FLUCTUATIONS NEAR EQUILIBRIUM



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Fluctuations Near Equilibrium

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This book is dedicated to the memory of my parents Bibudh Narayan Sen & Uma Sen and my grandmother Nirmala Sundari Devi

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TABLE OF CONTENTS

About the Author

Licensing

1: Statistical Mechanical Fluctuations and Time-independent Linear Responser

2: Statistical Mechanical Fluctuations

2.1: Gibbs's Derivation (1902)

2.2: Einstein's Independent Derivation (1904)

2.3: Keesom's Experiment and Opalescence

2.4: Ornstein-Zernike Correction

2.5: Bibliography

3: Critical Opalescence- From Einstein's Theory to Correlation Functions

3.1: Introduction

3.2: Local Fluctuations and the Dipole Picture

3.3: Wave Equation in an Inhomogeneous Medium

3.4: Green Function Solution

3.5: Born Approximation

3.6: Far-Field Limit

3.7: Scattered Intensity

3.8: Connection to Density Fluctuations

3.9: Structure Factor

3.10: Thermodynamic Limit and Critical Opalescence

3.11: Beyond Einstein- The Ornstein-Zernike Correction

3.12: The Wilson-Fisher Correction and Anomalous Scaling

3.13: Other examples

3.14: Comparison of Neutron Scattering at the Curie Point and Critical Opalescence

3.15: The Physical Mechanism

3.16: Technical Comparison

3.17: The Scattering Law

3.18: The Uniqueness of Neutrons

3.19: Summary of the Analogy

3.20: Bibliography

4: Thermodynamics and Statistical Mechanics- From Static Response to Dynamic Fluctuations

5: Einstein and Markov Equations for Brownian Motion- Historical Foundations and Modern Perspective

6: Power Balance and the Necessity of Dissipation- Pedagogical Derivation of the Generalized Langevin Equation

7: Classical Linear Response Theory and the Kubo Formula

8: Fluctuation-Dissipation Relations and Frequency-Dependent Johnson Nyquist Noise

- 8.1: Introduction
- 8.2: Theoretical Framework
- 8.3: Spectral Density and Bandwidth
- 8.4: Application of FTD to Electrical Resistance
- 8.5: Derivation of the Voltage Spectral Density
- 8.6: Derivation of the Voltage Spectral Density
- 8.7: Frequency-Dependent Noise Density
- 8.8: RC Circuit- Series Configuration
- 8.9: RC Circuit- Parallel Configuration
- 8.10: The L-R Shunted by C Equivalent Circuit Model
- 8.11: LCR Circuit and Charge Fluctuations
- 8.12: Johnson Noise Thermometry (JNT)
- 8.13: Conclusion
- 8.14: Appendix A
- 8.15: Appendix B
- 8.16: Appendix C
- 8.17: Appendix D
- 8.18: Bibliography

9: Onsager Relations

- 9.1: Introduction and Roadmap
- 9.2: Classical FDT from Liouville Dynamics
- 9.3: Proof of the Regression Hypothesis
- 9.4: Connection to the Power Spectral Density
- 9.5: Onsager-Casimir Reciprocal Relations
- 9.6: Modification by an External Magnetic Field
- 9.7: Summary and Logical Chain
- 9.8: Bibliography

10: Electrokinetics in a Tube
11: From Microscopic Reversibility to Macroscopic Irreversibility
12: Magalinski's Derivation of the Memory Function and the Generalized Langevin Equation for a System Coupled to a Bath of Harmonic Oscillators
13: Mori-Zwanzig Formulation
14: The Magalinski Model- A Physical Realization of Mori-Zwanzig Dynamics
15: Derivation of the Nakajima-Zwanzig and Mori-Zwanzig Formalisms
16: Quantum Linear Response Theory
17: Generalized Langevin Dynamics for an Arbitrary Potential- Thermal Renormalization and Stability
18: Quantum Mori-Zwanzig Formulation of the Magalinski Model
Index
Glossary
Detailed Licensing

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About the Author

Pabitra N. Sen completed his undergraduate studies in Calcutta (now Kolkata). He earned his Ph.D. in physics from the University of Chicago. Beginning in 1978, he served as a Scientific Advisor at Schlumberger-Doll Research. He is an elected Fellow of the American Institute of Physics and the Institute of Physics, Great Britain

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1: Statistical Mechanical Fluctuations and Time-independent Linear Responser

Thermodynamic equilibrium is never truly quiet. The density in a fluid is always fluctuating. The density fluctuations become large near a critical point giving rise to the critical opalescence. Similarly, a microscopic particle undergoes Brownian motion, driven by the relentless, random forces of surrounding molecules. These same fluctuations also give rise to viscous drag.

A simple resistor sitting isolated on a laboratory bench is seething at the atomic level. Its conduction electrons collide incessantly with the lattice in a random walk, producing a fluctuating voltage across its terminals. This Johnson noise-characterized by a zero mean but a nonzero variance-is not a defect; it is the audible signature of equilibrium itself.

The study of fluctuations near equilibrium is, in a deep sense, the study of what thermodynamic equilibrium actually is at the level of statistical mechanics. Macroscopic parameters- such as temperature, pressure, and chemical potential-are merely averages that conceal an underlying distribution. The central objective of this field is to determine the character of that distribution, how it evolves in time, and what it reveals about the underlying dynamics of the system.

The aim of this book is to discuss some aspects of fluctuations near equilibrium.

A central question of non-equilibrium statistical mechanics is how a macroscopic system responds to a weak external perturbation. While intuition might suggest that this requires driving the system out of equilibrium, one of the most profound results of twentieth-century physics states the opposite: the full linear response of any system is already encoded in the spontaneous fluctuations of that same system at thermal equilibrium.

These fluctuations govern dissipation and damping, determining the time-scale on which a system returns to equilibrium. For example, a pendulum (best observed in a mirror galvanometer) executes a constant, minute jiggling motion even when left alone. When deflected, the damping mechanism that restores it to equilibrium arises from the same microscopic fluctuations that drive its spontaneous motion.

The transition from microscopic, time-reversible processes to macroscopic, irreversible behavior is a central problem in statistical physics. This is often known as the reversibility paradox. The fundamental microscopic laws of physics, including both Newtonian and quantum mechanics, are reversible (except for the weak interactions), yet most macroscopic systems behave irreversibly. In the third part of the book we discuss this.

The book is divided into three parts. The first part, Chapters 2-5, deals with the statistical, time independent, fluctuations. The second part, Chapters 6-14, deals with time dependent statistical fluctuations. The third part, Chapters 15-19, deals with the origin of macroscopic irreversibility arising from microscopic reversible physics. I tried to stick to classical statistical mechanics throughout since the quantum mechanical formalism of the fluctuation-dissipation theorem and Kubo formula has been discussed in many places. However, I added an appendix covering the quantum mechanical case for convenience.

I am grateful to Professor M. S. Jhon who taught me about the importance of the Mori-Zwanzig formalism when we were graduate students at the University of Chicago.

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2: STATISTICAL MECHANICAL FLUCTUATIONS

This chapter examines the historical development of energy fluctuation theorems in statistical mechanics. We compare the formalisms introduced independently by J. Willard Gibbs and Albert Einstein, highlighting their mathematical equivalence and their significance in the transition toward a molecular understanding of radiation.

2.1: Gibbs's Derivation (1902)

2.2: Einstein's Independent Derivation (1904)

2.3: Keesom's Experiment and Opalescence

2.4: Ornstein-Zernike Correction

2.5: Bibliography

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2.1: Gibbs's Derivation (1902)

In his 1902 treatise, Elementary Principles in Statistical Mechanics, J. Willard Gibbs established the variance of energy by examining the properties of the canonical distribution [1].

2.1.1 The Partition Function

Following Gibbs, the probability of a system being in a state with energy between E and $E + dE$ is defined as:

$$P(E)dE = \frac{e^{-\beta E}}{Z}\rho(E)dE \tag{2.1}$$

where $\beta = 1/\left(k_B T\right), k_B$ is the Boltzmann constant, and T is the absolute temperature. The normalization condition requires:

$$Z = \int e^{-\beta E}\rho(E)dE \tag{2.2}$$

where $\rho(E)$ represents the density of states.

2.1.2 The Fluctuation Formula

By differentiating the average energy $\langle E\rangle$ with respect to the modulus, Gibbs demonstrated the relationship between the dispersion of energy and the heat capacity [4]. He arrived at the expression:

$$\overline{E^2} - \bar{E}^2 = \left(k_B T\right)^2 \frac{d\bar{E}}{d\left(k_B T\right)} \tag{2.3}$$

which is equivalent to the modern expression for energy variance:

$$\left\langle \Delta E^2 \right\rangle = k_B T^2 \frac{d\langle E\rangle}{dT} = k_B T^2 C_v, \tag{2.4}$$

where C_v is the heat capacity at constant volume. For a similar derivation using discrete states, one may refer to Reif[11].

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2.2: Einstein's Independent Derivation (1904)

Einstein was unaware of Gibbs's work when he published "On the General Molecular Theory of Heat"[2]. He followed a distinct but logically parallel path to arrive at the fluctuation-dissipation relation.

2.2.1 Step-by-Step Statistical Logic

Einstein utilized the canonical distribution $dW = Ce^{-\beta E}\omega(E)dE$. To find the variance, the following steps are employed:

1. Identity: Express the average energy as $\langle E\rangle = \frac{\int Ee^{-\beta E}\omega(E)dE}{\int e^{-\beta E}\omega(E)dE}$.
2. Differentiation: Calculate the derivative with respect to β, yielding $\frac{d\langle E\rangle}{d\beta} = -\left(\langle E^2\rangle - \langle E\rangle^2\right)$.
3. Conversion: Use the chain rule where $\frac{d}{d\beta} = \frac{dT}{d\beta}\frac{d}{dT} = -k_BT^2\frac{d}{dT}$.

Substituting the conversion into the derivative leads back to the fundamental fluctuation result:

$$\left\langle \Delta E^2\right\rangle = k_BT^2\frac{d\langle E\rangle}{dT} \tag{2.5}$$

This leads back to the same fundamental result as Gibbs's. Einstein applied this to blackbody radiation to suggest the dual nature of light. While the 1904 paper didn't explicitly claim that light is made of particles (photons), it proved that if you treat radiation using the laws of statistical mechanics, it behaves in a way that is strikingly inconsistent with pure wave theory and strikingly consistent with a "molecular" theory of heat. He noted that the fluctuations in radiation followed the same mathematical form as fluctuations in a gas composed of discrete particles. This suggested that radiation might not be a continuous wave but could have a "granular" or discrete structure.

Derivation of Particle Number Fluctuations

We will derive density fluctuations assuming discrete states. For continuous spectrum, the derivation will be similar as above with sums replaced by integrals over energy with proper density of states. To understand density fluctuations, we consider a subsystem of volume V in contact with a reservoir at temperature T and chemical potential μ. The number of particles N in this volume is not fixed. In the grand canonical ensemble, the probability of a system being in a state with N particles and energy E is given by:

$$P(E,N) = \frac{1}{\mathcal{Z}}e^{-\beta(E-\mu N)} \tag{2.6}$$

where $\mathcal{Z}$ is the grand partition function:

$$\mathcal{Z} = \sum_N\sum_i e^{-\beta(E_i-\mu N)} = \sum_N e^{\beta\mu N}Z_N(V,T) \tag{2.7}$$

Here $\beta = 1/k_BT$. The average number of particles is:

$$\langle N\rangle = \frac{1}{\mathcal{Z}}\sum_N Ne^{\beta\mu N}Z_N = \frac{1}{\beta}\frac{\partial\ln\mathcal{Z}}{\partial\mu} \tag{2.8}$$

To find the fluctuation, we take the second derivative:

$$\frac{\partial^2\ln\mathcal{Z}}{\partial\mu^2} = \beta\frac{\partial\langle N\rangle}{\partial\mu} = \beta^2\left(\langle N^2\rangle - \langle N\rangle^2\right) \tag{2.9}$$

Thus, the variance in particle number is:

$$\left\langle (\Delta N)^2\right\rangle = \frac{1}{\beta^2}\frac{\partial^2\ln\mathcal{Z}}{\partial\mu^2} = \frac{1}{\beta}\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{V,T} \tag{2.10}$$

Using the Gibbs-Duhem relation at constant $T(dP = \rho d\mu$, where $\rho = \langle N\rangle/V)$, we can transform the derivative:

$$\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{V,T}=\left(\frac{\partial\langle N\rangle}{\partial P}\right)_{V,T}\left(\frac{\partial P}{\partial\mu}\right)_{V,T}=\left(\frac{\partial\langle N\rangle}{\partial P}\right)_{V,T}\rho \tag{2.11}$$

Since $\langle N\rangle = V\rho$, and the isothermal compressibility is $\kappa_T = \frac{1}{\rho}\left(\frac{\partial\rho}{\partial P}\right)_T$, we find:

$$\left\langle(\Delta N)^2\right\rangle = \frac{\rho V}{\beta}\left(\frac{\partial\rho}{\partial P}\right)_T = \langle N\rangle\rho k_B T\kappa_T \tag{2.12}$$

Dividing by $\langle N\rangle^2$ and noting that relative density fluctuations $\frac{\Delta\rho}{\rho}$ are equivalent to $\frac{\Delta N}{\langle N\rangle}$ for a fixed volume, we arrive at the Einstein fluctuation formula [6]:

$$\frac{\left\langle(\Delta\rho)^2\right\rangle}{\rho^2} = \frac{k_B T\kappa_T}{V} \tag{2.13}$$

Thus, the relative root-mean-square fluctuation in the particle density of the given system is ordinarily $1\sqrt{N}$, and, therefore, negligible. However, there are exceptions, like the in phase transitions where at a critical point the compressibility diverges, so it is no longer intensive and a finite size scaling is required[3]. Thus, at the critical points, we encounter unusually large fluctuations in the particle density of the system. Such fluctuations indeed exist and account for phenomena like critical opalescence. We will describe this later in the chapter on Einstein's theory of critical opalescence.

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2.3: Keesom's Experiment and Opalescence

In 1911, W.H. Keesom[5] utilized this relationship to study ethylene. Because $\kappa_T \to \infty$ at the critical point, the fluctuations $\Delta\rho$ become macroscopic. Keesom observed that the scattering of light follows this divergence, confirming the link between microscopic statistical fluctuations and macroscopic thermodynamic observables.

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2.4: Ornstein-Zernike Correction

The previous derivation assumes fluctuations are local. The Ornstein-Zernike theory accounts for spatial correlations by introducing the correlation length ξ. The modified structure factor is:

$$S(k) \propto \frac{\kappa_T}{1 + k^2\xi^2} \tag{2.14}$$

In real space, the total correlation function $h(r) = g(r) - 1$ decays as:

$$h(r) \sim \frac{e^{-r/\xi}}{r} \tag{2.15}$$

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3: CRITICAL OPALESCENCE- FROM EINSTEIN'S THEORY TO CORRELATION FUNCTIONS

Critical opalescence is the dramatic increase in light scattering observed when the temperature T of a fluid approaches its critical value T_c. Critical opalescence arises when the size ξ of density fluctuations becomes comparable to the wavelength λ of the visible light, $\xi \propto (T - T_c)^{-\nu} \approx \lambda$. The exponent ν is the critical exponent

This phenomenon was first reported by French physicist Charles Cagniard de la Tour[1] in 1823 in mixtures of alcohol and water. In 1869, Thomas Andrews [2] demonstrated that at the critical point in carbon dioxide CO_2, the liquid-gas interface vanishes, and the substance exhibits critical opalescence. In 1908 the Polish physicist Marian Smoluchowski [3] became the first to ascribe the phenomenon of critical opalescence to large density fluctuations. In 1910 Albert Einstein [4] showed that the link between critical opalescence and Rayleigh scattering is quantitative

This phenomenon was first explained by Einstein [4] and Smoluchowski[3], who identified its origin in large-scale fluctuations of density and hence of the dielectric constant.

3.1: Introduction

3.2: Local Fluctuations and the Dipole Picture

3.3: Wave Equation in an Inhomogeneous Medium

3.4: Green Function Solution

3.5: Born Approximation

3.6: Far-Field Limit

3.7: Scattered Intensity

3.8: Connection to Density Fluctuations

3.9: Structure Factor

3.10: Thermodynamic Limit and Critical Opalescence

3.11: Beyond Einstein- The Ornstein-Zernike Correction

3.12: The Wilson-Fisher Correction and Anomalous Scaling

3.13: Other examples

3.14: Comparison of Neutron Scattering at the Curie Point and Critical Opalescence

3.15: The Physical Mechanism

3.16: Technical Comparison

3.17: The Scattering Law

3.18: The Uniqueness of Neutrons

3.19: Summary of the Analogy

3.20: Bibliography

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3.1: Introduction

The approach to the liquid-gas critical point is characterized by the divergence of the isothermal compressibility, defined as $\kappa_T = -V^{-1}(\partial V/\partial P)_T$. As the system nears the critical temperature T_c along the critical isochore, the vanishing of the second derivative of the Gibbs free energy leads to an asymptotic power-law divergence of the form $\kappa_T \sim |T - T_c|^{-\gamma}$, where γ is a universal critical exponent. This divergence is intrinsically linked to the Fluctuation-Dissipation Theorem, which relates κ_T to the integral of the pair correlation function $G(\mathbf{r}) = \langle \Delta\rho(\mathbf{r})\Delta\rho(0)\rangle$. Specifically, as the correlation length ξ diverges, the system exhibits density fluctuations across all length scales, manifesting macroscopically as critical opalescence. In the mean-field approximation, $\gamma = 1$, whereas renormalization group theory and experimental observations for systems in the 3D Ising universality class yield a value of $\gamma \approx 1.24$.

Near the critical point, the isothermal compressibility diverges,

$$\kappa_T \to \infty, \tag{3.1}$$

leading to long-wavelength density fluctuations that strongly scatter light.

In this chapter, we present a unified and pedagogical derivation of Einstein's theory, connecting:

- the dipole picture of scattering,
- the wave equation in an inhomogeneous medium,
- and the modern formulation in terms of correlation functions.

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3.2: Local Fluctuations and the Dipole Picture

Consider a small volume $V \ll \lambda^3$ with dielectric fluctuation

$$\varepsilon = \bar{\varepsilon} + \delta\varepsilon. \tag{3.2}$$

In Gaussian units, polarization is

$$\mathbf{P} = \frac{\varepsilon - 1}{4\pi}\mathbf{E}. \tag{3.3}$$

Thus, the fluctuating part induces a dipole moment

$$\mathbf{p} = \frac{V}{4\pi}\delta\varepsilon\mathbf{E}_0. \tag{3.4}$$

The radiated electric field from a dipole in the far field is

$$\mathbf{E}_{\text{scat}}(\mathbf{r}) = \frac{k^2}{r}(\hat{\mathbf{r}} \times \mathbf{p}) \times \hat{\mathbf{r}}e^{ikr}. \tag{3.5}$$

Summing contributions from all fluctuating regions leads naturally to a continuum description.

3.2.1 Radiated Power and Intensity

From Maxwell's equations, an accelerating dipole radiates power. The electric field E_{scat} of the scattered wave at a distance r in the far-field is:

$$E_{\text{scat}} = \frac{1}{c^2 r}\frac{\partial^2 p}{\partial t^2}\sin\phi = -\frac{\omega^2 p_0}{c^2 r}\sin\phi \tag{3.6}$$

where ϕ is the angle between the dipole axis and the observer. The scattered intensity I_{scat} is:

$$I_{\text{scat}} = I_0 \frac{\pi^2 V^2}{r^2\lambda^4}\left\langle(\Delta\epsilon)^2\right\rangle \frac{1+\cos^2\theta}{2} \tag{3.7}$$

For unpolarized incident light, we average $\sin^2\phi$ over all orientations, yielding the geometric factor $\frac{1+\cos^2\theta}{2}$, where θ is the scattering angle relative to the incident beam.

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3.3: Wave Equation in an Inhomogeneous Medium

The above is an intuitive derivation of the scattered intensity. It is more convenient to formulate the scattering formula in terms of the density correlation functions. The electric field satisfies

$$\nabla^2\mathbf{E}(\mathbf{r}) + k_0^2\varepsilon(\mathbf{r})\mathbf{E}(\mathbf{r}) = 0, \quad k_0 = \frac{\omega}{c}. \tag{3.8}$$

Decompose

$$\varepsilon(\mathbf{r}) = \bar{\varepsilon} + \delta\varepsilon(\mathbf{r}), \tag{3.9}$$

and define

$$k^2 = k_0^2\bar{\varepsilon}. \tag{3.10}$$

Then

$$\nabla^2\mathbf{E} + k^2\mathbf{E} = -k_0^2\delta\varepsilon(\mathbf{r})\mathbf{E}(\mathbf{r}). \tag{3.11}$$

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3.4: Green Function Solution

The Green function satisfies

$$\left(\nabla^2 + k^2\right) G(\mathbf{r}) = -\delta(\mathbf{r}), \quad G(\mathbf{r}) = \frac{e^{ikr}}{4\pi r}. \tag{3.12}$$

Thus,

$$\mathbf{E}_s(\mathbf{r}) = k_0^2 \int d^3r' G\left(\mathbf{r} - \mathbf{r}'\right) \delta\varepsilon\left(\mathbf{r}'\right) \mathbf{E}\left(\mathbf{r}'\right). \tag{3.13}$$

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3.5: Born Approximation

Assume weak scattering:

$$\mathbf{E}\left(\mathbf{r}'\right) = \mathbf{E}_0 e^{i\mathbf{k}_i \cdot \mathbf{r}'}. \tag{3.14}$$

Then

$$\mathbf{E}_s(\mathbf{r}) = k_0^2 \mathbf{E}_0 \int d^3r' \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{4\pi\left|\mathbf{r}-\mathbf{r}'\right|} \delta\varepsilon\left(\mathbf{r}'\right) e^{i\mathbf{k}_i \cdot \mathbf{r}'}. \tag{3.15}$$

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3.6: Far-Field Limit

Using

$$|\mathbf{r}-\mathbf{r}'| \approx r - \hat{\mathbf{r}}\cdot\mathbf{r}', \tag{3.16}$$

we obtain

$$\mathbf{E}_s(\mathbf{r}) = \frac{k_0^2 e^{ikr}}{4\pi r}\mathbf{E}_0 \int d^3r' \delta\varepsilon\left(\mathbf{r}'\right) e^{-i\mathbf{q}\cdot\mathbf{r}'}, \tag{3.17}$$

with

$$\mathbf{q} = \mathbf{k}_s - \mathbf{k}_i. \tag{3.18}$$

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3.7: Scattered Intensity

$$I(\mathbf{q}) = \left\langle |\mathbf{E}_s|^2 \right\rangle \tag{3.19}$$

$$= \frac{k_0^4}{16\pi^2 r^2} |\mathbf{E}_0|^2 \int d^3r d^3r' e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')} \left\langle \delta\varepsilon(\mathbf{r})\delta\varepsilon\left(\mathbf{r}'\right)\right\rangle \tag{3.20}$$

Define the dielectric correlation function

$$C_\varepsilon(\mathbf{R}) = \langle \delta\varepsilon(0)\delta\varepsilon(\mathbf{R})\rangle. \tag{3.21}$$

Then

$$I(\mathbf{q}) = \frac{k_0^4}{16\pi^2 r^2} |\mathbf{E}_0|^2 V \int d^3R e^{-i\mathbf{q}\cdot\mathbf{R}} C_\varepsilon(\mathbf{R}). \tag{3.22}$$

This, Equation 3.22, is an example which epitomizes the relationship between measurement and correlation function.

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3.8: Connection to Density Fluctuations

Now we use the relation

$$\delta\varepsilon = \left(\frac{\partial\varepsilon}{\partial\rho}\right)_T \delta\rho, \tag{3.23}$$

to connect between dielectric correlation function to density correlation function:

$$C_\varepsilon(\mathbf{R}) = \left(\frac{\partial\varepsilon}{\partial\rho}\right)^2 \langle\delta\rho(0)\delta\rho(\mathbf{R})\rangle. \tag{3.24}$$

Define the static structure factor

$$G(\mathbf{R}) = \langle\delta\rho(0)\delta\rho(\mathbf{R})\rangle. \tag{3.25}$$

Then Equation ??? becomes

$$I(\mathbf{q}) = \frac{k_0^4}{16\pi^2 r^2} |\mathbf{E}_0|^2 V \left(\frac{\partial\varepsilon}{\partial\rho}\right)^2 \int d^3R e^{-i\mathbf{q}\cdot\mathbf{R}} G(\mathbf{R}). \tag{3.26}$$

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3.9: Structure Factor

The static structure factor is generally defined as the Fourier transform of $G(\mathbf{R})$

$$S(\mathbf{q}) = \frac{1}{V}\int d^3 R e^{-i\mathbf{q}\cdot\mathbf{R}} G(\mathbf{R}) \tag{3.27}$$

The final result that relates the scattering intensity and the tatic structure factor is

$$I(\mathbf{q}) = \frac{k_0^4}{16\pi^2 r^2}\left|\mathbf{E}_0\right|^2 V^2 \left(\frac{\partial\varepsilon}{\partial\rho}\right)^2 S(\mathbf{q}) \tag{3.28}$$

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3.10: Thermodynamic Limit and Critical Opalescence

At $q = 0$:

$$S(0) = \left\langle (\delta\rho)^2 \right\rangle . \tag{3.29}$$

The relationship between density fluctuations and the isothermal compressibility κ_T is derived within the grand canonical ensemble as we have seen in previous chapter. The variance in the total particle number is given by:

$$\left\langle N^2 \right\rangle - \langle N \rangle^2 = \frac{1}{\beta} \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{V,T} \tag{3.30}$$

By applying the Gibbs-Duhem relation at constant temperature, $dP = \rho d\mu$, and utilizing the definition of compressibility $\kappa_T = \rho^{-1}(\partial\rho/\partial P)_T$, we obtain:

$$\left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{V,T} = V \left(\frac{\partial \rho}{\partial \mu} \right)_T = V\rho \left(\frac{\partial \rho}{\partial P} \right)_T = V\rho^2 \kappa_T \tag{3.31}$$

Combining these results and defining the density fluctuation $\delta\rho = (N - \langle N \rangle)/V$, we arrive at the fluctuation-dissipation relation:

$$\left\langle (\delta\rho)^2 \right\rangle = \frac{\rho^2 k_B T \kappa_T}{V} \tag{3.32}$$

This demonstrates that as the system approaches the critical point and $\kappa_T \to \infty$, the magnitude of density fluctuations diverges, leading to the phenomenon of critical opalescence. Thus, the thermodynamics gives

$$\left\langle (\delta\rho)^2 \right\rangle = \rho^2 k_B T \kappa_T. \tag{3.33}$$

Thus,

Label '3.33' multiply defined

Since $\kappa_T \to \infty$ at the critical point, the scattered intensity diverges, producing critical opalescence.

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3.11: Beyond Einstein- The Ornstein-Zernike Correction

While Einstein's result, Eq. (34), correctly predicts the divergence of scattering as $\kappa_T \to \infty$, it suffers from a physical inconsistency at the exact critical point. Einstein's derivation assumes that fluctuations in neighboring volume elements are uncorrelated. This implies a "flat" scattering intensity $I(\mathbf{q})$ that is independent of the scattering angle (or wave-vector q) for small q. However, as the correlation length ξ diverges, the assumption that $V \ll \lambda^3$ for independent fluctuating volumes fails, as fluctuations become correlated over distances comparable to or larger than the wavelength of light.

To resolve this, Ornstein and Zernike [5] proposed that the local free energy should depend not only on the local density $\rho(\mathbf{r})$ but also on its gradient $\nabla\rho(\mathbf{r})$. This leads to a modified expression for the static structure factor for $q = |\mathbf{q}|$:

$$S(q) = \frac{S(0)}{1 + q^2\xi^2} \tag{3.35}$$

where ξ is the correlation length. Substituting the thermodynamic relation for $S(0)$ from Eq. (35), the scattered intensity becomes:

$$I(q) \propto \frac{\rho^2 k_B T \kappa_T}{1 + q^2\xi^2} \tag{3.36}$$

This is the celebrated Ornstein-Zernike formula. It provides two critical corrections to Einstein's theory:

- Angular Dependence: Unlike the Einstein result, the intensity now decreases as q (and thus the scattering angle θ) increases.
- Finite Intensity at $q > 0$: Even when $\kappa_T \to \infty$ at the critical point, the scattered intensity remains finite for any non-zero scattering angle because $S(\mathbf{q}) \sim 1/q^2$.

This explains why the fluid does not become "infinitely" bright, but rather exhibits a specific angular dissymmetry in its opalescence as $T \to T_c$.

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3.12: The Wilson-Fisher Correction and Anomalous Scaling

Einstein's theory shows that light scattering directly measures density fluctuations via their correlation function. In modern language, critical opalescence arises from the divergence of the structure factor at small wave-vector, reflecting long-range correlations in the fluid. While the Ornstein-Zernike (OZ) theory significantly improves upon Einstein's result by accounting for the correlation length ξ, it remains a mean-field approximation. In the limit of $T \to T_c$ and $q\xi \gg 1$, the OZ formula predicts that the structure factor scales as $S(q) \sim q^{-2}$. However, exact

solutions and renormalization group calculations show that the correlation function $G(\mathbf{R})$ decays slightly differently at the critical point. To account for this, the anomalous critical exponent η is introduced, modifying the scaling of the structure factor to:

$$S(\mathbf{q}) \sim \frac{1}{q^{2-\eta}}. \tag{3.37}$$

For the 3D Ising universality class, $\eta \approx 0.036$, a small but physically significant deviation from the OZ prediction of $\eta = 0$ [6]. This Fisher correction implies that the density fluctuations are slightly more persistent over long distances than predicted by classical theory, representing the final refinement in our modern understanding of critical opalescence.

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3.13: Other examples

Ferromagnetic material has large fluctuations of magnetic domains near the Curie point [7]. And since neutron scattering is affected by magnetic moments of atoms, this creates critical opalescence. Specifically, if a beam of neutrons is fired at a ferromagnetic material, then as it approaches the Curie point, it would start scattering the neutrons as if it is turning opaque to neutrons.

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3.14: Comparison of Neutron Scattering at the Curie Point and Critical Opalescence

Comparing neutron scattering at the Curie point to critical opalescence reveals a profound unity in how matter behaves near a second-order phase transition. The both systems develops large-scale fluctuations and produce the divergence of the correlation length.

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3.15: The Physical Mechanism

The underlying physics for both phenomena is described by the Ornstein-Zernike theory. As a system approaches a critical point T_c, the spatial correlation length ξ grows significantly.

- **Critical Opalescence:** In a fluid (like CO_2) near its liquid-gas critical point, density fluctuations become so large that their spatial extent matches the wavelength of visible light. This causes the light to scatter strongly, making a normally transparent fluid appear milky or "opaque."
- **Neutron Scattering at the Curie Point:** In a ferromagnet (like Iron or Nickel), the "density" being measured is the local magnetization. Near the Curie temperature T_c, the spins begin to fluctuate in large, correlated clusters. Because neutrons have a magnetic moment, they interact with these magnetic fluctuations.

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3.16: Technical Comparison

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3.17: The Scattering Law

In both systems, the scattering intensity $I(\mathbf{q})$ is proportional to the static structure factor $S(\mathbf{q})$. Near the critical point, for small scattering vectors $\mathbf{q}$, this follows the Lorentzian form:

$$S(\mathbf{q}) \propto \frac{\chi}{1 + q^2\xi^2} \tag{3.38}$$

where:

- χ is the susceptibility (magnetic or isothermal compressibility).
- ξ is the correlation length, which diverges as $\xi \sim |T - T_c|^{-\nu}$.

As $T \to T_c$, the denominator $1 + q^2\xi^2$ becomes dominated by the q^2 term for any fixed q, leading to a massive increase in forward scattering.

Table 3.1: Comparison of critical phenomena in fluids and magnets.

Feature	Critical Opalescence (Fluids)	Magnetic Scattering (Curie Point)
Probe	Visible Light (Photons)	Thermal/Cold Neutrons
Fluctuating Variable	Local Number Density $n(\mathbf{r})$	Local Magnetization M(r)
Scattering Length	$\sim 4000 - 7000\text{Å}$	$\sim 1 - 10\text{Å}$
Interaction	Electromagnetic (Dielectric constant)	Magnetic (Dipolar interaction)
Observation	Fluid becomes "milky" or opaque	Divergence in "Small Angle Scattering"

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3.18: The Uniqueness of Neutrons

While critical opalescence is a spectacular visual effect, neutron scattering provides deeper insight into the dynamics of the transition:

- 1.Wavelength Match: The wavelength of thermal neutrons is comparable to interatomic distances. This allows researchers to probe fluctuations at the microscopic scale.
- 2.Inelastic Scattering: Neutrons can exchange energy with the system. Near the Curie point, one observes "Critical Slowing Down," where the characteristic relaxation time of the spin fluctuations diverges:

$$\tau \propto \xi^{z} \tag{3.39}$$

where z is the dynamic critical exponent.

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3.19: Summary of the Analogy

Critical opalescence is essentially the "optical version" of the magnetic critical scattering observed with neutrons. If our eyes were sensitive to magnetic fields and could "see" neutrons, a magnet at its Curie point would appear to "glow" or become cloudy with magnetic turbulence, exactly like a fluid at its critical point.

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4: Thermodynamics and Statistical Mechanics- From Static Response to Dynamic Fluctuations

4.1 The Statistical Basis of Response

In thermodynamics, the response of a system to an external field is deeply connected to the spontaneous fluctuations of the system at equilibrium. This relationship allows us to relate macroscopic response coefficients, such as susceptibility, to microscopic statistical variances [7, [6, 3].

4.2 Linear Response to a Conjugate Field

Consider a system in thermal equilibrium at temperature T with an unperturbed Hamiltonian H_0. When an external field h is applied to an observable A, the total Hamiltonian becomes $H = H_0 - hA$.

The partition function Z in the canonical ensemble is:

$$Z(h, \beta) = \mathrm{Tr}\left[e^{-\beta(H_0 - hA)}\right] \tag{4.1}$$

where $\beta = 1/(k_B T)$. The equilibrium expectation value $\langle A \rangle$ is related to the derivative of the partition function:

$$\langle A \rangle = \frac{1}{\beta}\frac{\partial \ln Z}{\partial h} \tag{4.2}$$

The static susceptibility χ, defined as the rate of change of the average value $\langle A \rangle$ with respect to the field h, is derived from Eq. 4.2 as:

$$\chi = \left.\frac{\partial \langle A \rangle}{\partial h}\right|_{h \to 0} = \beta\left(\langle A^2 \rangle - \langle A \rangle^2\right) = \frac{\mathrm{Var}(A)}{k_B T} \tag{4.3}$$

As shown in Eq. 4.3, the macroscopic response is determined entirely by the equilibrium variance [?].

4.3 Cross-Correlations and Generalized Response

If we measure the response of a different observable, B, to the field h conjugate to A, the thermal average is governed by the covariance C_{BA} :

$$\langle B \rangle = \frac{1}{Z}\mathrm{Tr}\left(Be^{-\beta(H_0 - hA)}\right) \tag{4.4}$$

$$\frac{\partial \langle B \rangle}{\partial h} = \beta C_{BA} \tag{4.5}$$

Here,

$$C_{BA} = \langle BA \rangle - \langle B \rangle \langle A \rangle \tag{4.6}$$

is the cross correlation.

4.4 Cross-Correlations and Generalized Response

If we measure the response of a different observable B to the field h conjugate to A, the thermal average is:

$$\langle B \rangle = \frac{1}{Z}\mathrm{Tr}\left(Be^{-\beta(H_0 - hA)}\right) \tag{4.7}$$

To find the response, we differentiate with respect to h :

$$\frac{\partial\langle B\rangle}{\partial h}=\frac{\beta \operatorname{Tr}\left(BAe^{-\beta H}\right)}{Z}-\frac{\operatorname{Tr}\left(Be^{-\beta H}\right)}{Z}\frac{\beta \operatorname{Tr}\left(Ae^{-\beta H}\right)}{Z}, \tag{4.8}$$

remembering $H=H_0-hA$. Simplifying the terms into expectation values, we obtain:

$$\frac{\partial\langle B\rangle}{\partial h}=\beta(\langle BA\rangle-\langle B\rangle\langle A\rangle)=\beta C_{BA} \tag{4.9}$$

where C_{BA} is the cross-correlation (or covariance) between A and B. A, B are classical observable and therefore they commute.

4.5 Physical Applications

4.5.1 Curie's Law in Paramagnets

Equation (9) above gives, for a magnetic response in an external field, H_{ext}

$$\chi=\frac{\partial\langle M\rangle}{\partial H_{ext}}=\beta\left(\left\langle M^2\right\rangle-\langle M\rangle^2\right) \tag{4.10}$$

For a system where the mean magnetization is zero:

$$\chi=\beta\left\langle M^2\right\rangle \tag{4.11}$$

where the variance $\left\langle M^2\right\rangle=N\mu^2$ drives the response.Thus, for a paramagnetic material, like oxygen, with N non-interacting spins and magnetic moment μ, the perturbation is $-\mu\cdot\mathbf{H}$. The magnetization M_z is conjugate to the external field $H_{\text{ext},z}$ [5]. In the limit $H_{\text{ext},z}\to 0$, the susceptibility follows Curie's Law [4]:

$$\chi_{zz}=\frac{N\mu^2}{3k_BT}=\frac{C}{T} \tag{4.12}$$

The factor of $1/3$ comes from averaging $\cos^2(\theta)$, where the angle between each magnetic moment and the field is assumed to be uniformly distributed.

4.5.2 Quantum Treatment: The Brillouin Function

In the quantum mechanical regime[5, 6], the magnetic moment is quantized. The magnetization M for N spins with total angular momentum J is given by:

$$M=Ng_J\mu_BJB_J(x),\quad x=\frac{g_J\mu_BJH}{k_BT} \tag{4.13}$$

where $B_J(x)$ is the Brillouin function:

$$B_J(x)=\frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}x\right)-\frac{1}{2J}\coth\left(\frac{1}{2J}x\right) \tag{4.14}$$

In the limit of high temperature $(x\ll 1)$, the susceptibility $\chi=M/H$ reduces to Curie's Law:

$$\chi=\frac{Ng_J^2\mu_B^2J(J+1)}{3k_BT} \tag{4.15}$$

where the effective moment $\mu_{eff}^2=g_J^2\mu_B^2J(J+1)$ replaces the classical μ^2.

In the quantum model, the magnetization is derived by taking the thermal average of the discrete magnetic moments $g_J\mu_Bm_J$. In the high-temperature (low-field) limit, the susceptibility χ is proportional to the average of the squares of the magnetic quantum numbers m_J :

$$\langle m_J^2 \rangle = \frac{1}{2J+1} \sum_{m_J=-J}^{J} m_J^2 \tag{4.16}$$

Using the identity for the sum of squares $\sum_{k=1}^{n} k^2 = \frac{n(n+1)(2n+1)}{6}$, the summation over the $2J+1$ states yields:

$$\sum_{m_J=-J}^{J} m_J^2 = \frac{1}{3} J(J+1)(2J+1) \tag{4.17}$$

Normalizing by the number of states, we find $\langle m_J^2 \rangle = \frac{1}{3} J(J+1)$. This demonstrates that the factor of 1/3 persists in the quantum regime due to the isotropic distribution of the total angular momentum across the three spatial dimensions.

4.5.3 Heat Capacity and Energy Fluctuations

In the canonical ensemble, the internal energy E fluctuates. The average energy $\langle E \rangle$ is given by $-\frac{\partial \ln Z}{\partial \beta}$. The constant-volume heat capacity C_V is defined as the rate of change of energy with respect to temperature [?]:

$$C_V = \left(\frac{\partial \langle E \rangle}{\partial T} \right)_V = \left(-\frac{1}{k_B T^2} \right) \frac{\partial \langle E \rangle}{\partial \beta} \tag{4.18}$$

Differentiating the average energy with respect to β using the quotient rule:

$$\frac{\partial \langle E \rangle}{\partial \beta} = -\left[\frac{\sum E_i^2 e^{-\beta E_i}}{Z} - \left(\frac{\sum E_i e^{-\beta E_i}}{Z} \right)^2 \right] = -\left(\langle E^2 \rangle - \langle E \rangle^2 \right) \tag{4.19}$$

Substituting this back, we arrive at the energy fluctuation relation:

$$C_V = \frac{\langle E^2 \rangle - \langle E \rangle^2}{k_B T^2} = \frac{\mathrm{Var}(E)}{k_B T^2} \tag{4.20}$$

Equation 4.20 demonstrates that a system with high thermal inertia also exhibits large spontaneous energy fluctuations.

4.5.4 Analogous Equilibrium Effects

The following table summarizes the most significant macroscopic response functions and the microscopic fluctuations that drive them:

Table 4.1: Analogies between response functions and spontaneous fluctuations.

Property	Symbol	Response to...	Underlying Fluctuation
Heat Capacity	C_V	Temperature (T)	Energy (E)
Isothermal Compressibility	κ_T	Pressure (P)	Particle Number (N) or Volume (V)
Magnetic Susceptibility	χ	Magnetic Field (H)	Magnetization (M)
Electric Polarizability	α	Electric Field (E)	Dipole Moment (P)

4.6 Transition to Dynamic Response

The Dynamic Fluctuation-Dissipation Theorem (FDT) is the time-dependent evolution of the static identities discussed above. While the static case considers the variance, the dynamic case utilizes the Time-Correlation Function, $C(t) = \langle A(t)A(0) \rangle$, which describes how a fluctuation persists or decays over time. The FDT states that the way a system dissipates energy from an external field is identical to how it spontaneously relaxes from a natural thermal fluctuation. This will be discussed later in detail.

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5: Einstein and Markov Equations for Brownian Motion- Historical Foundations and Modern Perspective

Einstein's 1905 theory of Brownian motion represents the first systematic application of a continuous Markov process in physics. Without invoking microscopic equations of motion, Einstein introduced a probabilistic evolution law for the position of a suspended particle, derived the diffusion equation, and connected the diffusion constant to thermodynamic quantities. This work provided decisive evidence for the molecular nature of matter and established the conceptual foundations of stochastic processes in physics. In this chapter we reconstruct Einstein's reasoning in modern notation, clarify its Markov structure, connect it to subsequent developments by Smoluchowski and Langevin, and discuss its relation to the Fokker-Planck equation and the fluctuation-dissipation relation.

5.1 Introduction

In 1905 Albert Einstein published his seminal paper On the movement of small particles suspended in a stationary liquid demanded by the molecular kinetic theory of heat (Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen" [1]. In it, he provided a quantitative theory of the irregular motion observed by Robert Brown in 1827. The work played a decisive role in establishing the atomic theory of matter. Independently, Smoluchowski [2] developed a discrete random-walk picture

Einstein used both thermodynamic and probabilistic arguments. Beyond its historical importance, Einstein's analysis introduced a new type of physical reasoning. Instead of writing Newton's equations for a particle bombarded by molecules, Einstein described the system probabilistically. He postulated an evolution equation for the probability density of the particle's position and derived macroscopic irreversibility from statistical independence of successive displacements. Independently, Smoluchowski [2] developed a discrete random-walk picture.

Although Einstein did not use the term "Markov process," his construction satisfies precisely the defining properties of a continuous-time Markov process. In modern language, Brownian motion is a diffusion process whose generator is the Laplacian. Einstein's paper thus represents the first clear appearance of Markovian dynamics in physics[3].

5.2 Part I: The Thermodynamic Derivation

Einstein first used thermodynamic reasoning.

Diffusion current:

$$J_{\text{diff}} = -D\frac{\partial n}{\partial x}. \tag{5.1}$$

Drift current under force F :

$$J_{\text{drift}} = \mu n F. \tag{5.2}$$

Here n is the particle density, and μ the mobility. At equilibrium,

$$J_{\text{diff}} + J_{\text{drift}} = 0. \tag{5.3}$$

Using $n \propto e^{-U/kT}$, Einstein obtained

$$D = \mu kT. \tag{5.4}$$

With Stokes' law,

$$\mu = \frac{1}{6\pi\eta a}, \tag{5.5}$$

leading to

$$D = \frac{kT}{6\pi\eta a}. \tag{5.6}$$

Equation 5.4 is the first example of a fluctuation-dissipation relation.

5.3 Part II: The Markovian Derivation

Let $P(x,t)$ denote the probability density of finding the Brownian particle at position x at time t.

Einstein considered a short time interval τ and introduced $\varphi(\Delta)$, the probability density for a displacement Δ during that interval.

His central assumption was:

Displacements occurring in non-overlapping time intervals are statistically independent.

Additionally:

- The medium is homogeneous.
- There is no systematic drift.
- The displacement distribution is symmetric.

Under these assumptions, the probability density evolves according to

$$P(x,t+\tau) = \int_{-\infty}^{\infty} P(x-\Delta,t)\varphi(\Delta)d\Delta \tag{5.7}$$

Equation 5.7 is precisely the Chapman-Kolmogorov equation for a time-homogeneous Markov process.

5.4 Derivation of the Diffusion Equation

Assume τ is small and that $P(x,t)$ is smooth. Expand the left-hand side:

$$P(x,t+\tau) = P(x,t) + \tau\frac{\partial P}{\partial t} + O\left(\tau^2\right). \tag{5.8}$$

Expand the integrand:

$$P(x-\Delta,t) = P(x,t) - \Delta\frac{\partial P}{\partial x} + \frac{\Delta^2}{2}\frac{\partial^2 P}{\partial x^2} + \cdots. \tag{5.9}$$

Using normalization and symmetry,

$$\int \varphi(\Delta)d\Delta = 1 \tag{5.10}$$

$$\int \Delta\varphi(\Delta)d\Delta = 0 \tag{5.11}$$

$$\int \Delta^2\varphi(\Delta)d\Delta = \left\langle\Delta^2\right\rangle \tag{5.12}$$

we obtain

$$\frac{\partial P}{\partial t} = \frac{\left\langle\Delta^2\right\rangle}{2\tau}\frac{\partial^2 P}{\partial x^2}. \tag{5.13}$$

Define

$$D = \frac{\left\langle\Delta^2\right\rangle}{2\tau}. \tag{5.14}$$

The diffusion equation follows:

$$\frac{\partial P}{\partial t} = D\frac{\partial^2 P}{\partial x^2}. \tag{5.15}$$

5.5 Solution and Experimental Prediction

For initial condition $P(x,0) = \delta(x)$,

$$P(x,t) = \frac{1}{\sqrt{4\pi Dt}}\exp\left(-\frac{x^2}{4Dt}\right). \tag{5.16}$$

The mean-square displacement is

$$\left\langle x^2(t)\right\rangle = 2Dt. \tag{5.17}$$

Equation 5.17 provided a direct experimental prediction. Jean Perrin later verified this relation and measured Avogadro's number [4].

5.6 First Fluctuation-Dissipation Relation [4]

The first fluctuation-dissipation theorem, famously known as the Einstein relation, connects the diffusion coefficient D (representing fluctuations) to the mobility μ (representing dissipation) of a particle in thermal equilibrium, Equation 5.4

$$D = \mu k_B T$$

In terms of the velocity autocorrelation function, the relation is expressed via the Green-Kubo formula:

$$D = \int_0^\infty \left\langle u\left(t_0\right) u\left(t_0+t\right)\right\rangle dt \tag{5.18}$$

This demonstrates that the macroscopic transport properties of a system are determined by the correlation of its microscopic thermal fluctuations. We now derive the above equation.

First recast equation Equation 5.17 in the following form

$$D = \lim_{t\to\infty}\frac{1}{2t}\left\langle [x(t)-x(0)]^2\right\rangle \tag{5.19}$$

where the average $\rangle$ is taken over an ensemble in thermal equilibrium. Since we have

$$x(t) - x(0) = \int_0^t u\left(t'\right) dt'$$

equation Equation 5.19 is transformed as

$$\begin{aligned} D &= \lim_{t\to\infty}\frac{1}{2t}\int_0^t dt_1 \int_0^t dt_2 \left\langle u\left(t_1\right) u\left(t_2\right)\right\rangle \\ &= \lim_{t\to\infty}\frac{1}{t}\int_0^t dt_1 \int_0^{t-t_1} dt' \left\langle u\left(t_1\right) u\left(t_1+t'\right)\right\rangle \\ &= \int_0^\infty \left\langle u\left(t_0\right) u\left(t_0+t\right)\right\rangle dt \end{aligned} \tag{5.20}$$

where we assumed that

$$\lim_{t\to\infty}\left\langle u\left(t_0\right) u\left(t_0+t\right)\right\rangle = 0. \tag{5.21}$$

Therefore the Einstein relation, Equation 5.4 can be written as the first fluctuation-dissipation theorem:

$$\mu = \frac{1}{m\gamma} = \frac{D}{kT} = \frac{1}{kT}\int_0^\infty \langle u\left(t_0\right) u\left(t_0+t\right)\rangle \, dt \tag{5.22}$$

If a periodic external force

$$F = F_0 \cos \omega t, \quad -\infty < t$$

is applied, the mobility is defined by

$$\langle u(t)\rangle = \mathrm{Re}\left[\mu(\omega) F_0 e^{i\omega t}\right] \tag{5.23}$$

where $\mu(\omega)$ is the complex mobility or the admittance. Now we have a frequency dependent FDT

$$\mu(\omega) = \frac{1}{kT}\int_0^\infty \langle u\left(t_0\right) u\left(t_0+t\right)\rangle \, e^{-i\omega t} dt \tag{5.24}$$

We will see that they are really Kubo formula [4] for linear response where the macroscopic response function is given by time correlation function of microscopic currents. Here these relations Eqs.(5.22, 5.24), follow directly from the definitions. Remarkably, no perturbation theory was required.

Marian Smoluchowski's Contributions to Brownian Motion

While Albert Einstein is often the first name associated with the theory of Brownian motion (1905), Marian Smoluchowski [2] independently developed a nearly identical theory published in 1906. His approach was rooted in the kinetic theory of gases and collisions, providing a more "physically direct" microscopic mechanism compared to Einstein's thermodynamic derivation. The following discussion follows cosely Fulinski's article[6].

CHAPTER 5. EINSTEIN AND MARKOV EQUATIONS FOR BROWNIAN MOTION:HISTORICAL FOUNDATION

1. Kinetic-Probabilistic Derivation

Unlike Einstein, who viewed Brownian motion through the lens of diffusion and osmotic pressure, Smoluchowski analyzed the individual collisions between the suspended particle and the molecules of the surrounding fluid.

- He modeled the motion as a random walk.
- He calculated the cumulative effect of thousands of unobservable molecular impacts, proving that a statistical imbalance in these impacts results in the observable jittery movement.
- He arrived at a formula for the mean square displacement (MSD) that was virtually identical to Einstein's, differing only by a small numerical factor due to specific assumptions about collision geometry.

2. The Smoluchowski Equation

In 1916, he generalized the description of Brownian motion to include the effects of external force fields (such as gravity or electric fields). This resulted in the Smoluchowski equation, a specific form of the Fokker-Planck equation:

$$\frac{\partial P}{\partial t} = \nabla \cdot \left[D\nabla P - \frac{\mathbf{F}}{\gamma} P\right] \tag{5.25}$$

where P is the probability density, D is the diffusion coefficient, and $\mathbf{F}$ is the external force. This remains a fundamental tool in soft matter physics and chemical kinetics.

3. Verification of the Atomic Hypothesis

Smoluchowski was a fierce defender of the atomistic view of matter. Along with Einstein and Jean Perrin, his work provided the theoretical "smoking gun" that atoms actually existed. By showing that macroscopic fluctuations (Brownian motion) were the

direct result of microscopic "graininess" (atoms), he helped defeat the "Energisist" school of thought.

4. Theory of Coagulation

Smoluchowski applied his Brownian motion theories to the study of colloids. He developed the first mathematical description of how particles in a suspension collide and stick together-a process known as Smoluchowski coagulation. This is still the standard model for understanding the stability of aerosols and colloidal suspensions.

Summary Comparison

Feature	Einstein (1905)	Smoluchowski (1906)
Primary Tool	Thermodynamics & Diffusion	Kinetic Theory & Random Walks
Perspective	Macroscopic/Statistical	Microscopic/Statistical
Key Result	$D = \frac{kT}{6\pi\eta a}$	Nearly identical result via collisions
Main Impact	Founded the theory of fluctuations	Linked diffusion to molecular scale

5.7 The Langevin Equation

In 1908 Langevin [7] introduced the "Equation of Motion" method, which is, Langevin's approach is notably different from Einstein's (1905) or Smoluchowski's (1906). While Einstein used a diffusion equation approach, Langevin introduced a stochastic differential equation,

$$m\frac{d^2x}{dt^2} = -6\pi\eta a\frac{dx}{dt} + X \tag{5.26}$$

where X is the the stochastic force. This paper is the formal birth of the Langevin Equation. EquationEquation 5.26 is generally recast in a more familiar form as

$$m\dot{v} = -\gamma v + \xi(t), \tag{5.27}$$

where $\xi(t)$ is a rapidly fluctuating force. The second Fluctuation-Dissipation Theorem relates $< \xi(t)\xi(0) >$ to the damping γ or the generalized memory function $\gamma(t)$. We will discuss this in more detail in the following chapters, especially those on Noise, Magalinski's model and Mori-Zwanzig formulation of the generalized Langevin equation.

5.8 Derivation of the Diffusion Equation result from the Langevin Equation

The Langevin equation provides a microscopic description of Brownian motion. We derive the macroscopic diffusion equation by considering the stochastic evolution of a particle's position using the specific notation $m\dot{v} = -\gamma v + \xi(t), \gamma$ is the friction coefficient and $\xi(t)$ is the stochastic force (random noise).

The random force $\xi(t)$ is assumed to be Gaussian, white, noise with the properties:

$$\langle \xi(t) \rangle = 0, \quad \langle \xi(t)\xi\left(t'\right) \rangle = 2\gamma k_B T\delta\left(t - t'\right) \tag{5.28}$$

For the Generalized Langevin Equation, GLE, the damping is time dependent and the equation above, Eq. 5.28 becomes

$$\langle \xi(t) \rangle = 0, \quad \langle \xi(t)\xi\left(t'\right) \rangle = 2\gamma k_B T\gamma\left(t - t'\right) \tag{5.29}$$

Equation 5.29 is called the second fluctuation-dissipation theorem[4]. It will be proven classically from classical mechanics in the chapter on Noise.

5.9 The Over-damped Limit

In the limit of high friction or long times $(t \gg m/\gamma)$, the inertial term $m\dot{v}$ is neglected. Equation 5.27 simplifies to:

$$\gamma v(t) = \xi(t) \Longrightarrow \frac{dx}{dt} = \frac{1}{\gamma}\xi(t) \tag{5.30}$$

5.10 Statistical Moments

For a small time interval Δt, the change in position is:

$$\Delta x = \int_t^{t+\Delta t} \frac{1}{\gamma}\xi\left(t'\right) dt' \tag{5.31}$$

The first and second moments are:

$$\langle \Delta x \rangle = 0 \tag{5.32}$$

$$\left\langle (\Delta x)^2 \right\rangle = \frac{1}{\gamma^2}\int_t^{t+\Delta t}\int_t^{t+\Delta t} \left\langle \xi\left(t'\right)\xi\left(t''\right)\right\rangle dt' dt'' = \frac{2\gamma k_B T}{\gamma^2}\Delta t = \frac{2k_B T}{\gamma}\Delta t \tag{5.33}$$

Here we have used Eq. (5.28

Defining the diffusion coefficient $D = \frac{k_B T}{\gamma}$, we arrive at the diffusion equation result:

$$\left\langle (\Delta x)^2 \right\rangle = D\Delta t \tag{5.34}$$

5.11 Modern Interpretation

Equation 5.7 defines a continuous-time Markov process. Taking the limit $\tau \to 0$ yields the generator

$$\mathcal{L} = D\frac{\partial^2}{\partial x^2}. \tag{5.35}$$

The diffusion equation is the corresponding Fokker-Planck equation.

More generally, expansion of Equation 5.7 yields the Kramers-Moyal series. Einstein's derivation truncates at second order because the increment distribution has finite variance.

Thus Brownian motion is the scaling limit of a random walk with independent increments, anticipating later work by Wiener and Kolmogorov.

5.12 The Master Equation (Discrete States)

For systems with discrete states (e.g., energy levels), we define $P_n(t)$ as the probability of being in state n. By defining transition rates w_{nm} (probability per unit time of $m \to n$), we derive the "probability balance":

$$\frac{dP_n(t)}{dt} = \sum_{m \neq n} [\underbrace{w_{nm}P_m(t)}_{\text{Gain}} - \underbrace{w_{mn}P_n(t)}_{\text{Loss}} \tag{5.36}$$

5.13 Connecting the Two: The Kramers-Moyal Expansion

To bridge the discrete Master Equation and the continuous Fokker-Planck Equation, we consider transitions $w(x, z)$ where z is the jump size. The continuous Master Equation is:

$$\frac{\partial P(x,t)}{\partial t} = \int [w(x-z,z)P(x-z,t) - w(x,-z)P(x,t)]dz$$

Expanding the integrand $w(x-z,z)P(x-z,t)$ as a Taylor series in z :

$$\frac{\partial P(x,t)}{\partial t} = \sum_{n=1}^{\infty} \frac{(-1)^n}{n!}\frac{\partial^n}{\partial x^n}\left[a_n(x)P(x,t)\right]$$

where the jump moments are $a_n(x) = \int z^n w(x,z)dz$.

5.14 The Fokker-Planck Equation

Truncating the expansion at $n = 2$ (the Diffusion limit) yields the general framework for particles under external forces:

$$\frac{\partial P(x,t)}{\partial t} = -\frac{\partial}{\partial x}[A(x,t)P(x,t)] + \frac{\partial^2}{\partial x^2}[B(x,t)P(x,t)] \tag{5.37}$$

- Drift Term $A(x,t)$: Corresponds to $a_1(x)$, the average velocity due to external forces.
- Diffusion Term $B(x,t)$: Corresponds to $a_2(x)/2$, the stochastic spreading.

5.15 Conceptual Significance

Einstein's theory achieved several conceptual breakthroughs:

- Introduction of probabilistic evolution laws in physics.
- Derivation of irreversible macroscopic behavior from statistical independence.
- First quantitative link between fluctuation strength and dissipative transport coefficient.
- Establishment of diffusion as a universal scaling limit.

The modern theory of stochastic processes, linear response, and nonequilibrium statistical mechanics can be traced to this 1905 paper.

5.16 Conclusion

Einstein's treatment of Brownian motion marks the birth of Markovian stochastic dynamics in physics. From a simple assumption of independent increments, he derived the diffusion equation and connected fluctuations to dissipation through thermodynamic reasoning.

This synthesis of probability theory and physics laid the foundation for stochastic differential equations, Fokker-Planck theory, and the fluctuation-dissipation framework that underlies modern statistical mechanics.

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6: Power Balance and the Necessity of Dissipation- Pedagogical Derivation of the Generalized Langevin Equation

The well-known power absorption formula shows that an undamped oscillator undergoes an "energy catastrophe" due to resonant singularities, i.e., the system energy grows linearly in time, without bound, violating the postulates of equilibrium statistical mechanics. An undamped oscillator driven by stochastic forcing absorbs power at a constant rate, leading to $\langle E \rangle \propto t \to \infty$, which contradicts the finite energy expected in thermal equilibrium. A calculation using the generalized Langevin equation (GLE) shows that the memory-dependent damping kernel regulates the susceptibility to arrest energy growth through exact frequency-by-frequency power balance. Under the fluctuation-dissipation theorem, this mechanism naturally recovers the equipartition theorem $\langle E \rangle = k_B T$, demonstrating that dissipation is not merely phenomenological but rather a thermodynamic necessity for systems in thermal contact.

6.1 Introduction

The interplay between fluctuations and dissipation lies at the heart of non-equilibrium statistical mechanics. A fundamental question concerns the mechanism by which macroscopic systems driven by random forces reach steady states. Phenomenologically, one introduces damping forces to model energy dissipation [4, 5]; however, the deeper connection between stochastic driving and dissipative response reveals a more profound principle: dissipation is not an independent ingredient but rather emerges as a thermodynamic necessity for maintaining equilibrium in the presence of fluctuations.

A particularly transparent framework for studying this balance is provided by the harmonic oscillator subjected to stochastic forcing. The linearity of the system allows the response to be characterized entirely by a frequency-dependent susceptibility. This enables exact derivations of energy balance relations in frequency space and precise identification of the mechanisms preventing unbounded energy growth.

A direct model going from microscopic Newtonian motion to macroscopic dissipative equations was given in a landmark paper by Magalinski [1] in 1959. Magalinski solved a mechanical model of the motion of a harmonic oscillator which is coupled to N other harmonic oscillators and showed that it undergoes Brownian motion, i.e., obeys the generalized Langevin equation [4] with a non-Markovian memory kernel. This stands in contrast to heuristic derivations of the Langevin equation where a stochastic force and a dissipative drag are postulated. Magalinski's model derives these effects analytically.

The rigorous, model-independent derivation of the GLE typically uses projection operator

techniques [3, 2]. While rigorous, these methods can obscure the fundamental physical requirement that links dissipation to thermal fluctuations.

Here, we adopt a complementary pedagogical route: we demonstrate that the structure of the GLE, including the crucial relationship between the damping kernel and the noise spectrum, follows uniquely from fundamental principles of energy balance, stationarity, and causality.

Our analysis proceeds as follows. First, using the well-known power dissipation formula, we demonstrate the "energy catastrophe" that befalls an undamped oscillator: resonant singularities in the susceptibility lead to infinite power absorption and linear energy growth, violating equilibrium. Second, we show how the GLE introduces a frequency-dependent dissipation mechanism that exactly balances stochastic energy injection at every frequency, ensuring a stable thermal state consistent with the fluctuation-dissipation theorem. For completeness, we provide a derivation of the general spectral form of power injection for linear systems. In Appendix, we prove the well-known result that only the imaginary (dissipative) part of the susceptibility contributes to net energy absorption. The logical chain connecting these results is summarized in Table 6.1.

This work is intended to provide both pedagogical value for students entering the field and conceptual clarity for researchers: dissipation emerges not as an ad hoc phenomenological addition but as a logical consequence of demanding thermodynamic consistency.

Table 6.1: Summary of the logical chain from susceptibility structure to thermodynamic consistency.

System	Susceptibility	Consequence
Undamped oscillator	$\mathrm{Im}[\chi(\omega)] \propto \delta(\omega \pm \omega_0)$	Energy catastrophe: $\langle E \rangle \to \infty$
GLE (general)	Finite $\mathrm{Im}[\chi(\omega)]$	Exact power balance: $\langle P \rangle = 0$
GLE + FDT	$S_F(\omega) = 2k_B T \tilde{\gamma}'(\omega)$	Equipartition: $\langle E \rangle = k_B T$

6.2 Fourier and Spectral Conventions

We adopt the following Fourier transform pair for a time-dependent function $F(t)$:

$$F(\omega) = \int_{-\infty}^{\infty} dt F(t) e^{i\omega t} \tag{6.1}$$

$$F(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} F(\omega) e^{-i\omega t} \tag{6.2}$$

This convention is symmetric and facilitates the treatment of both positive and negative frequencies on equal footing.

For a wide-sense stationary stochastic process, the autocorrelation function depends only on the time difference:

$$C_F(\tau) = \langle F(t+\tau) F(t) \rangle, \tag{6.3}$$

where $\langle \cdot \rangle$ denotes the ensemble average. According to the Wiener-Khinchin theorem [6], the two-sided power spectral density (PSD) $S_F(\omega)$ is defined as:

$$S_F(\omega) = \int_{-\infty}^{\infty} d\tau C_F(\tau) e^{i\omega\tau} \tag{6.4}$$

Note the sign convention: with our forward Fourier transform using $e^{i\omega t}$, consistency requires the PSD to also use $e^{i\omega\tau}$. This ensures proper matching in the spectral correlation identity derived below.

An important consequence of stationarity is the spectral correlation identity. For a stationary process, taking the Fourier transforms of $F(t)$ at two different frequencies ω and ω' and using Equation 6.3, one obtains:

$$\begin{aligned} \langle F(\omega) F(\omega') \rangle &= \iint dt dt' e^{i\omega t} e^{i\omega' t'} \langle F(t) F(t') \rangle \\ &= \int d\tau e^{i\omega\tau} C_F(\tau) \int dt' e^{i(\omega+\omega')t'} \\ &= 2\pi \delta(\omega + \omega') S_F(\omega) \end{aligned} \tag{6.5}$$

This result, which follows directly from the stationarity condition (which implies $C_F(t, t') = C_F(t - t')$) and the definitions above (see, e.g., Ref. [6]), will be used in Sec. 6.4 to evaluate the average injected power. Note that this identity is distinct from the Wiener-Khinchin theorem itself; it is a consequence of stationarity in the two-frequency domain.

6.3 Linear Response and Susceptibility

Consider a causal linear system where the displacement $x(t)$ responds to an external force $F(t)$ via a retarded Green's function $\chi(t)$:

$$x(t) = \int_{-\infty}^{t} dt' \chi(t - t') F(t') . \tag{6.6}$$

The causality requirement states that $\chi(t) = 0$ for $t < 0$.

In frequency space:

$$x(\omega) = \chi(\omega) F(\omega), \tag{6.7}$$

where $\chi(\omega)$ is the susceptibility. The velocity is:

$$\dot{x}(\omega) = -i\omega\chi(\omega) F(\omega). \tag{6.8}$$

For a physical system with real-valued $\chi(t)$:

$$\chi(-\omega) = \chi^*(\omega), \tag{6.9}$$

implying $\mathrm{Re}[\chi(\omega)]$ is even and $\mathrm{Im}[\chi(\omega)]$ is odd.

6.4 General Derivation of Injected Power

This formula is presented in most standard texts on statistical physics; see for example Landau and Lifshitz [7] (section 123 on generalized susceptibility), Martin [8], Cao [7], and Dattagupta [10]. An alternate derivation using linear response theory directly is given in Appendix.

The instantaneous power injected by the stochastic force is $P_{\text{in}}(t) = \dot{x}(t) F(t)$. For a stationary process:

$$\langle P_{\text{in}} \rangle = \langle \dot{x}(t) F(t) \rangle. \tag{6.10}$$

Writing $\dot{x}(t)$ and $F(t)$ as inverse Fourier transforms and using the spectral correlation identity Equation 6.5:

$$\langle P_{\text{in}} \rangle = \int \frac{d\omega}{2\pi} \int \frac{d\omega'}{2\pi} e^{-i(\omega+\omega')t} \left\langle \dot{x}(\omega) F(\omega') \right\rangle. \tag{6.11}$$

Substituting $\dot{x}(\omega) = -i\omega\chi(\omega) F(\omega)$ and applying Equation 6.5:

$$\left\langle \dot{x}(\omega) F(\omega') \right\rangle = -i\omega\chi(\omega) \left\langle F(\omega) F(\omega') \right\rangle = -i\omega\chi(\omega) \cdot 2\pi\delta(\omega + \omega') S_F(\omega). \tag{6.12}$$

Integrating over ω' using the delta function:

$$\langle P_{\text{in}} \rangle = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} (-i\omega)\chi(\omega) S_F(\omega). \tag{6.13}$$

6.4.1 Parity analysis

Writing $\chi(\omega) = \chi'(\omega) + i\chi''(\omega)$, where χ' is even and χ'' is odd:

$$-i\omega\left[\chi' + i\chi''\right] S_F = \left[-i\omega\chi' + \omega\chi''\right] S_F. \tag{6.14}$$

Since $S_F(\omega)$ is real and even (because $C_F(\tau)$ is real and even), the term $-i\omega\chi'(\omega) S_F(\omega)$ is purely imaginary and odd (product of odd ω and even functions), and integrates to zero. The term $\omega\chi''(\omega) S_F(\omega)$ is real and even (product of two odd functions and an even function) and gives the net contribution.

This can be seen from the parity table:

Term	Components	Parity product	Net parity
$-i\omega\chi' S_F$	ω (odd) × χ' (even) × S_F (even)	odd × even × even	odd (vanishes)
$\omega\chi'' S_F$	ω(odd) × χ''(odd) × S_F(even)	odd × odd × even	even (survives)

Therefore:

$$\langle P_{\text{in}} \rangle = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \omega\, \mathrm{Im}[\chi(\omega)] S_F(\omega). \tag{6.15}$$

This fundamental result shows that energy absorption is controlled exclusively by the imaginary (dissipative) part of the

susceptibility.

6.5 The Undamped Energy Catastrophe

For an undamped harmonic oscillator:

$$m\ddot{x}(t) + m\omega_0^2 x(t) = F(t), \tag{6.16}$$

the susceptibility is formally:

$$\chi_0(\omega) = \frac{1}{m\left(\omega_0^2 - \omega^2\right)}. \tag{6.17}$$

6.5.1 Causal prescription

To satisfy causality, we introduce infinitesimal damping:

$$\chi_0(\omega) = \lim_{\epsilon \to 0^+} \frac{1}{m\left(\omega_0^2 - \omega^2 - i\epsilon\omega\right)}. \tag{6.18}$$

Applying the Sokhotski-Plemelj theorem [11, 12]:

$$\lim_{\epsilon \to 0^+} \frac{1}{x - i\epsilon} = \mathcal{P}\left(\frac{1}{x}\right) + i\pi\delta(x), \tag{6.19}$$

we first perform a partial fraction decomposition of the susceptibility. Writing $\omega_0^2 - \omega^2 = (\omega_0 - \omega)(\omega_0 + \omega)$ and treating the $i\epsilon\omega$ term to leading order in ϵ :

$$\chi_0(\omega) = \lim_{\epsilon \to 0^+} \frac{1}{m(\omega_0 - \omega)(\omega_0 + \omega) - i\epsilon\omega}. \tag{6.20}$$

Near $\omega \approx +\omega_0$ the factor $(\omega_0 + \omega) \approx 2\omega_0$, and near $\omega \approx -\omega_0$ the factor $(\omega_0 - \omega) \approx 2\omega_0$. We decompose into simple poles by writing:

$$\frac{1}{(\omega_0 - \omega)(\omega_0 + \omega)} = \frac{1}{2\omega_0}\left(\frac{1}{\omega_0 - \omega} + \frac{1}{\omega_0 + \omega}\right), \tag{6.21}$$

which can be verified immediately by combining the right-hand side over the common denominator $(\omega_0 - \omega)(\omega_0 + \omega)$. Incorporating the $i\epsilon$ prescription consistently at each pole (the sign of i $\epsilon\omega$ at $\omega \approx +\omega_0$ is positive, and at $\omega \approx -\omega_0$ is negative), the full causal expression becomes:

$$\chi_0(\omega) = \lim_{\epsilon \to 0^+} \frac{1}{2m\omega_0}\left[\frac{1}{\omega_0 - \omega - i\epsilon} + \frac{1}{\omega_0 + \omega + i\epsilon}\right]. \tag{6.22}$$

Applying Equation 6.19 to each term:

$$\frac{1}{\omega_0 - \omega - i\epsilon} \to \mathcal{P}\frac{1}{\omega_0 - \omega} + i\pi\delta(\omega_0 - \omega), \tag{6.23}$$

$$\frac{1}{\omega_0 + \omega + i\epsilon} \to \mathcal{P}\frac{1}{\omega_0 + \omega} - i\pi\delta(\omega_0 + \omega), \tag{6.24}$$

where the sign difference in the delta term in Equation ??? arises because the $i\epsilon$ appears with the opposite sign, so the Plemelj formula gives $-i\pi\delta$ rather than $+i\pi\delta$.

Taking the imaginary part of χ_0 and using $\delta(\omega_0 - \omega) = \delta(\omega - \omega_0)$:

$$\mathrm{Im}\left[\chi_0(\omega)\right] = \frac{\pi}{2m\omega_0}\left[\delta(\omega - \omega_0) - \delta(\omega + \omega_0)\right]. \tag{6.25}$$

This sign structure is essential: it ensures $\omega\,\mathrm{Im}\left[\chi_0(\omega)\right] \geq 0$ everywhere, which is required for the power absorbed to be non-negative.

6.5.2 Power and energy growth

Substituting Equation 6.25 into Equation 6.15 and evaluating each delta function contribution separately:

$$\begin{aligned}\langle P_{\text{in}}\rangle &= \int \frac{d\omega}{2\pi}\omega\cdot\frac{\pi}{2m\omega_0}\left[\delta\left(\omega-\omega_0\right)-\delta\left(\omega+\omega_0\right)\right]S_F(\omega)\\ &= \frac{1}{4m\omega_0}\left[\omega_0 S_F\left(\omega_0\right)-\left(-\omega_0\right)S_F\left(-\omega_0\right)\right]\\ &= \frac{1}{4m\omega_0}\left[\omega_0 S_F\left(\omega_0\right)+\omega_0 S_F\left(-\omega_0\right)\right]\\ &= \frac{S_F\left(\omega_0\right)}{2m},\end{aligned} \tag{6.26}$$

where in the last step we used $S_F\left(-\omega_0\right)=S_F\left(\omega_0\right)$ (since S_F is even).

Since $S_F\left(\omega_0\right)>0$, the energy grows linearly:

$$\langle E(t)\rangle = \langle E(0)\rangle + \langle P_{\text{in}}\rangle\cdot t\to\infty. \tag{6.27}$$

This energy catastrophe violates equilibrium statistical mechanics, demonstrating that dissipation is thermodynamically necessary.

6.6 The Generalized Langevin Equation

The GLE incorporates memory-dependent damping:

$$m\ddot{x}(t)+m\omega_0^2 x(t)+\int_{-\infty}^{t}\gamma\left(t-t'\right)\dot{x}\left(t'\right)dt'=F(t). \tag{6.28}$$

6.6.1 Susceptibility

In frequency space, the susceptibility takes the form:

$$\chi(\omega)=\frac{1}{m\left(\omega_0^2-\omega^2\right)-i\omega\tilde{\gamma}(\omega)}, \tag{6.29}$$

where we define the one-sided Fourier transform of the memory kernel:

$$\tilde{\gamma}(\omega)=\int_0^\infty \gamma(t)e^{i\omega t}dt \tag{6.30}$$

Because $\gamma(t)$ is real, we have the symmetry $\tilde{\gamma}(-\omega)=\tilde{\gamma}^*(\omega)$.

Writing $\tilde{\gamma}(\omega)=\tilde{\gamma}'(\omega)+i\tilde{\gamma}''(\omega)$ with $\tilde{\gamma}'=\mathrm{Re}[\tilde{\gamma}]$ and $\tilde{\gamma}''=\mathrm{Im}[\tilde{\gamma}]$, the denominator of Equation ??? becomes:

$$D(\omega)=\left[m\left(\omega_0^2-\omega^2\right)+\omega\tilde{\gamma}''(\omega)\right]-i\omega\tilde{\gamma}'(\omega). \tag{6.31}$$

Taking the imaginary part of $\chi=1/D$:

$$\mathrm{Im}[\chi(\omega)]=\frac{\omega\tilde{\gamma}'(\omega)}{|D(\omega)|^2}=\omega\tilde{\gamma}'(\omega)|\chi(\omega)|^2. \tag{6.32}$$

Note that $|D(\omega)|^2=\left[m\left(\omega_0^2-\omega^2\right)+\omega\tilde{\gamma}''(\omega)\right]^2+\omega^2\left[\tilde{\gamma}'(\omega)\right]^2$, which in general includes a contribution from the imaginary part $\tilde{\gamma}''(\omega)$ of the memory kernel. Only in the Markovian limit $\gamma(t)=\gamma\delta(t)$ does $\tilde{\gamma}''=0$ exactly.

6.6.2 Dissipated power

We now derive the dissipated power explicitly. The friction force in the GLE is $F_\gamma(t)=-\int_{-\infty}^{t}\gamma\left(t-t'\right)\dot{x}\left(t'\right)dt'$, so the

instantaneous power dissipated is:

$$P_{\text{diss}}(t) = \dot{x}(t)F_\gamma(t) = -\dot{x}(t)\int_{-\infty}^{t} \gamma\left(t-t'\right)\dot{x}\left(t'\right)dt' \tag{6.33}$$

Taking the ensemble average and using stationarity with $\tau = t - t' \geq 0$:

$$\langle P_{\text{diss}}\rangle = -\int_0^\infty \gamma(\tau)\langle \dot{x}(t)\dot{x}(t-\tau)\rangle d\tau \tag{6.34}$$

Expressing the velocity correlator via its spectral density $S_{\dot{x}}(\omega) = \omega^2|\chi(\omega)|^2 S_F(\omega)$ and applying the same Parseval/Fourier analysis as above, the friction force in frequency space is:

$$F_\gamma(\omega) = -i\omega\tilde{\gamma}(\omega)x(\omega) = -i\omega\tilde{\gamma}(\omega)\chi(\omega)F(\omega). \tag{6.35}$$

Then:

$$\begin{aligned}\langle P_{\text{diss}}\rangle &= -\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\tilde{\gamma}^*(\omega)\omega^2|\chi(\omega)|^2 S_F(\omega)\\ &= -\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\omega^2\,\mathrm{Re}[\tilde{\gamma}(\omega)]|\chi(\omega)|^2 S_F(\omega)\\ &= -\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\omega^2\tilde{\gamma}'(\omega)|\chi(\omega)|^2 S_F(\omega)\end{aligned} \tag{6.36}$$

where the imaginary part of $\tilde{\gamma}(\omega)$ drops out upon integration because the resulting integrand is odd. Comparing with Eqs. Equation 6.15 and Equation 6.32:

$$\langle P_{\text{in}}\rangle = \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\omega^2\tilde{\gamma}'(\omega)|\chi(\omega)|^2 S_F(\omega). \tag{6.37}$$

6.6.3 Power balance

The total average power is the sum of injected and dissipated contributions:

$$\begin{aligned}\langle P\rangle &= \langle P_{\text{in}}\rangle + \langle P_{\text{diss}}\rangle\\ &= \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\omega^2\tilde{\gamma}'(\omega)|\chi(\omega)|^2 S_F(\omega) - \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\omega^2\tilde{\gamma}'(\omega)|\chi(\omega)|^2 S_F(\omega) = 0\end{aligned} \tag{6.38}$$

Here $\langle P_{\text{diss}}\rangle$ is defined as negative (energy leaving the system via friction), so the balance $\langle P\rangle = 0$ means power injected by the noise is exactly removed by the friction force. Therefore:

$$\langle P_{\text{in}}\rangle + \langle P_{\text{diss}}\rangle = 0. \tag{6.39}$$

This balance holds frequency by frequency, not merely in total, preventing the energy catastrophe.

6.6.4 The general principle

This confirms that the form of the GLE with a memory kernel is consistent with energy balance for any noise spectrum $S_F(\omega)$. However, the specific forms of $\tilde{\gamma}(\omega)$ and $S_F(\omega)$ are fixed by the fluctuation-dissipation theorem, as we show in the next section.

6.7 Equipartition from the FDT

The fluctuation-dissipation theorem (FDT) [4] relates the noise power spectrum to the dissipative part of the memory kernel:

$$S_F(\omega) = 2k_B T\tilde{\gamma}'(\omega). \tag{6.40}$$

This is sometimes called the "second fluctuation-dissipation theorem" to distinguish it from the Kubo relation (the "first" FDT) connecting the equilibrium correlation function of a dynamical variable to the corresponding linear response function [4]. Both

forms express the same underlying principle: the bath fluctuations that drive the system are precisely matched to the dissipation they cause.

6.7.1 Markovian limit

For $\gamma(t) = \gamma\delta(t)$, the memory kernel is instantaneous and $\tilde{\gamma}(\omega) = \gamma$ (real, frequency-independent). Then $\tilde{\gamma}'' = 0$ and:

$$\chi(\omega) = \frac{1}{m\left(\omega_0^2 - \omega^2\right) - i\omega\gamma}. \tag{6.41}$$

The mean kinetic energy is:

$$\langle T\rangle = \frac{m}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\omega^2|\chi(\omega)|^2 S_F(\omega). \tag{6.42}$$

Substituting Equation ??? with $\tilde{\gamma}'(\omega) = \gamma$:

$$\langle T\rangle = \frac{m}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\omega^2\frac{2k_BT\gamma}{\left[m\left(\omega_0^2 - \omega^2\right)\right]^2 + \omega^2\gamma^2} \tag{6.43}$$

Simplifying:

$$\langle T\rangle = \frac{k_BT\gamma}{2\pi}\int_{-\infty}^{\infty}\frac{\omega^2 d\omega}{\left(\omega_0^2 - \omega^2\right)^2 + \left(\gamma^2/m^2\right)\omega^2}. \tag{6.44}$$

Note that the damping coefficient in the denominator appears as γ/m; for notational simplicity, we absorb m into γ in what follows (or equivalently, set $m = 1$ temporarily and restore dimensions at the end). With this understanding, we evaluate:

$$I = \int_{-\infty}^{\infty}\frac{\omega^2 d\omega}{\left(\omega_0^2 - \omega^2\right)^2 + \gamma^2\omega^2} \tag{6.45}$$

The integral is evaluated by contour methods. The integrand $f(z) = z^2/\left[\left(z^2 - \omega_0^2\right)^2 + \gamma^2 z^2\right]$ has poles where $m\left(\omega_0^2 - \omega^2\right) - i\omega\gamma = 0$, i.e., at:

$$z = \pm\sqrt{\omega_0^2 - \gamma^2/4} - i\gamma/2 \quad \text{(underdamped case)}. \tag{6.46}$$

Both poles lie in the lower half of the complex ω-plane (negative imaginary parts), consistent with causality. Closing the contour in the upper half-plane (where the integrand vanishes) encloses no poles, so we instead close in the lower half-plane and pick up residues at the two poles. A standard residue calculation [11, 12] gives:

$$I = \frac{\pi}{\gamma}. \tag{6.47}$$

For completeness, this result can also be verified by partial fractions, writing the denominator as $\left(\omega^2 - \omega_+^2\right)\left(\omega^2 - \omega_-^2\right)$ in the underdamped case $\omega_0 > \gamma/2$; the residues at both lower-half-plane poles sum to π/γ, independently of ω_0.

Therefore:

$$\langle T\rangle = \frac{k_BT\gamma}{2\pi}\cdot\frac{\pi}{\gamma} = \frac{k_BT}{2}. \tag{6.48}$$

Similarly, by the same contour integral (or by symmetry of the Lorentzian), $\langle V\rangle = \frac{1}{2}m\omega_0^2\left\langle x^2\right\rangle = k_BT/2$, giving:

$$\langle E\rangle = \langle T\rangle + \langle V\rangle = k_BT. \tag{6.49}$$

6.8 Discussion and Conclusions

The key results, summarized in Table 6.1, are:

- 1.Energy absorption is governed exclusively by $\mathrm{Im}[\chi(\omega)]$ [Equation 6.15], a consequence of parity alone.
- 2.Undamped oscillators exhibit divergent energy growth [Equation 6.27], violating equilibrium - the "energy catastrophe."
- 3.The GLE provides exact, frequency-by-frequency power balance [Equation 6.39], derived explicitly from both the injected and dissipated power contributions.
- 4.Under the FDT, equipartition emerges naturally [Equation 6.49], with the result $\langle E \rangle = k_B T$ confirmed via contour integration.

Our analysis demonstrates that, although dissipation is generally introduced as a phenomenological term, it turns out to be a thermodynamic necessity: without it, any oscillator coupled to a thermal reservoir would accumulate energy without bound. The GLE with a memory kernel provides the unique consistent framework that avoids this catastrophe and yields thermodynamically correct steady states.

A standard undamped oscillator driven by stochastic forcing undergoes an energy catastrophe. Because it lacks a mechanism to shed energy, the resonant singularities in the susceptibility cause the average energy to grow linearly in time:

$$\langle E(t) \rangle \propto t \to \infty. \tag{6.50}$$

This naturally violates the Equipartition Theorem, which requires $\langle E \rangle = k_B T$. This chapter demonstrates that the GLE introduces a memory-dependent damping kernel $\gamma(t)$ that regulates energy growth through exact frequency-by-frequency power balance.

The most significant intuitive takeaway is that absorption (energy in) and dissipation (energy out) are two sides of the same coin: both are governed by the kernel $\tilde{\gamma}(\omega)$.

The heat bath acts as both a source of fluctuations and a sink for energy. The coupling strength $\tilde{\gamma}(\omega)$ between the system and the bath determines both roles:

- Dissipation: As the particle moves, it collides with bath molecules, transferring kinetic energy back to the bath (drag).
- Absorption: Even at rest, bath molecules "kick" the particle due to their thermal energy (noise).

The Generalized Langevin Equation ensures that the energy leaving the system is exactly balanced by the gateway for energy entering it, so that the system reaches a stable thermal state at temperature T.

Appendix I: Colored Noise and the Drude Memory Kernel

In the main text, we focused primarily on the Markovian limit where the friction is local in time. Here, we extend the analysis to a frequency-dependent (Drude) memory kernel and its corresponding "colored" noise spectrum.

6.8.1 The Drude Model for Memory

A common physical model for memory is the Drude-like exponential decay of the friction kernel:

$$\gamma(t) = \frac{\gamma_0}{\tau_c} e^{-t/\tau_c} \Theta(t), \tag{6.51}$$

where γ_0 is the static friction coefficient, τ_c is the correlation time of the bath, and $\Theta(t)$ is the Heaviside step function. In the limit $\tau_c \to 0$, we use the fact that $\frac{1}{\tau_c} e^{-t/\tau_c}$ acts as a delta sequence for $t \geq 0$, giving $\int_0^\infty \frac{1}{\tau_c} e^{-t/\tau_c} \phi(t) dt \to \phi(0)$ for any test function $\phi(t)$. Thus:

$$\gamma(t) \to \gamma_0 \delta(t) \quad (\tau_c \to 0)\,, \tag{6.52}$$

recovering the Markovian kernel with friction coefficient γ_0 (no additional factor of 2).

Taking the Fourier transform of Equation 6.51:

$$\begin{aligned} \tilde{\gamma}(\omega) &= \int_0^\infty \frac{\gamma_0}{\tau_c} e^{-t/\tau_c} e^{i\omega t} dt \\ &= \frac{\gamma_0}{\tau_c} \int_0^\infty e^{-(1/\tau_c - i\omega)t} dt \\ &= \frac{\gamma_0}{\tau_c} \cdot \frac{1}{1/\tau_c - i\omega} = \frac{\gamma_0}{1 - i\omega\tau_c}. \end{aligned} \tag{6.53}$$

The real (dissipative) part of the kernel is:

$$\tilde{\gamma}'(\omega) = \mathrm{Re}[\tilde{\gamma}(\omega)] = \frac{\gamma_0}{1+\omega^2\tau_c^2}. \tag{6.54}$$

6.8.2 Colored Noise (Ornstein-Uhlenbeck)

According to the FDT, Equation ???, the noise $F(t)$ must have a PSD proportional to $\tilde{\gamma}'(\omega)$:

$$S_F(\omega) = 2k_BT\tilde{\gamma}'(\omega) = \frac{2k_BT\gamma_0}{1+\omega^2\tau_c^2}. \tag{6.55}$$

This is the characteristic spectrum of the Ornstein-Uhlenbeck process. Unlike white noise, the power in colored noise rolls off at high frequencies ($\omega \gg 1/\tau_c$), reflecting the finite response time of the environment.

6.8.3 Verification of Power Balance

The susceptibility $\chi(\omega)$ for the Drude GLE is:

$$\chi(\omega) = \left[m\left(\omega_0^2 - \omega^2\right) - i\omega\left(\frac{\gamma_0}{1-i\omega\tau_c}\right)\right]^{-1}. \tag{6.56}$$

The injected power, using Equation 6.37, is:

$$\langle P_{\text{in}} \rangle = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\omega^2\tilde{\gamma}'(\omega)|\chi(\omega)|^2 S_F(\omega). \tag{6.57}$$

Substituting $S_F(\omega) = 2k_BT\tilde{\gamma}'(\omega)$:

$$\langle P_{\text{in}} \rangle = 2k_BT\int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\omega^2\left(\frac{\gamma_0}{1+\omega^2\tau_c^2}\right)^2|\chi(\omega)|^2. \tag{6.58}$$

By the same argument as in Sec. 6.6, the dissipated power $\langle P_{\text{diss}} \rangle$ involves the identical integral with a negative sign. The balance $\langle P_{\text{in}} \rangle + \langle P_{\text{diss}} \rangle = 0$ is thus satisfied frequency by frequency, even with the frequency-dependent damping $\tilde{\gamma}'(\omega)$.

6.8.4 Equipartition in the Non-Markovian Case

While the integrals are more complex, the equipartition theorem still holds. The mean kinetic energy is:

$$\langle T \rangle = \frac{m}{2}\int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\omega^2|\chi(\omega)|^2 S_F(\omega). \tag{6.59}$$

By substituting the Drude forms and using the method of residues, it can be shown that the contribution of the memory pole at $\omega = i/\tau_c$ exactly compensates for the modified response of the oscillator, yielding $\langle T \rangle = \frac{1}{2}k_BT$. This confirms that the spectral shape of the colored noise (the "color") is perfectly matched to the memory of the dissipation, preserving the thermodynamic state.

Appendix II: Alternate Derivation of Power Absorption

To provide an independent derivation of Equation 6.15, we use the linear response relation directly in the time domain. In a stationary process, the velocity can be written as:

$$\dot{x}(t) = \int_{-\infty}^{\infty} \dot{\chi}\left(t-t'\right)F\left(t'\right)dt' \tag{6.60}$$

where $\chi(t)$ is the retarded response function (satisfying $\chi(t) = 0$ for $t < 0$) and $\dot{\chi}$ denotes its time derivative. The upper limit is written as ∞ rather than t because causality ($\chi(\tau) = 0$ for $\tau < 0$) already enforces that only $t' \leq t$ contributes.

Therefore:

$$\langle F(t)\dot{x}(t)\rangle = \left\langle F(t)\int_{-\infty}^{\infty}\dot{\chi}\left(t-t'\right)F\left(t'\right)dt'\right\rangle. \tag{6.61}$$

By stationarity, $\langle F(t)F\left(t'\right)\rangle = C_F\left(t-t'\right)$, so:

$$\langle F(t)\dot{x}(t)\rangle = \int_{-\infty}^{\infty}\dot{\chi}\left(t-t'\right)C_F\left(t-t'\right)dt' \tag{6.62}$$

Changing variables to $\tau = t - t'$, and using the fact that $\dot{\chi}(\tau) = 0$ for $\tau < 0$, the lower limit is effectively 0:

$$\langle F(t)\dot{x}(t)\rangle = \int_{0}^{\infty}\dot{\chi}(\tau)C_F(\tau)d\tau \tag{6.63}$$

The right-hand side is a standard half-line integral of the product $\dot{\chi}(\tau)C_F(\tau)$. To pass to frequency space we note that, since $\dot{\chi}(\tau) = 0$ for $\tau < 0$, extending the lower limit to $-\infty$ introduces no new contribution:

$$\int_{0}^{\infty}\dot{\chi}(\tau)C_F(\tau)d\tau = \int_{-\infty}^{\infty}\dot{\chi}(\tau)C_F(\tau)d\tau. \tag{6.64}$$

This is simply a convolution evaluated at $\tau = 0$. By the convolution theorem and Parseval's relation:

$$\int_{-\infty}^{\infty}\dot{\chi}(\tau)C_F(\tau)d\tau = \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}(-i\omega)\chi(\omega)S_F(\omega). \tag{6.65}$$

Separating real and imaginary parts of $\chi(\omega) = \chi'(\omega) + i\chi''(\omega)$, and using the same parity argument as in Sec. 6.4, the χ' term is odd and vanishes, yielding:

$$\langle P_{\text{in}}\rangle = \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\omega\,\text{Im}[\chi(\omega)]S_F(\omega), \tag{6.66}$$

in agreement with Equation 6.15.

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7: Classical Linear Response Theory and the Kubo Formula

The preceding chapters established the statistical mechanics of equilibrium fluctuations. We now develop the dynamical theory: how a system responds to a weak external perturbation, and how that response is entirely encoded in the spontaneous equilibrium fluctuations. Three complementary routes to the same result are presented in sequence. First, we derive the Kubo formula directly from Liouville dynamics-the most fundamental and assumption-free path. Second, we approach the same physics through the Generalized Langevin Equation (GLE), making contact with friction kernels, noise, and causality. Third, we reverse the logic and show how the Kubo relation follows from the Fluctuation-Dissipation Theorem (FDT) together with the Wiener-Khinchin theorem, yielding the Green-Kubo relations for transport coefficients as a corollary. All three routes are classical; the quantum generalization is treated in the final chapter.

7.1 Correlation Functions, Susceptibility, and the FDT: Overview

The "memory" of a system's fluctuations is captured by the equilibrium auto-correlation function of an observable $A(t)$:

$$C(t) = \langle A(t)A(0)\rangle. \tag{7.1}$$

When a small time-dependent external force $h(t)$ couples linearly to A, the system's mean response is governed by the causal susceptibility $\chi(t)$:

$$\langle \Delta A(t)\rangle = \int_{-\infty}^{t} \chi\left(t-t'\right) h\left(t'\right) dt' \tag{7.2}$$

In the frequency domain, $\chi(\omega) = \chi'(\omega) + i\chi''(\omega)$; the imaginary part $\chi''(\omega) > 0$ represents the energy irreversibly dissipated by the system. In the classical limit $\hbar\omega \ll k_B T$, the FDT asserts:

$$\chi''(\omega) = \frac{\beta\omega}{2} S(\omega), \tag{7.3}$$

where $\beta = (k_B T)^{-1}$ and $S(\omega) = 2\int_0^\infty C(t)\cos(\omega t)dt$ is the one-sided power spectral density. The following three sections prove this relation by different methods, each illuminating a different facet of the physics.

7.2 Derivation I: Microscopic Route via Liouville Dynamics

7.2.1 Poisson Brackets and the Liouville Equation

We consider a classical system whose state is a point $\Gamma = (\mathbf{q}, \mathbf{p})$ in phase space. The Poisson bracket of two phase-space functions f and g is

$$\{f, g\} = \sum_i \left(\frac{\partial f}{\partial q_i}\frac{\partial g}{\partial p_i} - \frac{\partial f}{\partial p_i}\frac{\partial g}{\partial q_i} \right). \tag{7.4}$$

The phase-space probability density $\rho(\Gamma, t)$ evolves according to the Liouville equation:

$$\frac{\partial \rho}{\partial t} = \{H, \rho\} \equiv -L\rho, \tag{7.5}$$

where $L \equiv -\{H, \cdot\}$ is the Liouville operator. We apply a perturbation $\Delta H = -A(\Gamma)h(t)$, so the full Hamiltonian is $H = H_0 - Ah(t)$.

7.2.2 A Key Thermal Identity

The unperturbed equilibrium distribution is the canonical ensemble $\rho_0 = e^{-\beta H_0}/Z_{\text{part}}$, where $Z_{\text{part}} = \int e^{-\beta H_0(\Gamma)} d\Gamma$. Using the chain rule for Poisson brackets, $\{A, f(g)\} = (df/dg)\{A, g\}$, which follows from $\partial f(g)/\partial p_i = (df/dg)\left(\partial g/\partial p_i\right)$ and likewise for q_i, we compute

$$\{A,\rho_0\} = \left\{A, \frac{e^{-\beta H_0}}{Z_{\text{part}}}\right\} = \frac{1}{Z_{\text{part}}} \frac{d\left(e^{-\beta H_0}\right)}{dH_0} \{A, H_0\} = -\beta\rho_0 \{A, H_0\}. \tag{7.6}$$

Since Hamilton's equations give $\dot{A} = \{A, H_0\}$, this yields the fundamental thermal identity:

$$\{A,\rho_0\} = -\beta\rho_0\dot{A}. \tag{7.7}$$

7.2.3 First-Order Perturbation Theory

Writing $\rho(t) = \rho_0 + \Delta\rho(t)$ and linearising the Liouville equation in $h(t)$:

$$\frac{\partial\Delta\rho}{\partial t} = \{H_0, \Delta\rho\} + \{-Ah(t), \rho_0\}. \tag{7.8}$$

The second term becomes $h(t)\beta\rho_0\dot{A}$ via Equation 7.7. Solving with the propagator $e^{L_0(t-t')}$:

$$\Delta\rho(t) = \beta\rho_0 \int_{-\infty}^{t} h(t') \dot{A}(t'-t)\, dt' \tag{7.9}$$

The mean deviation $\langle\Delta A(t)\rangle = \int A(\Gamma)\Delta\rho(t)d\Gamma$. Shifting time evolution to the observable (passing to the Heisenberg picture) and using the stationarity of the equilibrium average:

$$\langle\Delta A(t)\rangle = \int_{-\infty}^{t} h(t')\, \beta \left\langle \dot{A}(0) A(t-t') \right\rangle_0 dt' \tag{7.10}$$

By time-translation invariance, $\frac{d}{dt}\langle A(0)A(t)\rangle = \langle A(0)\dot{A}(t)\rangle = -\langle\dot{A}(0)A(t)\rangle$, so we identify the susceptibility as

$$\chi(t-t') = -\beta\frac{d}{dt} C(t-t')\, \theta(t-t'). \tag{7.11}$$

This is the Kubo formula in the time domain: the linear response function is the negative β-scaled time derivative of the equilibrium correlation function, multiplied by the Heaviside step θ to enforce causality.

7.2.4 Connection to the Spectral Density

Taking the Fourier transform of Equation 7.11:

$$\chi(\omega) = -\beta \int_0^\infty \dot{C}(t) e^{i\omega t} dt \tag{7.12}$$

Integration by parts, with $C(\infty) \to 0$, gives $\chi(\omega) = \beta C(0) + i\omega\beta \int_0^\infty C(t)e^{i\omega t}dt$. The imaginary part is:

$$\chi''(\omega) = \omega\beta \int_0^\infty C(t)\cos(\omega t)dt = \frac{\beta\omega}{2} S(\omega) \tag{7.13}$$

recovering the classical FDT stated in Section 7.1. The quantum generalization, which replaces the factor $\beta\omega/2$ with $\left(1 - e^{-\beta\hbar\omega}\right)/(2\hbar)$, is treated in Kubo [4] and in the final chapter of this book.

7.3 Derivation II: The Generalized Langevin Equation Route

The Liouville derivation is exact but abstract. A complementary, more physical route proceeds through the stochastic equation of motion for a distinguished degree of freedom embedded in a thermal bath.

7.3.1 The Generalized Langevin Equation

Consider a particle of mass m in a harmonic potential with intrinsic frequency ω_0, subject to non-Markovian friction described by a memory kernel $\gamma(t)$ [3, 5, 3]. The equation of motion is:

$$m\ddot{x}(t) + m\omega_0^2 x(t) + m\int_{-\infty}^{t} \gamma\left(t-t'\right)\dot{x}\left(t'\right)dt' = F_{\text{ext}}(t) + f(t), \tag{7.14}$$

where $F_{\text{ext}}\ (t)$ is a deterministic external force and $f(t)$ is the random (fluctuating) force exerted by the bath. The memory kernel encodes the retarded friction: the drag at time t depends on the particle's velocity at all earlier times $t' < t$.

7.3.2 Mean Response and the Deterministic Equation

Taking the ensemble average of Eq. (B.10) and using $\langle f(t)\rangle = 0$, the mean displacement $\bar{x}(t) = \langle x(t)\rangle$ satisfies:

$$m\ddot{\bar{x}}(t) + m\omega_0^2\bar{x}(t) + m\int_{-\infty}^{t} \gamma\left(t-t'\right)\dot{\bar{x}}\left(t'\right)dt' = F_{\text{ext}}(t). \tag{7.15}$$

The random force drops out entirely at this level: it governs fluctuations, not the mean response. This separation is the point of departure for the two Fluctuation-Dissipation relations below.

7.3.3 Susceptibility and the Green's Function

The causal Green's function $G(t)$ (also called the response function) is defined as the mean displacement produced by an impulsive force $F_{\text{ext}}\ (t) = \delta(t)$, with $G(t) = 0$ for $t < 0$. The susceptibility is its one-sided Fourier transform:

$$\chi(\omega) = \int_0^\infty G(t)e^{i\omega t}dt \tag{7.16}$$

Fourier-transforming Equation 7.15 and denoting the transform of $\gamma(t)$ by $\tilde{\gamma}(\omega)$, one finds

$$\chi(\omega) = \frac{1}{m\left(\omega_0^2 - \omega^2\right) - i\omega m\tilde{\gamma}(\omega)}. \tag{7.17}$$

The complex mobility $\mu(\omega) = -i\omega\chi(\omega)$ relates the force to the mean velocity in the frequency domain.

7.3.4 The Two Fluctuation-Dissipation Relations

The noise $f(t)$, which vanishes on average, carries statistical information that is tightly constrained by thermal equilibrium.

Second FDT (noise-friction relation). The power spectral density of the random force, $S_{ff}(\omega) = \int_{-\infty}^{\infty}\langle f(t)f(0)\rangle e^{i\omega t}dt$, is related to the real part of the frequency-dependent friction by:

$$S_{ff}(\omega) = 2k_B T m\,\mathrm{Re}[\tilde{\gamma}(\omega)]. \tag{7.18}$$

This is the Second Fluctuation-Dissipation Theorem: the spectral density of the bath noise is proportional to the dissipative part of the friction kernel. For Markovian (white-noise) friction $\gamma(t) = 2\gamma_0\delta(t), \mathrm{Re}[\tilde{\gamma}] = \gamma_0$ and one recovers the Langevin relation $\langle f(t)f(0)\rangle = 2\gamma_0 k_B T\delta(t)$.

First FDT (Kubo formula for mobility). The complementary relation connects the response (mobility) to the equilibrium velocity autocorrelation:

$$\mu(\omega) = \frac{1}{k_B T}\int_0^\infty e^{i\omega t}\langle v(t)v(0)\rangle_{\text{eq}}\,dt \tag{7.19}$$

This is the First Fluctuation-Dissipation Theorem (equivalently, the Kubo formula for the mobility): the admittance of the system equals the β-weighted one-sided transform of the velocity autocorrelation. Taking $\omega \to 0$ yields the Einstein-Green-Kubo formula for the DC mobility, connecting it to the integral of the velocity autocorrelation.

7.3.5 Causality and the Kramers-Kronig Relations

Causality requires $G(t) = 0$ for $t < 0$. This condition is equivalent to $\chi(\omega)$ being analytic in the closed upper half of the complex frequency plane. By Cauchy's theorem applied to the contour integral of $\chi\left(\omega'\right)/\left(\omega' - \omega\right)$, one obtains the Kramers-Kronig relations:

$$\mathrm{Re}[\chi(\omega)] = \frac{2}{\pi}\mathcal{P}\int_0^\infty \frac{\omega' \,\mathrm{Im}\left[\chi\left(\omega'\right)\right]}{\omega'^2-\omega^2}d\omega', \tag{7.20}$$

$$\mathrm{Im}[\chi(\omega)] = -\frac{2\omega}{\pi}\mathcal{P}\int_0^\infty \frac{\mathrm{Re}\left[\chi\left(\omega'\right)\right]}{\omega'^2-\omega^2}d\omega', \tag{7.21}$$

where $\mathcal{P}$ denotes the Cauchy principal value. These relations are model-independent consequences of causality: a measurement of $\chi''(\omega)$ over all frequencies uniquely determines $\chi'(\omega)$, and vice versa. Combined with the FDT, they imply that the full equilibrium noise spectrum determines both the reactive and dissipative parts of the linear response.

7.4 Derivation III: From the FDT and Wiener-Khinchin to the Kubo Formula

The two preceding sections derived the FDT from microscopic dynamics. It is illuminating to run the argument in the opposite direction: assuming the classical FDT as a postulate (or as experimentally established), one can derive the Kubo relation and the Green-Kubo transport formulas. This route is the one most directly useful for practical calculations.

7.4.1 Starting Point: The Classical FDT

In the classical limit $k_BT \gg \hbar\omega$, the FDT relates the power spectral density $S_{AA}(\omega)$ of an observable $A(t)$ to the dissipative part of the susceptibility:

$$S_{AA}(\omega) = \frac{2k_BT}{\omega}\mathrm{Im}[\chi(\omega)]. \tag{7.22}$$

7.4.2 Spectral Density via the Wiener-Khinchin Theorem

The Wiener-Khinchin theorem [18, 19] states that the power spectral density is the Fourier transform of the equilibrium autocorrelation function $C_{AA}(t) = \langle A(t)A(0)\rangle$:

$$S_{AA}(\omega) = \int_{-\infty}^{\infty}\langle A(t)A(0)\rangle e^{i\omega t}dt \tag{7.23}$$

For a classical equilibrium system the correlation function is stationary and even, $C(t) = C(-t)$, so:

$$S_{AA}(\omega) = 2\,\mathrm{Re}\int_0^\infty \langle A(t)A(0)\rangle e^{i\omega t}dt = 2\int_0^\infty \langle A(t)A(0)\rangle\cos(\omega t)dt \tag{7.24}$$

7.4.3 Linear Response and Susceptibility

The mean response to an external force $f(t)$ linearly coupled to A is

$$\delta\langle A(t)\rangle = \int_{-\infty}^{t}\phi\left(t-t'\right)f\left(t'\right)dt' \tag{7.25}$$

where the response function $\phi(t)$ (causal, so $\phi(t) = 0$ for $t < 0$) is related to the susceptibility by

$$\chi(\omega) = \int_0^\infty \phi(t)e^{i\omega t}dt = \int_0^\infty \phi(t)[\cos(\omega t) + i\sin(\omega t)]dt \tag{7.26}$$

The dissipative part is therefore

$$\mathrm{Im}[\chi(\omega)] = \int_0^\infty \phi(t)\sin(\omega t)dt \tag{7.27}$$

7.4.4 The Kubo Relation in the Time Domain

Substituting Eqs. Equation 7.24 and Equation 7.27 into the FDT (A.29):

$$\int_{-\infty}^{\infty}\langle A(t)A(0)\rangle e^{i\omega t}dt=\frac{2k_BT}{\omega}\int_0^{\infty}\phi(t)\sin(\omega t)dt \tag{7.28}$$

Using the symmetry of $C(t)$ and inverting the Fourier relation (see, e.g., Zwanzig [3]), the time-domain identity for $t>0$ is the Kubo relation:

$$\phi(t)=-\frac{1}{k_BT}\frac{d}{dt}\langle A(t)A(0)\rangle. \tag{7.29}$$

This is the same result as Equation 7.11 derived from Liouville dynamics, now obtained by a purely spectral argument.

7.4.5 The Frequency-Domain Kubo Formula

Inserting Equation 7.29 into the definition of $\chi(\omega)$ and integrating by parts:

$$\chi(\omega)=\int_0^{\infty}\left(-\frac{1}{k_BT}\frac{d}{dt}\langle A(t)A(0)\rangle\right)e^{i\omega t}dt=\frac{1}{k_BT}\left[\langle A(0)^2\rangle+i\omega\int_0^{\infty}\langle A(t)A(0)\rangle e^{i\omega t}dt\right]. \tag{7.30}$$

Equation 7.30 is the standard frequency-domain Kubo formula: the susceptibility is the β -weighted Laplace transform of the correlation function.

7.4.6 Green-Kubo Relations for Transport Coefficients

For transport coefficients, one identifies the observable A with a current and takes the DC $(\omega\to 0)$ limit of Equation 7.30. For electrical conductivity, with $A=J$ (current density):

$$\sigma(\omega)=\frac{1}{Vk_BT}\int_0^{\infty}\langle J(t)J(0)\rangle e^{i\omega t}dt \tag{7.31}$$

which at $\omega=0$ reduces to the DC Green-Kubo formula $\sigma_{\mathrm{DC}}=(Vk_BT)^{-1}\int_0^{\infty}\langle J(t)J(0)\rangle dt$. Analogous formulas hold for viscosity, thermal conductivity, and diffusion coefficients, all expressible as time integrals of appropriate equilibrium current-current correlations.

7.5 Defining and Contrasting the Two Types of Fluctuation-Dissipation Theorems

The Fluctuation-Dissipation Theorem (FDT), pioneered by Ryogo Kubo, bridges the gap between microscopic fluctuations and macroscopic dissipative responses. In the context of the Generalized Langevin Equation (GLE), two distinct forms of the FDT are identified: the First Kind (1FDT) and the Second Kind (2FDT) [12].

7.5.1 The First Fluctuation-Dissipation Theorem (1FDT)

The 1FDT is rooted in Linear Response Theory (LRT). It establishes a direct relationship between the linear response of a system to a small external perturbation and the correlation of its spontaneous fluctuations in thermal equilibrium.

- Core Principle: It relates the generalized susceptibility (or mobility) of a system to the auto-correlation function of a physical observable (e.g., velocity).
- Physical Interpretation: This theorem validates Onsager's regression hypothesis-the idea that the relaxation of a system perturbed from equilibrium follows the same laws as the decay of a spontaneous, internal fluctuation.
- Mathematical Relation: For a classical system, the response function $\chi(t)$ is related to the equilibrium correlation function $C(t)$ by:

$$\chi(t)=-\beta\frac{d}{dt}C(t)\theta(t) \tag{7.32}$$

where $\beta=(k_BT)^{-1}$ and $\theta(t)$ is the Heaviside step function.

7.5.2 The Second Fluctuation-Dissipation Theorem (2FDT)

The 2FDT arises within the framework of the Generalized Langevin Equation (GLE) and is often referred to as the Generalized Nyquist Theorem.

- Core Principle: It relates the stochastic random force acting on a particle to the frictional memory kernel that characterizes the energy dissipation to the surrounding heat bath.
- Physical Interpretation: It ensures a balance between the random impacts from the environment (fluctuations) and the systematic drag (dissipation). This balance ensures the system reaches thermal equilibrium rather than heating up indefinitely.
- Mathematical Relation: The auto-correlation of the random force $F_{\text{ext}}(t)$ is proportional to the memory kernel $\gamma(t)$:

$$\langle F_{ext}(t)F_{ext}(0)\rangle = k_B T\gamma(t) \tag{7.33}$$

7.5.3 Contrast and Comparison

Table 7.1: Comparison between the First Kind (1FDT) and Second Kind (2FDT) fluctuationdissipation relations, highlighting their respective frameworks and physical roles.

Feature		First Kind (1FDT)	Second Kind (2FDT)
Primary work	Frame-	Linear Response Theory (LRT)	Generalized Langevin Equation (GLE)
Related ties	Quanti-	Response function vs. Correla- tion function	Random force vs. Memory kernel
Level of tion	Descrip-	Macro/Mesoscopic (Observable response)	Microscopic/Stochastic (Dynam- ics)
Equilibrium tus	Sta-	Relates non-equilibrium response to equilibrium fluctuations	Relates noise and friction within the heat bath
Robustness		Can break down far from equilib- rium	Often valid in non-equilibrium steady states

7.6 Summary and Logical Connections

The table below collects the key results of this chapter and their derivation routes.

7.7 Summary and Logical Connections

The table below collects the key results of this chapter and their derivation routes.

Table 7.2: Key results for linear response, fluctuation-dissipation relations, and their physical origins.

Result	Key equation	Origin
Thermal identity	$\{A, \rho_0\} = -\beta\rho_0\dot{A}$	Chain rule for Poisson brackets
Kubo formula (time domain)	$\chi(t) = -\beta\dot{C}(t)\theta(t)$	Liouville + first-order perturbation
Classical FDT	$\chi''(\omega) = \frac{\beta\omega}{2}S(\omega)$	Kubo formula + spectral decomposition
GLE susceptibility	Equation 7.17	Fourier transform of mean GLE
Second FDT	$S_{ff}(\omega) = 2k_B T m\,\mathrm{Re}[\tilde{\gamma}(\omega)]$	Equilibrium constraint on noise
First FDT (mobility)	$\mu(\omega) = \beta\int_0^\infty \langle vv\rangle e^{i\omega t}dt$	Kubo formula for velocity
Kramers-Kronig	Eqs. (A.17)-(A.18)	Causality (analyticity in upper half-plane)
Kubo relation (from FDT)	$\phi(t) = -(k_B T)^{-1}\dot{C}(t)$	FDT + Wiener-Khinchin (reverse route)
Green-Kubo (conductivity)	Equation 7.31	DC limit of frequency-domain Kubo formula

The central message is that all dissipative and transport properties of a system at thermal equilibrium are encoded in equilibrium time-correlation functions. Whether one starts from Liouville dynamics, the stochastic GLE, or the FDT itself, the same family of results emerges: susceptibility, mobility, conductivity, and noise are not independent quantities-they are different faces of the same underlying fluctuation statistics.

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8: FLUCTUATION-DISSIPATION RELATIONS AND FREQUENCY-DEPENDENT JOHNSON NYQUIST NOISE

This chapter presents a pedagogical and self-contained derivation of Johnson-Nyquist formula that relates the voltage fluctuations due to the thermal noise to the impedance in linear electrical circuits using linear response theory. Spectral densities and measurement bandwidth are carefully defined following Nyquist's original formulation. Explicit expressions are derived for voltage fluctuations across a resistor in R, RC (series and parallel), and LCR circuits. Reactive elements are shown to shape but not generate noise, producing frequency-dependent Johnson-Nyquist relations governed by circuit susceptibility. We demonstrate that while pure resistors exhibit frequency-independent (white) Johnson-Nyquist noise, circuits containing reactive elements can display frequency-dependent colored noise spectra. Specifically, we analyze pure resistors, series RC circuits, parallel RC circuits, and series LCR resonators, showing how circuit topology determines whether the noise spectrum is white or colored. We explain the physical origin of frequency dependence through the concept of effective resistance and current redistribution at different frequencies. Analogies with the generalized Langevin equation are explained.

8.1: Introduction
8.2: Theoretical Framework
8.3: Spectral Density and Bandwidth
8.4: Application of FTD to Electrical Resistance
8.5: Derivation of the Voltage Spectral Density
8.6: Derivation of the Voltage Spectral Density
8.7: Frequency-Dependent Noise Density
8.8: RC Circuit- Series Configuration
8.9: RC Circuit- Parallel Configuration
8.10: The L-R Shunted by C Equivalent Circuit Model
8.11: LCR Circuit and Charge Fluctuations
8.12: Johnson Noise Thermometry (JNT)
8.13: Conclusion
8.14: Appendix A
8.15: Appendix B
8.16: Appendix C
8.17: Appendix D
8.18: Bibliography

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8.1: Introduction

The Johnson-Nyquist noise [1, 2] is a cornerstone of non-equilibrium statistical mechanics. Despite its foundational importance, pedagogical treatments often leave a gap between the formal Fluctuation-Dissipation Theorem (FDT) of Kubo[3] and the practical reality of Johnson-Nyquist noise. This chapter addresses this gap by providing a self-contained derivation of the FDT from Liouville dynamics and applying the framework to macroscopic circuit topologies.

8.1.1 The Evolution of Noise Theory

Johnson and Nyquist established that a resistor at temperature T exhibits equilibrium voltage fluctuations with a flat, low-frequency spectrum [1, 2]. While their results describe frequency-independent "white" noise, we demonstrate that noise can be frequency-dependent-or "colored"- in complex electrical networks [4].

Importantly, this transition from white to colored noise is not a modification of the fluctuation strength itself. Instead, it is a consequence of frequency-dependent dissipation encoded in the circuit's complex impedance $Z(\omega)$. By introducing the concept of "effective resistance" and analyzing current redistribution in various RC and LCR configurations, we provide an intuitive physical framework for spectral shaping.

8.1.2 Literature and Motivation

The relationship between spectral density and dissipation is a fundamental result of statistical mechanics known as the FDT. While the topic of noise has been addressed in various forms-notably by Reichel [5], Bleaney [6], Ginzburg and Pitaevskii [7], Clerk [8], and Devoret [9]-a persistent gap remains in the literature.

Standard texts often follow one of two paths: they either rely on the original derivation [2] using transmission lines [10, 11] or focus on the quantum mechanical version[7, 8, 9] of the FDT [4, 12, 13, 14]. Conversely, engineering handbooks [15, 16] often provide practical formulas without a rigorous link to the underlying statistical mechanics.

This chapter is motivated by a central question: "Can we apply microscopic statistical analysis to macroscopic voltage fluctuations?" The answer is a definitive yes. We offer a unified, step-by-step trajectory from microscopic Liouville dynamics to the frequency-dependent Nyquist formula, assuming a constant temperature T high enough for the classical FDT to hold.

8.1.3 Core Theoretical Framework

In an ideal system with frequency-independent resistance R, the voltage noise spectral density $S_V(\omega)$ is given by the standard Nyquist relation:

$$S_V(\omega) = 4k_B T R \tag{8.1}$$

Here k_B is the Boltzmann constant.

However, real-world measurement systems-such as those used in Johnson Noise Thermometry (JNT) [17]-incorporate leads and amplifiers that introduce parasitic capacitance C and inductance L. For any arbitrary linear impedance $Z(\omega)$, the FDT generalizes the relation to:

$$S_V(\omega) = 4k_B T \,\mathrm{Re}[Z(\omega)] \tag{8.2}$$

This chapter derives Equation 8.2 and explores how reactive elements shape, but do not generate, noise. We further bridge the disciplinary divide by mapping these electrical fluctuations onto the Generalized Langevin Equation (GLE) and mechanical jitter in optical traps, offering a more intuitive grasp of dissipation than is typically found in specialized reviews.

8.1.4 Structure of the Chapter

The structure of this chapter is as follows: Section 2 establishes the FDT framework. Section 3 defines Spectral Density and our bandwidth conventions. Section 4 applies FDT to electrical impedance to derive the Johnson-Nyquist relation, while Section 5 focuses on the Voltage Spectral Density. Section 6 discusses noise via the Equipartition theorem in RC circuits, and Section 7 explores frequency-dependent noise density.

Sections 8 through 11 consider specific circuit configurations: RC (series and parallel), $L-R$ shunted by C, and LCR charge fluctuations. Section 12 discusses the physical concept of effective resistance. Section 13 provides an overview of Johnson Noise Thermometry (JNT), followed by concluding remarks in Section 14.

Detailed derivations are provided in the Appendices: Microscopic FDT from Liouville dynamics (Appendix A), spectral density connections (Appendix B), and the mechanical-electrical analogy (Appendix C and D).

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8.2: Theoretical Framework

The "memory" of a system's fluctuations is quantified by the auto-correlation function $C(t)$ of an observable $A(t)$:

$$C(t) = \langle A(t)A(0)\rangle \tag{8.3}$$

When a small time-dependent external force $h(t)$ is applied, the system responds according to the susceptibility $\chi(t)$. The linear response is given by:

$$\langle \Delta A(t)\rangle = \int_{-\infty}^{t} \chi\left(t-t'\right) h\left(t'\right) dt' \tag{8.4}$$

Throughout, we assume a constant temperature T that is high enough such that the classical FDT holds. In the frequency domain, the susceptibility is a complex function $\chi(\omega) = \chi'(\omega) + i\chi''(\omega)$. The imaginary part, $\chi''(\omega)$, represents the energy dissipated by the system. In the classical limit $\hbar\omega \ll k_B T$, the FDT relates these via:

$$\chi''(\omega) = \frac{\beta\omega}{2} S(\omega) \tag{8.5}$$

where $\beta = (k_B T)^{-1}$.

FDT needed here is proven in an appendix, solely from classical statistical mechanics. It is important to emphasize the fundamental nature of FDT-it does not depend on particular physical system like a damped oscillator or a dissipative circuit. Furthermore, it is not a limiting form of a quantum phenomenon, it can be realized in classical physics starting with Louiville' s equation.

Physical Interpretation of FDT

- The equality demonstrates that fluctuations and dissipation are two sides of the same coin:
- The dissipation $\chi''(\omega)$ describes how the system loses energy to its environment (the bath).
- The Fluctuations $S(\omega)$ describe how the environment kicks the system due to its own thermal energy.

The conversion factor of $k_B T$ ensures that the energy that the system loses through dissipation ("friction") is exactly balanced by the energy it gains from thermal noise, allowing the system to reach and maintain thermodynamic equilibrium.

The Quantum Fluctuation-Dissipation Theorem, which is required to account for quantum effects at high frequencies or low temperatures, utilizes the Callen-Welton [12] form of the FDT:

$$S(\omega) = \frac{2}{\omega}\left[\frac{\hbar\omega}{e^{\hbar\omega/k_B T}-1} + \frac{\hbar\omega}{2}\right]\chi''(\omega) = \hbar\coth\left(\frac{\hbar\omega}{2k_B T}\right)\chi''(\omega) \tag{8.6}$$

Here $\hbar$ is the Planck's constant.

In the limit where $\hbar\omega \ll k_B T$, we expand the exponential term $e^{\hbar\omega/k_B T} \approx 1 + \frac{\hbar\omega}{k_B T}$. The zero-point energy term $\frac{\hbar\omega}{2}$ becomes negligible.

$$\frac{\hbar\omega}{e^{\hbar\omega/k_B T}-1} \approx \frac{\hbar\omega}{1+\frac{\hbar\omega}{k_B T}-1} = k_B T \tag{8.7}$$

Substituting this back into the spectral density recovers the classical Nyquist result in the classical limit $\hbar\omega \ll k_B T . k_B T$: The thermal energy scale is the product of the Boltzmann constant k_B times the absolute temperature T. The Planck's constant $\hbar$ times frequency ω is the energy of photons. $S_V(\omega)$ is the power spectral density of the fluctuations. At 60 Hz and room temperatures, the thermal energy $\left(\approx 0.0259\mathrm{eV}\right)$ is much larger than the quantum energy $\left(\approx 2.48\times 10^{-13}\mathrm{eV}\right)$, thus $\hbar\omega \ll k_B T$.

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8.3: Spectral Density and Bandwidth

Fourier convention: We adopt the convention

$$V(\omega) = \int_{-\infty}^{\infty} dt V(t) e^{i\omega t} \tag{8.8}$$

with inverse

$$V(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega V(\omega) e^{-i\omega t}. \tag{8.9}$$

For any voltage signal $V(t)$, the voltage noise spectral density $S_V(\omega)$ is defined by

$$\langle V(t)V(0)\rangle = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} S_V(\omega) e^{-i\omega t}. \tag{8.10}$$

For real-valued signals, $S_V(\omega)$ is an even function: $S_V(-\omega) = S_V(\omega)$.

Equation 8.11, below, is the Wiener-Khinchin theorem [18, 19]: the power spectral density $S_V(\omega)$ is the Fourier transform of the autocorrelation function $C(t) = \langle V(t)V(0)\rangle$, or equivalently

$$S_V(\omega) = \int_{-\infty}^{\infty} \langle V(t)V(0)\rangle e^{+i\omega t} dt \tag{8.11}$$

Setting $t = 0$ in Eq. (4) gives

$$\langle V^2 \rangle = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} S_V(\omega), \tag{8.12}$$

which is Parseval's theorem: the total mean-square equals the integral of the spectral density over all frequencies [18].

A voltmeter with a bandpass filter that passes only $|\omega| \in [\omega_1, \omega_2]$ contributes from both the positive-frequency band $[\omega_1, \omega_2]$ and its mirror image $[-\omega_2, -\omega_1]$:

$$\langle V^2 \rangle_{\text{meas}} = \int_{-\omega_2}^{-\omega_1} \frac{d\omega}{2\pi} S_V(\omega) + \int_{\omega_1}^{\omega_2} \frac{d\omega}{2\pi} S_V(\omega). \tag{8.13}$$

Since $S_V(-\omega) = S_V(\omega)$ for a real signal, the two integrals are equal, giving

$$\langle V^2 \rangle_{\text{meas}} = 2 \int_{\omega_1}^{\omega_2} \frac{d\omega}{2\pi} S_V(\omega). \tag{8.14}$$

Finally, substituting $\omega = 2\pi f, d\omega = 2\pi df$:

$$= 2 \int_{f_1}^{f_2} S_V(2\pi f) df = \int_{f_1}^{f_2} G_V(f) df \tag{8.15}$$

where $G_V(f) \equiv 2S_V(2\pi f)$ is the one-sided spectral density. The factor of 2 in the definition of G_V absorbs both the factor from folding negative frequencies and the Jacobian of the $\omega \to f$ substitution. Collecting these steps:

A voltmeter sensitive to frequencies in the band $\omega \in [\omega_1, \omega_2]$ measures the mean-square voltage

$$\langle V^2 \rangle = 2 \int_{\omega_1}^{\omega_2} \frac{d\omega}{2\pi} S_V(\omega) = \int_{f_1}^{f_2} G_V(f) df \tag{8.16}$$

where $\Delta f = (f_2 - f_1)$ is the measurement bandwidth, exactly as in Nyquist's original analysis. The one-sided spectral density $G_V(f) = 2S_V(2\pi f)$ absorbs both the folding of negative frequencies and the Jacobian of the $\omega \to f$ substitution, which explains

the factor of 4 commonly found in engineering books [20] versus the factor of 2 in statistical mechanics texts.

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8.4: Application of FTD to Electrical Resistance

We now apply the FDT to a circuit element directly, using the charge q as the fluctuating observable conjugate to the voltage V (the external "force"). This is the natural choice because $V = dU/dq$, making (V, q) a thermodynamically conjugate pair, and the current $I = \dot{q}$ follows from it. For a general linear network, the complex impedance $Z(\omega)$ relates the voltage $\tilde{V}(\omega)$ and current $\tilde{I}(\omega)$ in the frequency domain as:

$$\tilde{V}(\omega) = Z(\omega)\tilde{I}(\omega). \tag{8.17}$$

Using the convention $\tilde{I}(\omega) = -i\omega\tilde{q}(\omega)$ (where $\tilde{q}(\omega) = \int q(t)e^{i\omega t}dt$), the relationship between the applied voltage and the resulting charge displacement is given by:

$$\tilde{V}(\omega) = -i\omega Z(\omega)\tilde{q}(\omega). \tag{8.18}$$

8.4.1 Complex Charge Susceptibility

The charge susceptibility $\chi_q(\omega)$, which characterizes the linear response of the displacement q to the driving force V, is defined as:

$$\chi_q(\omega) \equiv \frac{\tilde{q}(\omega)}{\tilde{V}(\omega)} = \frac{1}{-i\omega Z(\omega)} = \frac{i}{\omega Z(\omega)}. \tag{8.19}$$

Decomposing the impedance into its resistive and reactive components, $Z(\omega) = R(\omega) + iX(\omega)$, we express the susceptibility as:

$$\chi_q(\omega) = \frac{i}{\omega[R(\omega) + iX(\omega)]} = \frac{X(\omega) + iR(\omega)}{\omega|Z(\omega)|^2}. \tag{8.20}$$

Identifying the real (χ_q') and imaginary (χ_q'') components, we obtain:

$$\chi_q'(\omega) = \frac{X(\omega)}{\omega|Z(\omega)|^2}, \quad \chi_q''(\omega) = \frac{R(\omega)}{\omega|Z(\omega)|^2}. \tag{8.21}$$

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8.5: Derivation of the Voltage Spectral Density

The Fluctuation-Dissipation Theorem (FDT) relates the equilibrium charge fluctuations $S_q(\omega)$ to the dissipative part of the susceptibility:

$$S_q(\omega) = \frac{2k_BT}{\omega}\chi_q''(\omega) = \frac{2k_BT}{\omega}\left(\frac{R(\omega)}{\omega|Z(\omega)|^2}\right). \tag{8.22}$$

To find the voltage spectral density $S_V(\omega)$, we apply the transfer function $|\tilde{V}/\tilde{q}|^2 = \omega^2|Z(\omega)|^2$:

$$S_V(\omega) = \omega^2|Z(\omega)|^2 S_q(\omega) = \omega^2|Z(\omega)|^2 \cdot \frac{2k_BTR(\omega)}{\omega^2|Z(\omega)|^2}. \tag{8.23}$$

The frequency-dependent factors in the denominator cancel exactly, yielding the generalized Nyquist result:

$$S_V(\omega) = 2k_BT\,\mathrm{Re}[Z(\omega)] \tag{8.24}$$

where $\mathrm{Re}[Z(\omega)] = R(\omega)$.

Equation 8.24 demonstrates that only the dissipative (resistive) component of the impedance contributes to the generation of equilibrium noise. Reactive components (capacitance and inductance) do not generate fluctuations themselves; rather, they redistribute energy and shape the resulting noise spectrum.

In the case of a pure frequency-independent resistor, where $\mathrm{Re}[Z(\omega)] = R$, we recover the classic white-noise spectrum:

$$S_V^{(R)}(\omega) = 2k_BTR. \tag{8.25}$$

The cancellation of the ω^2 terms is a fundamental consequence of the fact that a pure resistor lacks an intrinsic timescale.

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8.6: Derivation of the Voltage Spectral Density

In complex networks, the real part of the impedance $\mathrm{Re}[Z(\omega)]$ represents frequency-dependent dissipation.

8.6.1 The Complex Impedance and Spectrum

For a resistor R in parallel with a capacitor C :

$$\mathrm{Re}[Z(\omega)] = \frac{R}{1+(\omega RC)^2} \tag{8.26}$$

The frequency-dependent one-sided noise power spectral density is then:

$$G_V(\omega) = \frac{4k_BTR}{1+(\omega RC)^2} \tag{8.27}$$

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8.7: Frequency-Dependent Noise Density

Consider a resistor R in series with a capacitor C. The impedance is

$$Z(\omega) = R + \frac{1}{i\omega C}. \tag{8.28}$$

The voltage across the capacitor is

$$V_C(\omega) = \frac{Z_C(\omega)}{Z(\omega)} V(\omega), \quad Z_C = \frac{1}{i\omega C}. \tag{8.29}$$

The capacitor voltage spectral density is defined as

$$S_{V_C}(\omega) \equiv \langle |V_C(\omega)|^2 \rangle = \left| \frac{Z_C}{Z} \right|^2 S_V^{(R)}(\omega). \tag{8.30}$$

Explicitly,

$$S_{V_C}(\omega) = \frac{2k_B T R}{1 + (\omega RC)^2}. \tag{8.31}$$

The measured voltage fluctuation is

$$\langle V_C^2 \rangle = \int \frac{d\omega}{2\pi} S_{V_C}(\omega) = \frac{k_B T}{C}, \tag{8.32}$$

consistent with equipartition.

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8.8: RC Circuit- Series Configuration

For a resistor and capacitor in parallel, the admittance is

$$Y(\omega) = \frac{1}{R} + i\omega C. \tag{8.33}$$

The voltage across both elements is identical. The voltage spectral density across the resistor (and capacitor) is

$$S_V^{(\mathrm{RC}\|)}(\omega) = \frac{2k_B T R}{1 + (\omega RC)^2}. \tag{8.34}$$

Thus, the parallel RC circuit also acts as a low-pass filter for thermal noise, with cutoff frequency $\omega_c = 1/RC$.

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8.9: RC Circuit- Parallel Configuration

The stray capacitors are best modeled as a resistance R in series with an inductance L, all in parallel with a capacitance C. Coaxial cable capacitance (typically 50-100 pF/m) is the main source of the stray capacitance. The complex impedance $Z(\omega)$ of this network is:

$$Z(\omega) = \frac{R + i\omega L}{1 - \omega^2 LC + i\omega RC} \tag{8.35}$$

According to the generalized fluctuation-dissipation theorem, the noise power spectral density is proportional to the real part of the impedance, $\mathrm{Re}[Z(\omega)]$. Multiplying by the complex conjugate of the denominator, we find:

$$\mathrm{Re}[Z(\omega)] = \frac{R}{\left(1 - \omega^2 LC\right)^2 + (\omega RC)^2} \tag{8.36}$$

For low frequencies where $\omega^2 LC \ll 1$ and $(\omega RC)^2 \ll 1$, the expression can be approximated via Taylor expansion:

$$\mathrm{Re}[Z(\omega)] \approx R\left[1 + \omega^2\left(2LC - R^2C^2\right)\right] \tag{8.37}$$

This demonstrates that the noise spectrum is not "white" with characteristic frequencies determined by the time constants $\tau_L = L/R$ and $\tau_C = RC$.

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8.10: The L-R Shunted by C Equivalent Circuit Model

For a series LCR circuit,

$$Z(\omega) = R + i\left(\omega L - \frac{1}{\omega C}\right). \tag{8.38}$$

The voltage noise is generated solely by R, but the charge $q(\omega) = I(\omega)/i\omega$ fluctuates.

The charge noise spectral density is defined as

$$S_q(\omega) \equiv \left\langle |q(\omega)|^2 \right\rangle. \tag{8.39}$$

Using $I = V/Z$, one finds

$$S_q(\omega) = \frac{2k_BTR}{\left(1/C - L\omega^2\right)^2 + (R\omega)^2}. \tag{8.40}$$

The voltage across the resistor has spectral density

$$S_{V_R}^{(\mathrm{LCR})}(\omega) = 2k_BTR, \tag{8.41}$$

but the measurable voltages across L or C are resonantly enhanced.

In the high- Q limit, Equation 8.40 becomes Lorentzian near $\omega_0 = 1/\sqrt{LC}$. Writing $\omega = \omega_0 + \epsilon$ with $|\epsilon| \ll \omega_0$, the factor $(1/C - L\omega^2)$ $\approx -2L\omega_0\epsilon$ and $(R\omega)^2 \approx (R\omega_0)^2$, so the denominator becomes $4L^2\omega_0^2\epsilon^2 + R^2\omega_0^2 = \omega_0^2 4L^2\left[(\omega-\omega_0)^2 + (R/2L)^2\right]$. Hence for $Q = \omega_0 L/R$ $\gg 1$:

$$S_q(\omega) \approx \frac{k_BTRC}{2L}\frac{1}{(\omega-\omega_0)^2 + \left(\frac{R}{2L}\right)^2} = \frac{k_BTRC}{2L}\frac{1}{(\omega-\omega_0)^2 + \left(\frac{\omega_0}{2Q}\right)^2}. \tag{8.42}$$

While it is physically true that R is the dissipative element, in a formal FDT sense, the noise is a property of the entire system's impedance, i.e., while R is the source of dissipation, L and C act as the environment that shapes the correlation time of the fluctuations.

8.10.1 Summary of Results

Noise spectral densities and characteristic correlation times for various circuits are summarized below in Table 8.1.

Table 8.10.1*: Noise spectral densities and characteristic correlation times. For series configurations,* V_R *is listed to demonstrate consistent white noise characteristics.*

Circuit	Measured Voltage	$\mathrm{Re}[Z(\omega)]$	$S_V(\omega)$	Correlation Time τ
Pure R	V_R	R	$2k_BTR$ (white)	$\to 0$
Series RC	V_R	R	$2k_BTR$ (white)	$\to 0$
Series RC	V_C	R	$\frac{2k_BTR}{1+\omega^2R^2C^2}$ (colored)	RC
Parallel RC	$V_{R\|C}$	$\frac{R}{1+\omega^2R^2C^2}$	$\frac{2k_BTR}{1+\omega^2R^2C^2}$ (colored)	RC
Series LCR	V_R	R	$2k_BTR$ (white)	$2L/R$
Shunted $LR\|C$	V_R	$\frac{R}{(1-\omega^2LC)^2+(\omega RC)^2}$	$\frac{2k_BTR}{(1-\omega^2LC)^2+(\omega RC)^2}$ (colored)	$RC, \sqrt{LC}$

Note: For series RC, the noise across the resistor V_R is white, but the noise across the capacitor V_C is colored (low-pass filtered) as shown. For series LCR, voltages across L or C exhibit resonant enhancement but the resistor voltage remains white.

The distinction between white and colored noise in these entries depends on the choice of the measured observable. In series configurations, such as the series RC or LCR circuits, the same current flows through all elements. Because the dissipation occurs only within the resistor, the effective resistance $\mathrm{Re}[Z(\omega)]$ remains constant (R), and the voltage noise measured across that resistor (V_R) is white.

However, if the voltage is measured across a reactive element like the capacitor (V_C), the reactive impedance shapes the signal, resulting in a colored spectrum. This is not due to a change in the noise generation itself, but rather a frequency-dependent redistribution of the voltage. In contrast, parallel configurations exhibit naturally colored noise because the reactive elements provide alternative paths that make the total circuit dissipation frequency-dependent.

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8.11: LCR Circuit and Charge Fluctuations

The distinction between white and colored noise arises from how the circuit's real part of the impedance, $\mathrm{Re}[Z(\omega)]$, varies with frequency. This is best understood through the configurations shown in Figs. $8.11.1$: and $8.11.2$:.

Redistribution and Effective Resistance: In the Parallel RC configuration (Fig. $8.11.1$:), the capacitor provides an alternative path for the current. As frequency increases, the capacitor's impedance $1/i\omega C$ decreases, diverting current away from the resistor. This redistribution reduces the current through the resistor at high frequencies, which decreases the dissipated power and is reflected in the dropping $\mathrm{Re}[Z(\omega)]$. Consequently, the noise power spectral density $S_V(\omega)$ follows this drop, resulting in colored (low-pass) noise.

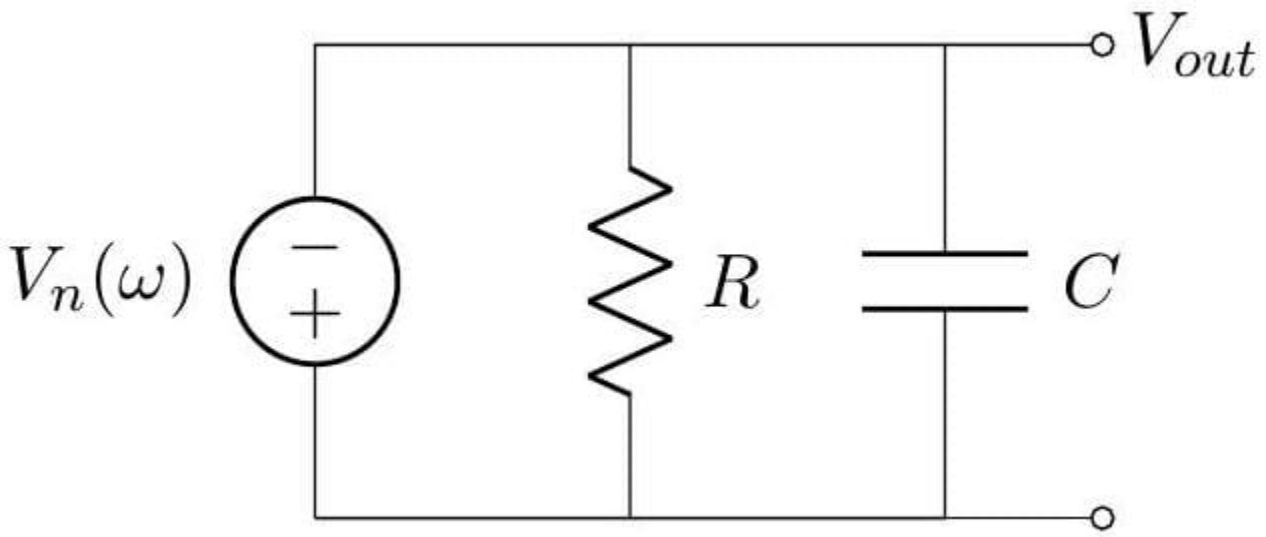


Figure $8.11.1$: Parallel RC circuit showing resistor noise source and capacitive current bypass responsible for frequency-dependent noise.

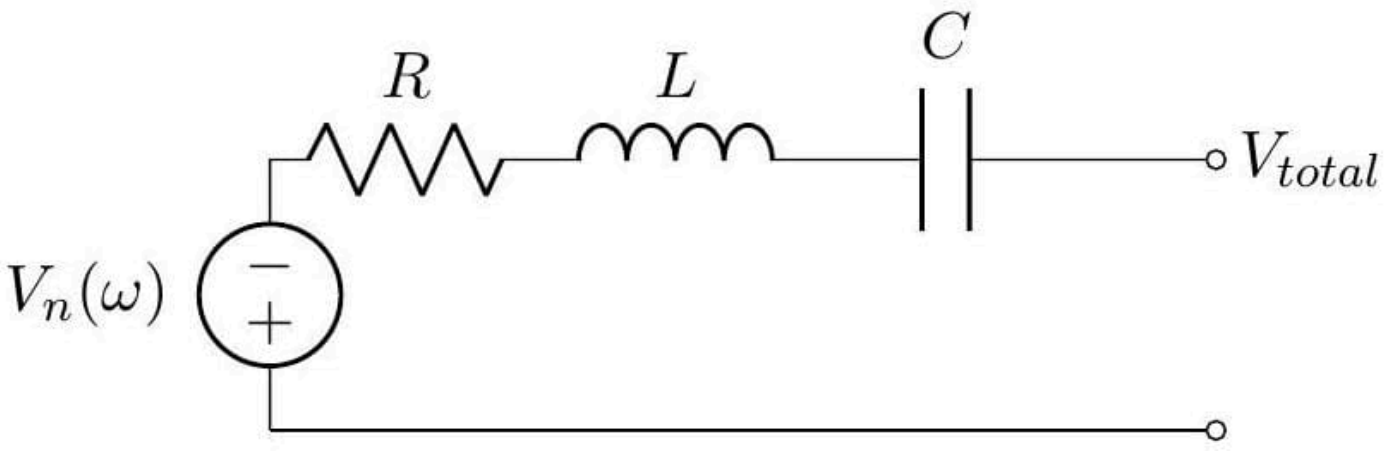


Figure $8.11.2$: Series LCR circuit. The same current flows through all elements, keeping the resistive dissipation constant.

Conversely, in Series configurations (Fig. 2), the same current must pass through the resistor regardless of the reactance of L or C. Because the dissipation mechanism (the resistor) is always fully engaged by the total current, the effective resistance $R(\omega)$ remains exactly R. Thus, while reactive elements may change the phase or the voltage measured across a single component, the total resistive part of the circuit impedance remains constant, and the noise remains white.

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8.12: Johnson Noise Thermometry (JNT)

A Johnson noise thermometer[17, 21, 22, 23] determines the absolute temperature T by measuring the mean-square voltage fluctuations $< V^2 >$ across a sensing resistor R, governed by the Nyquist formula given above Eq.(1):

$$S_V(\omega) = 4k_BTR.$$

However, in practical measurement systems [24, 25, 26], the sensing resistor is connected to amplifiers through leads and circuitry that introduce parasitic capacitance C and inductance L. As a result, the impedance becomes frequency dependent $Z(\omega)$, and R above is replaced by $\mathrm{Re}(Z)$ as in Eq.(2), and the "noise power" is integrated over a specific bandwidth where the ratio of the real part of the impedance to the total gain is precisely known.

Modern precision methods, such as those developed by NIST[24, 25], often utilize a dual-path cross-correlation technique or a combining of thermal noise with a synthesized reference signal to eliminate the influence of parasitic components. By measuring the complex transmission line characteristics using an alternating current (AC) quantized voltage source or a ratio-metric bridge, researchers can determine the exact attenuation and phase shift caused by the parasitics. This allows for the "de-embedding" of the sensor's true noise from the hardware's electrical signature, ensuring the temperature remains traceable directly to the Boltzmann constant without being skewed by the physical wiring of the cryostat or probe.

A review of Johnson noise thermometry is beyond the scope of this book and one should consult the papers cited here and references there in. JNT is particularly important with the

recent redefinition of the kelvin, (symbol K). As of May 2019, the National Institute of Standards and Technology (NIST) redefined the kelvin (K) based on the Boltzmann constant (K_B) rather than the triple point of water. The magnitude is now fixed by taking the fixed numerical value of the Boltzmann constant K_B to be 1.380649×10^{-23} when expressed in the unit Joules per Kelvin JK^{-1} , which is equal to $kgm^2s^{-2}K^{-1}$.

Johnson noise thermometry (JNT) is critically important following the 2019 redefinition of the kelvin because it acts as a primary, purely electronic method to realize and disseminate thermodynamic temperature directly from the fixed Boltzmann constant. With the redefinition, the kelvin is no longer based on the triple point of water, allowing temperature to be measured independent of material properties, making JNT a versatile tool for high-accuracy.

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8.13: Conclusion

We have presented a comprehensive pedagogical treatment of thermal noise in linear electrical circuits based on the fluctuation-dissipation theorem.

In summary, while the Johnson-Nyquist noise is a cornerstone of non-equilibrium statistical mechanics, pedagogical treatments leave a gap between the formal Fluctuation-Dissipation Theorem (FDT) and Johnson-Nyquist noise. This chapter addresses this gap by providing a self-contained derivation of FTD from Liouville dynamics and applying the FTD to macroscopic circuit topology. We demonstrate that the transition from white to colored noise is not a modification of the fluctuation strength itself, but a consequence of frequency-dependent dissipation encoded in the circuit's impedance. By introducing the concept of "effective resistance" and analyzing current redistribution in parallel versus series RC and LCR configurations, we provide an intuitive physical framework for spectral shaping.

It is often tempting to view reactive elements as filters applied to a pre-existing noise signal. However, as shown through the FDT, the noise and the circuit topology are inseparable; the reactive elements define the system's ability to dissipate energy at specific frequencies, which fundamentally dictates the spectral signature of the thermal fluctuations at equilibrium. The key to understanding why some circuits exhibit white noise while others show colored noise lies in the concept of effective resistance $R(\omega)$. Series configurations maintain white noise because the dissipation occurs only in the resistive elements, and $R(\omega) = R$ is constant. Parallel configurations display genuinely colored noise because reactive elements provide alternate current paths, making the effective resistance frequency-dependent. The results demonstrate that colored noise arises, not from modified fluctuation strength, but from frequency-dependent dissipation encoded in the impedance. The frequency dependencies play important role in Johnson-Nyquist thermometry.

Finally, we unify these concepts through the Generalized Langevin Equation and mechanical-electrical analogies, offering a robust foundation for understanding fluctuations in both electronic systems and modern applications like optical trapping and precision metrology.

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8.14: Appendix A

As noted above, we have not seen a classical derivation of FDT in the literature. The classical FTD is generally obtained by taking a limit of the quantum mechanical FTD, as explained above, Below we provide a self-contained derivation of FTD from Liouville dynamics.

To prove the response-correlation relation Equation 8.5, or its time domain version, $\chi(t) = -\beta \dot{C}(t)\theta(t)$, we consider a classical system in phase space $\Gamma = (\mathbf{q}, \mathbf{p})$.

A.1 Poisson Brackets and Liouville Equation

The Poisson bracket of any two phase-space functions f and g is defined as:

$$\{f, g\} = \sum_i \left(\frac{\partial f}{\partial q_i} \frac{\partial g}{\partial p_i} - \frac{\partial f}{\partial p_i} \frac{\partial g}{\partial q_i} \right) \tag{8.1}$$

The evolution of the phase-space density $\rho(\Gamma, t)$ is governed by the Liouville equation:

$$\frac{\partial \rho}{\partial t} = \{H, \rho\} = -L\rho \tag{8.2}$$

where L is the Liouville operator. We consider a perturbation $\Delta H = -A(\Gamma)h(t)$, so the total Hamiltonian is $H = H_0 - Ah(t)$.

A.2 Proof of the Thermal Identity

The equilibrium distribution is the canonical ensemble $\rho_0 = e^{-\beta H_0}/Z_{\text{part}}$, where the partition function $Z_{\text{part}} = \int e^{-\beta H_0(\Gamma)} d\Gamma$ and the integral is over phase space. Next, we show that $\{A, \rho_0\} = -\beta \rho_0 \dot{A}$. Using the chain rule for Poisson brackets, $\{A, f(g)\} = \frac{df}{dg}\{A, g\}$ which follows from the chain rule of calculus, $\frac{\partial f(g)}{\partial p_i} = \frac{df}{dg}\frac{\partial g}{\partial p_i}$, $\frac{\partial f(g)}{\partial q_i} = \frac{df}{dg}\frac{\partial g}{\partial q_i}$, we find

$$\{A, \rho_0\} = \left\{ A, \frac{1}{Z_{\text{part}}} e^{-\beta H_0} \right\} = \frac{1}{Z_{\text{part}}} \frac{d\left(e^{-\beta H_0}\right)}{dH_0} \{A, H_0\} \tag{8.3}$$

$$\{A, \rho_0\} = -\beta \left(\frac{1}{Z_{\text{part}}} e^{-\beta H_0} \right) \{A, H_0\} = -\beta \rho_0 \{A, H_0\} . \tag{8.4}$$

From Hamilton's equations, the time evolution of any observable A under the unperturbed Hamiltonian H_0 is $\dot{A} = \{A, H_0\}$. Substituting this yields the identity:

$$\{A, \rho_0\} = -\beta \rho_0 \dot{A} \tag{8.5}$$

A.3 First-Order Perturbation and Correlation

Let $\rho(t) = \rho_0 + \Delta\rho(t)$. Inserting this into the Liouville equation and keeping only terms linear in $h(t)$:

$$\frac{\partial \Delta\rho}{\partial t} = \{H_0, \Delta\rho\} + \{-Ah(t), \rho_0\} \tag{8.6}$$

Using the identity from Eq. (16), the second term becomes $h(t)\beta\rho_0\dot{A}$. Solving this first-order differential equation for $\Delta\rho(t)$ via the propagator $e^{L_0 t}$ gives:

$$\Delta\rho(t) = \int_{-\infty}^{t} e^{L_0(t-t')} \{-Ah(t'), \rho_0\} dt' = \beta\rho_0 \int_{-\infty}^{t} h(t') \dot{A}(t'-t) dt' \tag{8.7}$$

The observed change $\langle \Delta A(t) \rangle$ is the phase-space average $\int A(\Gamma)\Delta\rho(t)d\Gamma$. By shifting the time evolution from the density to the observable (Heisenberg picture) and using the stationarity of the equilibrium ensemble:

$$\langle \Delta A(t) \rangle = \int_{-\infty}^{t} h\left(t'\right) \left[\beta \left\langle \dot{A}(0) A\left(t - t'\right) \right\rangle_0 \right] dt' \tag{8.8}$$

Using time-reversal symmetry of Hamiltonian dynamics, since $\frac{d}{dt}\langle A(0)A(t)\rangle = \langle A(0)\dot{A}(t)\rangle = -\langle \dot{A}(0)A(t)\rangle$, we identify the susceptibility as:

$$\chi\left(t - t'\right) = -\beta \frac{d}{dt} C\left(t - t'\right) \theta\left(t - t'\right) \tag{8.9}$$

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8.15: Appendix B

The Fourier transform of the response function is:

$$\chi(\omega) = -\beta \int_0^\infty \dot{C}(t) e^{i\omega t} dt \tag{8.1}$$

Integrating by parts:

$$\chi(\omega) = -\beta \left[C(t) e^{i\omega t} \right]_0^\infty + i\omega\beta \int_0^\infty C(t) e^{i\omega t} dt \tag{8.2}$$

Assuming $C(\infty) \to 0$, we have $\chi(\omega) = \beta C(0) + i\omega\beta \int_0^\infty C(t) e^{i\omega t} dt$. The imaginary part is:

$$\chi''(\omega) = \omega\beta \int_0^\infty C(t) \cos(\omega t) dt \tag{8.3}$$

Since the two-sided power spectral density is $S(\omega) = 2 \int_0^\infty C(t) \cos(\omega t) dt$, we obtain:

$$\chi''(\omega) = \frac{\beta\omega}{2} S(\omega) \tag{8.4}$$

This is Equation ??? above. The quantum version of the fluctuation dissipation theory[12] can be found in Kubo[4]. It is addressed in most statistical physics books[13, 14].

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8.16: Appendix C

The thermal noise in electrical circuits is mathematically isomorphic to the Brownian motion of a mechanical oscillator. This relationship is formalized via the Generalized Langevin Equation (GLE), which incorporates memory effects into the dissipation process.

C.1 The Generalized Langevin Equation

For a particle of mass m moving in a potential $U(x)$, the GLE is given by:

$$m\ddot{x}(t) = -\int_{-\infty}^{t} \gamma\left(t-t'\right)\dot{x}\left(t'\right)dt' - \nabla U(x) + F_p(t) \tag{8.1}$$

where $\gamma(t)$ is the memory kernel representing friction and $F_p(t)$ is the fluctuating thermal force. The FDT ensures that the power spectral density of the force $S_F(\omega)$ is directly related to the real part of the Fourier-transformed friction $\tilde{\gamma}(\omega)$:

$$S_F(\omega) = 2k_B T\,\mathrm{Re}[\tilde{\gamma}(\omega)] \tag{8.2}$$

C.2 Comparison of Systems

The analogy between the electrical and the mechanical systems are summarized below in Table 8.2, which maps the parameters of the electrical circuits discussed in the main text to their mechanical equivalents. This mapping allows for the translation of circuit results (like low-pass filtering) directly into mechanical contexts (like viscous damping).

C.3 Visualizing the Analogy

The correspondence between the LCR circuit and the mechanical oscillator is not merely symbolic but structural. As shown in Figure 3, the mass m provides inertia (equivalent to inductance L), the damper γ provides dissipation (equivalent to resistance R), and the spring k provides the restoring force (equivalent to the inverse capacitance $1/C$).

Table 8.16.2*: Analogy between Electrical and Mechanical Systems.*

Electrical Parameter	Mechanical Equivalent	Physical Role
Voltage (V)	Force (F)	Driving influence / Fluctuation
Current (I)	Velocity $(v=\dot{x})$	Rate of flow/change
Charge (q)	Displacement (x)	State variable
Resistance (R)	Friction coefficient (γ)	Dissipation (Energy loss)
Inductance (L)	Mass (m)	Inertia (Kinetic energy storage)
Capacitance (C)	Compliance $(1/k)$	Potential energy storage
Impedance (Z)	Mechanical Impedance (Z_m)	Ratio of Force to Velocity

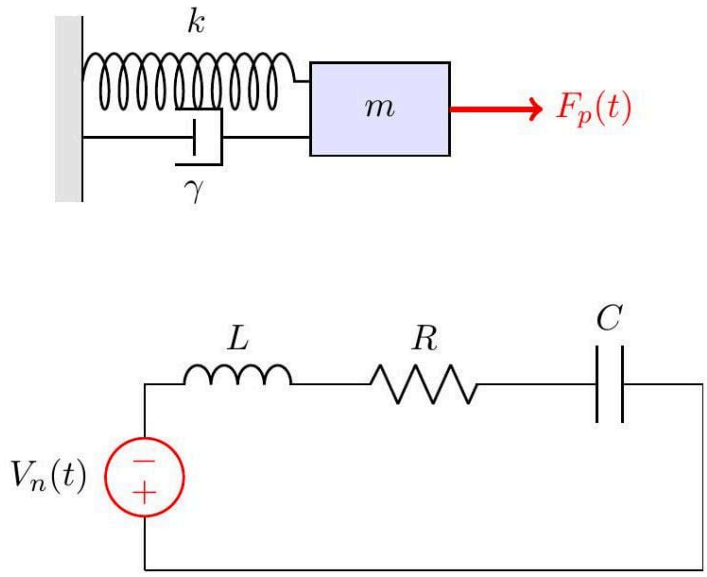


Figure 8.16.3: Top: Mechanical mass-spring-damper system. Bottom: The equivalent series LCR circuit. The stochastic terms (F_p and V_n) represent the external driving force and voltage respectively

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8.17: Appendix D

While the FDT describes fundamental equilibrium fluctuations, experimentalists must distinguish these from non-thermal noise sources that often dominate measurements.

D.1 Electronic "Hum"

In the circuits analyzed in Sections 8-10, "hum" refers to periodic interference, typically at 50/60 Hz, arising from AC power line coupling. Unlike the white Johnson noise with two-sided spectral density $S_V(\omega) = 2k_BTR$, hum manifests as sharp spectral peaks at the line frequency and its harmonics. While reactive elements like capacitors can filter high-frequency thermal noise, they are often less effective against low-frequency hum, which requires specialized notch filtering or differential signaling to mitigate.

D.2 Optical Trap "Jitter"

In optical tweezers, "jitter" refers to the stochastic displacement of a trapped bead.

- Thermal Jitter: This is the mechanical equivalent of Johnson-Nyquist noise. A laser provides a harmonic potential $U(x) = \frac{1}{2}kx^2$, and the bead undergoes Brownian motion. The displacement spectral density follows a Lorentzian shape:

$$S_x(\omega) = \frac{2k_BT\gamma}{k^2 + (\omega\gamma)^2} \tag{8.1}$$

This is functionally identical to the noise spectrum of the parallel RC circuit (Eq. 12).

- Technical Jitter: This arises from laser intensity fluctuations or mechanical vibrations. While thermal jitter is a fundamental limit dictated by T, technical jitter is an engineering constraint.

The distinction is critical: in electronics, we minimize "hum" to reach the thermal floor; in optical traps, we often measure the "jitter" as a probe to extract the local temperature or viscoelastic properties of the medium.

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9: ONSAGER RELATIONS

This Chapter gives a self-contained, step-by-step derivation showing that the Onsager Regression Hypothesis and the Onsager-Casimir Reciprocal Relations both follow rigorously from the Fluctuation-Dissipation Theorem (FDT). Starting from the Liouville equation and canonical equilibrium, we derive the key identity $\chi(t) = -\beta \dot{C}(t)\theta(t)$ linking the linear-response function to the equilibrium auto-correlation function. We prove that a macroscopic perturbation decays with the same normalized time dependence as a spontaneous microscopic fluctuation. For the reciprocal relations we present two complementary proofs: first, via the Green-Kubo formula and time-reversal parity of currents; second, via the entropy-production formalism and the Gaussian orthogonality relation $\langle A_i X_j \rangle = -k_{\mathrm{B}} \delta_{ij}$. Both routes arrive at $L_{ij} = \epsilon_i \epsilon_j L_{ji}$, and the modification under an external magnetic field is derived in full generality.

9.1: Introduction and Roadmap

9.2: Classical FDT from Liouville Dynamics

9.3: Proof of the Regression Hypothesis

9.4: Connection to the Power Spectral Density

9.5: Onsager-Casimir Reciprocal Relations

9.6: Modification by an External Magnetic Field

9.7: Summary and Logical Chain

9.8: Bibliography

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9.1: Introduction and Roadmap

Lars Onsager's regression hypothesis [1, 2] asserts a deep symmetry between the macroscopic and microscopic worlds: the laws governing the decay of spontaneous microscopic fluctuations in an equilibrium system are identical to the laws governing the relaxation of macroscopic perturbations. In Onsager's own words,

> "We shall now admit the hypothesis that the average decay of fluctuations occurs according to the laws of macroscopic theory."

With the development of Linear Response Theory by Kubo [4, 5] and others [6], this became not merely a postulate but a theorem-a direct consequence of the Fluctuation-Dissipation Theorem (FDT).

The importance of this connection extends well beyond a single elegant result. The FDT underlies the Einstein relation between diffusivity and mobility, the Johnson-Nyquist formula for thermal noise in resistors, and the Green-Kubo expressions for viscosity and thermal conductivity. In every case the same logic is at work: an equilibrium system, when slightly displaced, must relax in a way that is completely determined by how its own internal fluctuations behave at equilibrium.

The Onsager reciprocal relations extend this insight to coupled transport processes-thermoelectricity, cross-diffusion, the Hall effect-by showing that the matrix of transport coefficients is constrained by time-reversal symmetry of the microscopic equations of motion. Crucially, the second law of thermodynamics alone is insufficient: it only enforces that the symmetric part of the Onsager matrix $\mathbf{L}$ is positive semidefinite. The symmetry $L_{ij} = L_{ji}$ itself is a consequence of microscopic reversibility [8].

Outline. The argument proceeds in five stages.

- 1.Section 15.2: Starting from the Liouville equation and first-order perturbation theory, we derive $\chi(t) = -\beta \dot{C}(t)\theta(t)$, the classical FDT.
- 2.Section 9.3: We apply this to a suddenly removed perturbation and prove the Regression Hypothesis.
- 3.Section 9.4: We Fourier-transform the FDT to connect the dissipative susceptibility $\chi''(\omega)$ to the power spectral density $S(\omega)$.
- 4.Section 9.5: We derive the Onsager-Casimir reciprocal relations via two independent routes: (A) the Green-Kubo formula with time-reversal parity, and (B) the entropy-production formalism with the Gaussian orthogonality condition.
- 5.Section 9.6: We generalise to the case where an external magnetic field breaks time-reversal invariance, yielding $L_{ij}(\mathbf{B}) = \epsilon_i \epsilon_j L_{ji}(-\mathbf{B})$.

Throughout, we work classically $(\hbar \to 0)$ except where the quantum Kubo formula is quoted explicitly. We set $\beta = 1/k_{\mathrm{B}}T$.

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9.2: Classical FDT from Liouville Dynamics

9.2.1 Setup and definitions

Consider a classical system with phase-space coordinates $\Gamma = (\mathbf{q}, \mathbf{p})$ and unperturbed Hamiltonian H_0. Let $A(\Gamma)$ be an observable of interest. The equilibrium auto-correlation function is

$$C(t) = \langle A(t)A(0)\rangle_0, \tag{9.1}$$

where $\langle\cdots\rangle_0$ denotes the canonical ensemble average with respect to $\rho_0 = e^{-\beta H_0}/Z_{\text{part}}$.

When a small external force $h(t)$ is applied through the perturbation $\Delta H = -A(\Gamma)h(t)$, the response of A is linear for small h :

$$\langle \Delta A(t)\rangle = \int_{-\infty}^{t} \chi\,(t-t')\,h\,(t')\,dt', \tag{9.2}$$

where causality is encoded by the upper limit t.

Rate of average decay. Differentiating Equation 9.2 with respect to t gives

$$\frac{d}{dt}\langle \Delta A(t)\rangle = \chi(0)h(t) + \int_{-\infty}^{t} \dot{\chi}\,(t-t')\,h\,(t')\,dt'. \tag{9.3}$$

The first term is the instantaneous kick from the current force; the second encodes the memory of all past forcing weighted by the decay rate of χ. For a spontaneous fluctuation there is no external force, so the relaxation rate is governed entirely by $\dot{\chi}(t)$. Since the FDT will identify $\chi(t) = -\beta\dot{C}(t)\theta(t)$, equation Equation 9.3 tells us directly that the rate of average decay of a fluctuation is proportional to $\ddot{C}(t)$-the curvature of the correlation function.

The goal of this section is to prove:

$$\chi(t) = -\beta\dot{C}(t)\theta(t). \tag{9.4}$$

9.2.2 Poisson brackets and the Liouville equation

The Poisson bracket of two phase-space functions f and g is

$$\{f, g\} = \sum_i \left(\frac{\partial f}{\partial q_i}\frac{\partial g}{\partial p_i} - \frac{\partial f}{\partial p_i}\frac{\partial g}{\partial q_i}\right). \tag{9.5}$$

The Liouville equation governing $\rho(\Gamma, t)$ is

$$\frac{\partial \rho}{\partial t} = \{H, \rho\} \equiv -\mathcal{L}\rho, \tag{9.6}$$

where $\mathcal{L} \equiv -\{H, \cdot\}$ is the Liouville operator. Hamilton's equations give $\dot{A} = \{A, H_0\}$ for any observable.

9.2.3 A key thermal identity

Theorem 9.1 (Thermal identity)

For the canonical equilibrium density $\rho_0 = e^{-\beta H_0}/Z_{\text{part}}$,

$$\{A, \rho_0\} = -\beta\rho_0\dot{A}. \tag{9.7}$$

Proof. Using the chain rule $\{A, f(g)\} = f'(g)\{A, g\}$ with $f = e^{-\beta H_0}/Z_{\text{part}}$ and $g = H_0$:

$$\{A, \rho_0\} = \frac{1}{Z_{\text{part}}} \frac{d\left(e^{-\beta H_0}\right)}{dH_0} \{A, H_0\} = -\beta\rho_0 \{A, H_0\} = -\beta\rho_0 \dot{A}. \tag{9.8}$$

□

Physical meaning. Equation 9.7 is the classical analogue of the quantum identity $[A, \rho_0] = -i\beta\rho_0\dot{A}$ (with $\{,\} \to -i[,]/\hbar$ as $\hbar \to 0$). It encodes how the equilibrium distribution "knows about" dynamical quantities through β.

9.2.4 First-order perturbation of the density

Write $\rho(t) = \rho_0 + \Delta\rho(t)$ and insert into the Liouville equation with $H = H_0 - Ah(t)$. Keeping only terms linear in $h(t)$:

$$\frac{\partial \Delta\rho}{\partial t} = \{H_0, \Delta\rho\} - h(t) \{A, \rho_0\}. \tag{9.9}$$

Applying the thermal identity Equation 9.7 converts the second term: $-h(t) \{A, \rho_0\} = \beta h(t)\rho_0\dot{A}$. The formal solution via the unperturbed propagator $e^{\mathcal{L}_0(t-t')}$ is:

$$\Delta\rho(t) = \beta \int_{-\infty}^{t} e^{\mathcal{L}_0(t-t')} \left[\rho_0 \dot{A}(\Gamma)\right] h(t') \, dt'. \tag{9.10}$$

9.2.5 Computing the response and identifying $\chi(t)$

The observable response is $\langle \Delta A(t) \rangle = \int A(\Gamma)\Delta\rho(t)d\Gamma$. Shifting the time evolution from the density to the observable and using stationarity of the equilibrium ensemble:

$$\langle \Delta A(t) \rangle = \beta \int_{-\infty}^{t} h(t') \left\langle \dot{A}(0) A(t - t') \right\rangle_0 dt' \tag{9.11}$$

By time-translation invariance, $\left\langle \dot{A}(0) A(t - t') \right\rangle_0 = \left\langle \dot{A}(t' - t) A(0) \right\rangle_0$. Differentiating Equation 9.1 gives $\dot{C}(s) = \langle A(0)\dot{A}(s) \rangle_0$. Under time-reversal symmetry for an even-parity observable [1] $\langle A(0)\dot{A}(s) \rangle_0 = -\langle \dot{A}(0)A(s) \rangle_0$, so $\left\langle \dot{A}(0) A(t - t') \right\rangle_0 = -\dot{C}(t - t')$. Comparing with Equation 9.2 and invoking causality:

$$\chi(t) = -\beta\dot{C}(t)\theta(t). \tag{9.12}$$

This is the classical FDT. The response function is completely determined by the equilibrium correlation function; no separate knowledge of the out-of-equilibrium dynamics is needed.

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9.3: Proof of the Regression Hypothesis

9.3.1 Protocol: abrupt removal of a static force

Consider a static force f_0 applied for all $t \leq 0$ and then suddenly removed:

$$f(t) = f_0\theta(-t) = \begin{cases} f_0 & t \leq 0 \\ 0 & t > 0 \end{cases} \tag{9.13}$$

At $t = 0^-$the system is in a shifted equilibrium with mean $\langle \delta A(0) \rangle = \beta f_0 C(0)$, obtained by integrating Equation ??? against a constant force.

9.3.2 Relaxation for $t > 0$

For $t > 0$ there is no applied force, but the system was perturbed for all $t' \leq 0$. Inserting $f(t') = f_0\theta(-t')$ into Equation ??? and using Equation ???:

$$\begin{aligned} \langle \delta A(t) \rangle &= \int_{-\infty}^{0} \chi(t - t')\, f_0 dt' = -\beta f_0 \int_{-\infty}^{0} \dot{C}(t - t')\, dt' \\ &= -\beta f_0 \left[C(t - t') \right]_{t'=-\infty}^{t'=0} = -\beta f_0 [C(t) - C(\infty)] \end{aligned} \tag{9.14}$$

Since $C(\infty) = 0$ for any ergodic system (decorrelation at long times):

$$\langle \delta A(t) \rangle = \beta f_0 C(t), \quad t > 0. \tag{9.15}$$

9.3.3 The hypothesis as a ratio

Dividing the relaxation at time t by the initial displacement:

$$\frac{\langle \delta A(t) \rangle}{\langle \delta A(0) \rangle} = \frac{\beta f_0 C(t)}{\beta f_0 C(0)} = \frac{C(t)}{C(0)}. \tag{9.16}$$

Regression Hypothesis (proved). The normalised macroscopic relaxation (left-hand side) is identical to the normalised equilibrium auto-correlation function (right-hand side). The decay of a forced deviation from equilibrium follows the same temporal law as the spontaneous regression of a thermal fluctuation.

Physical interpretation. Equation 9.16 says the system cannot "tell the difference" between relaxing from a forced displacement and regressing from a rare spontaneous fluctuation. This is a consequence of the linearity of the response and the time-reversal symmetry of the microscopic equations of motion [7].

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9.4: Connection to the Power Spectral Density

Fourier-transforming Equation ??? with the convention $\chi(\omega) = \int_0^\infty \chi(t)e^{i\omega t}dt$ gives the dissipative (imaginary) part of the susceptibility directly in terms of the equilibrium fluctuation spectrum.

9.4.1 Derivation

$$\begin{aligned}\chi(\omega) &= -\beta \int_0^\infty \dot{C}(t)e^{i\omega t}dt \\ &= -\beta \left[C(t)e^{i\omega t}\right]_0^\infty + i\omega\beta \int_0^\infty C(t)e^{i\omega t}dt \\ &= \beta C(0) + i\omega\beta \int_0^\infty C(t)e^{i\omega t}dt, \end{aligned} \tag{9.17}$$

where $C(t)e^{i\omega t} \to 0$ as $t \to \infty$ by decorrelation. Since $C(t)$ is real and even ($C(t) = C(-t)$ from time-reversal symmetry of equilibrium dynamics), the integral in Equation 9.17 contributes purely real and imaginary parts. Taking the imaginary part:

$$\chi''(\omega) \equiv \operatorname{Im}\chi(\omega) = \omega\beta \int_0^\infty C(t)\cos(\omega t)dt \tag{9.18}$$

Defining the two-sided power spectral density via the Wiener-Khinchin theorem,

$$S(\omega) = \int_{-\infty}^\infty C(t)e^{i\omega t}dt = 2\int_0^\infty C(t)\cos(\omega t)dt \tag{9.19}$$

we obtain the classical FDT in the frequency domain:

$$\chi''(\omega) = \frac{\beta\omega}{2}S(\omega). \tag{9.20}$$

Remark 9.1. The factor of ω reflects that χ'' describes dissipation (energy absorbed per cycle scales as frequency), while $S(\omega)$ is the fluctuation spectrum. At low frequencies both vanish, but their ratio approaches a finite constant controlled by the zero-frequency diffusion coefficient (Einstein relation).

9.4.2 Generalisation to cross-correlations

When the driving force $f(t)$ couples to observable B while we monitor observable A, the same Liouville calculation yields the cross-susceptibility

$$\chi_{AB}(t) = -\beta\dot{C}_{AB}(t)\theta(t), \quad C_{AB}(t) \equiv \langle A(t)B(0)\rangle_0, \tag{9.21}$$

which is the natural generalisation of Equation ???. In the frequency domain:

$$\chi''_{AB}(\omega) = \frac{\beta\omega}{2}S_{AB}(\omega), \quad S_{AB}(\omega) = \int_{-\infty}^\infty C_{AB}(t)e^{i\omega t}dt. \tag{9.22}$$

Note that C_{AB} is generically not symmetric, i.e. $C_{AB}(t) \neq C_{BA}(t)$ in general. This asymmetry is the classical seed of the Onsager reciprocal relations derived in the next section.

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9.5: Onsager-Casimir Reciprocal Relations

9.5.1 Phenomenological setup

Consider a system near equilibrium characterised by thermodynamic variables $\{A_i\}$ with thermodynamic forces

$$X_i = \frac{\partial S}{\partial A_i}, \quad J_i = \frac{dA_i}{dt}, \tag{9.23}$$

where S is the total entropy. The fluxes are assumed to depend linearly on the forces:

$$J_i = \sum_j L_{ij} X_j. \tag{9.24}$$

The entropy production rate is therefore

$$\dot{S} = \sum_i J_i X_i = \sum_{i,j} L_{ij} X_i X_j, \tag{9.25}$$

so the second law of thermodynamics ($\dot{S} \geq 0$) requires only that the symmetric part of $\mathbf{L}$ be positive semidefinite. The reciprocity $L_{ij} = L_{ji}$ is an additional, stronger statement that follows from microscopic reversibility-not from thermodynamics alone.

The Onsager matrix L encodes all transport phenomena: thermal conductivity, electrical conductivity, thermoelectric coefficients, diffusion, and their cross-effects.

We now present two independent proofs of the reciprocal relations, each illuminating a different facet of the underlying physics.

9.5.2 Proof A: Green-Kubo formula and time-reversal parity

Green-Kubo formula for L_{ij}

Let the perturbation Hamiltonian be $H'(t) = -\sum_j X_j(t) B_j$, where B_j are observables conjugate to the forces. The Kubo formula for the quantum retarded response function is

$$\chi_{ij}(t) = \frac{1}{\hbar} \theta(t) \left\langle [J_i(t), B_j(0)] \right\rangle_0, \tag{9.26}$$

where $[\cdot, \cdot]$ is the commutator. In the classical (low-frequency) limit, via $[,]/i\hbar \to \{,\}, and using$ the cross-FDT Equation ???, the dc transport coefficients become

$$L_{ij} = \int_0^\infty \left\langle J_i(t) J_j(0) \right\rangle_0 dt \tag{9.27}$$

Time-reversal parity of fluxes

Let Θ denote the antiunitary time-reversal operator. The equilibrium state is Θ-invariant:

$$\left\langle \Theta \mathcal{O} \Theta^{-1} \right\rangle_0 = \langle \mathcal{O} \rangle_0 \quad \text{for any observable } \mathcal{O}. \tag{9.28}$$

We assign each flux a definite parity under time reversal:

$$\Theta J_i \Theta^{-1} = \epsilon_i J_i, \quad \epsilon_i = \pm 1, \tag{9.29}$$

which gives the dynamical relation

$$\Theta J_i(t) \Theta^{-1} = \epsilon_i J_i(-t). \tag{9.30}$$

Position-like quantities (density, concentration) have $\epsilon = +1$; velocity-like quantities (heat or charge currents) have $\epsilon = -1$.

Symmetry of the current correlator

Define $C_{ij}(t) = \langle J_i(t) J_j(0) \rangle_0$. Applying time-reversal invariance Equation 9.28-Equation 9.30:

$$\begin{aligned} C_{ij}(t) &= \left\langle \Theta J_i(t) J_j(0) \Theta^{-1} \right\rangle_0 \\ &= \left\langle \left(\Theta J_i(t) \Theta^{-1}\right) \left(\Theta J_j(0) \Theta^{-1}\right) \right\rangle_0 \\ &= \epsilon_i \epsilon_j \left\langle J_i(-t) J_j(0) \right\rangle_0 . \end{aligned} \tag{9.31}$$

Applying stationarity, $\langle J_i(-t) J_j(0) \rangle_0 = \langle J_j(t) J_i(0) \rangle_0 = C_{ji}(t)$:

$$C_{ij}(t) = \epsilon_i \epsilon_j C_{ji}(t). \tag{9.32}$$

Deriving the reciprocal relations

Substituting Equation 9.32 into the Green-Kubo formula Equation 9.27:

$$L_{ij} = \int_0^\infty C_{ij}(t) dt = \epsilon_i \epsilon_j \int_0^\infty C_{ji}(t) dt = \epsilon_i \epsilon_j L_{ji} \tag{9.33}$$

Hence the Onsager-Casimir reciprocal relations:

$$L_{ij} = \epsilon_i \epsilon_j L_{ji}. \tag{9.34}$$

When all relevant fluxes share the same time-reversal parity ($\epsilon_i \epsilon_j = 1$), this reduces to the original Onsager symmetry $L_{ij} = L_{ji}$. The mixed-parity case ($\epsilon_i \epsilon_j = -1$) yields the Casimir antisymmetry $L_{ij} = -L_{ji}$ [8], relevant for cross-effects between charge and heat currents in a magnetic field.

9.5.3 Proof B: Entropy-production and Gaussian fluctuations

This alternative proof works entirely at the level of fluctuation statistics, without invoking the Green-Kubo integral explicitly. It follows closely the original reasoning of Onsager [1, 3].

Equilibrium fluctuation measure

Near equilibrium, the joint distribution of the variables $\{A_i\}$ (each with zero mean) is approximately Gaussian:

$$P(\{A_i\}) \propto \exp\left(\frac{S}{k_B}\right), \quad S \approx S_{eq} - \frac{1}{2} \sum_{i,j} g_{ij} A_i A_j, \tag{9.35}$$

where g_{ij} is a symmetric positive-definite matrix (the inverse of the fluctuation covariance matrix, $g = \langle AA \rangle^{-1}$). The thermodynamic forces Equation 9.23 are therefore linear in the A_i :

$$X_k = \frac{\partial S}{\partial A_k} = -\sum_j g_{kj} A_j. \tag{9.36}$$

Orthogonality relation

Lemma 9.2 (Gaussian orthogonality). Under the distribution Equation 9.35,

$$\langle A_i X_j \rangle = -k_B \delta_{ij}. \tag{9.37}$$

Proof. $\langle A_i X_j \rangle = -\sum_k g_{jk} \langle A_i A_k \rangle = -\sum_k g_{jk} \left(g^{-1}\right)_{ki} = -\delta_{ji}$. □

Connecting time derivatives of correlators to L_{ij}

By the Regression Hypothesis (Section 9.3), the decay of $\langle A_k \rangle$ conditioned on an initial fluctuation $\{A_i\}$ follows the same linear law as a macroscopic relaxation:

$$\frac{d}{dt}\langle A_k(t)A_i(0)\rangle = \sum_j L_{kj}\langle X_j(t)A_i(0)\rangle\,. \tag{9.38}$$

Setting $t = 0$ and using the orthogonality relation Equation 9.37:

$$\frac{d}{dt}C_{ki}(t)\Big|_{t=0} = \sum_j L_{kj}\langle X_j A_i\rangle = -k_{\mathrm{B}}L_{ki}. \tag{9.39}$$

Time-reversal symmetry of the correlator

The three-step argument exploiting microscopic reversibility:

1. Time-reversal invariance. Under microscopic reversibility, for even-parity variables:

$$\langle A_i(t)A_k(t+\tau)\rangle = \langle A_i(t)A_k(t-\tau)\rangle\,. \tag{9.40}$$

2. Stationarity. Shifting the time origin by τ :

$$\langle A_i(t)A_k(t-\tau)\rangle = \langle A_i(t+\tau)A_k(t)\rangle\,. \tag{9.41}$$

3. Commutativity. Classical phase-space functions commute:

$$\langle A_i(t+\tau)A_k(t)\rangle = \langle A_k(t)A_i(t+\tau)\rangle\,. \tag{9.42}$$

Combining these three steps:

$$C_{ik}(\tau) \equiv \langle A_i(t)A_k(t+\tau)\rangle = \langle A_k(t)A_i(t+\tau)\rangle \equiv C_{ki}(\tau). \tag{9.43}$$

Hence for even-parity variables the cross-correlator is symmetric: $C_{ik}(\tau) = C_{ki}(\tau)$.

Concluding reciprocity

Differentiating both sides at $\tau = 0$ and applying Equation 9.39:

$$-k_{\mathrm{B}}L_{ik} = -k_{\mathrm{B}}L_{ki}, \tag{9.44}$$

and therefore

$$L_{ij} = L_{ji}. \tag{9.45}$$

The analogous argument for odd-parity variables (which pick up a sign under time reversal) yields the Casimir extension $L_{ij} = -L_{ji}$ in the mixed case, consistent with Equation 9.34.

Remark 9.2. Proofs A and B are complementary, not redundant. Proof A makes the role of the current-current Green-Kubo correlator explicit and extends immediately to quantum systems via Equation 9.26. Proof B is closer to Onsager's original argument and makes the Gaussian fluctuation assumption and the orthogonality relation Equation 9.37 explicit-ingredients that are sometimes hidden in the Green-Kubo approach.

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9.6: Modification by an External Magnetic Field

A static magnetic field B is odd under time reversal: $\Theta \mathbf{B} \Theta^{-1} = -\mathbf{B}$. Therefore, microscopic reversibility at field B maps trajectories to those of the system at $-B$. The equilibrium correlation identity becomes

$$\langle J_i(t) J_j(0) \rangle_{\mathbf{B}} = \epsilon_i \epsilon_j \langle J_j(t) J_i(0) \rangle_{-\mathbf{B}} . \tag{9.46}$$

After integration via the Green-Kubo formula:

$$L_{ij}(\mathbf{B}) = \epsilon_i \epsilon_j L_{ji}(-\mathbf{B}). \tag{9.47}$$

At $\mathbf{B} = 0$, strict symmetry $L_{ij} = \epsilon_i \epsilon_j L_{ji}$ is recovered. At nonzero $\mathbf{B}$, the symmetry is between the matrix at field +B and the transposed matrix at field -B. This is the full Onsager-Casimir generalisation [8].

Physical example. In thermoelectric transport, the Seebeck coefficient S_{AB} (voltage per temperature gradient) and the Peltier coefficient Π_{BA} (heat flux per current) are related by $\Pi_{BA}(\mathbf{B}) = T S_{AB}(-\mathbf{B})$, a consequence of Equation 9.47.

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9.7: Summary and Logical Chain

Step-by-step proof outline:

1. Start from microscopic dynamics that are time-reversal invariant at $\mathbf{B} = 0$.
2. The thermal identity $\{A, \rho_0\} = -\beta\rho_0\dot{A}$ (Theorem 15.2.1) converts the first-order Liouville perturbation into an equilibrium correlator.
3. Integration over the forcing history yields the classical FDT, $\chi(t) = -\beta\dot{C}(t)\theta(t)$.
4. Applying the FDT to a suddenly removed static force proves Onsager's Regression Hypothesis: macroscopic relaxation and microscopic regression are both governed by $C(t)/C(0)$.
5. Fourier-transforming the FDT yields $\chi''(\omega) = \frac{1}{2}\beta\omega S(\omega)$, linking dissipation to the equilibrium fluctuation spectrum.
6. Route A: The Green-Kubo formula expresses L_{ij} as $\int_0^\infty \langle J_i(t)J_j(0)\rangle_0\, dt$. Time-reversal parity gives $C_{ij}(t) = \epsilon_i\epsilon_j C_{ji}(t)$, and hence $L_{ij} = \epsilon_i\epsilon_j L_{ji}$.
7. Route B: The Regression Hypothesis applied to equilibrium fluctuation correlators, combined with the Gaussian orthogonality relation $\langle A_i X_j\rangle = -k_B\delta_{ij}$ and the symmetry $C_{ij}(\tau) = C_{ji}(\tau)$ from microscopic reversibility, directly gives $L_{ij} = L_{ji}$.
8. If a magnetic field B is present, time reversal maps $\mathbf{B} \to -\mathbf{B}$, yielding $L_{ij}(\mathbf{B}) = \epsilon_i\epsilon_j L_{ji}(-\mathbf{B})$.

The entire argument uses only three inputs: (i) canonical equilibrium statistics, (ii) linearity of the response, (iii) time-reversal invariance of the Hamiltonian dynamics. No phenomenological assumptions are needed.

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10: Electrokinetics in a Tube

This Chapter gives a self-contained, step-by-step derivation showing that the Onsager Regression Hypothesis and the Onsager-Casimir Reciprocal Relations both follow rigorously from the Fluctuation-Dissipation Theorem (FDT). Starting from the Liouville equation and canonical equilibrium, we derive the key identity $\chi(t) = -\beta \dot{C}(t)\theta(t)$ linking the linear-response function to the equilibrium auto-correlation function. We prove that a macroscopic perturbation decays with the same normalized time dependence as a spontaneous microscopic fluctuation. For the reciprocal relations we present two complementary proofs: first, via the Green-Kubo formula and time-reversal parity of currents; second, via the entropy-production formalism and the Gaussian orthogonality relation $\langle A_i X_j \rangle = -k_{\mathrm{B}} \delta_{ij}$. Both routes arrive at $L_{ij} = \epsilon_i \epsilon_j L_{ji}$, and the modification under an external magnetic field is derived in full generality.

9.1 Introduction and Roadmap

Lars Onsager's regression hypothesis [1, 2] asserts a deep symmetry between the macroscopic and microscopic worlds: the laws governing the decay of spontaneous microscopic fluctuations in an equilibrium system are identical to the laws governing the relaxation of macroscopic perturbations. In Onsager's own words,

> "We shall now admit the hypothesis that the average decay of fluctuations occurs according to the laws of macroscopic theory."

With the development of Linear Response Theory by Kubo [4, 5] and others [6], this became not merely a postulate but a theorem-a direct consequence of the Fluctuation-Dissipation Theorem (FDT).

The importance of this connection extends well beyond a single elegant result. The FDT underlies the Einstein relation between diffusivity and mobility, the Johnson-Nyquist formula for thermal noise in resistors, and the Green-Kubo expressions for viscosity and thermal conductivity. In every case the same logic is at work: an equilibrium system, when slightly displaced, must relax in a way that is completely determined by how its own internal fluctuations behave at equilibrium.

The Onsager reciprocal relations extend this insight to coupled transport processes-thermoelectricity, cross-diffusion, the Hall effect-by showing that the matrix of transport coefficients is constrained by time-reversal symmetry of the microscopic equations of motion. Crucially, the second law of thermodynamics alone is insufficient: it only enforces that the symmetric part of the Onsager matrix $\mathbf{L}$ is positive semidefinite. The symmetry $L_{ij} = L_{ji}$ itself is a consequence of microscopic reversibility [8].

Outline. The argument proceeds in five stages.

- 1.Section 15.2: Starting from the Liouville equation and first-order perturbation theory, we derive $\chi(t) = -\beta \dot{C}(t)\theta(t)$, the classical FDT.
- 2.Section 9.3: We apply this to a suddenly removed perturbation and prove the Regression Hypothesis.
- 3.Section 9.4: We Fourier-transform the FDT to connect the dissipative susceptibility $\chi''(\omega)$ to the power spectral density $S(\omega)$.
- 4.Section 9.5: We derive the Onsager-Casimir reciprocal relations via two independent routes: (A) the Green-Kubo formula with time-reversal parity, and (B) the entropy-production formalism with the Gaussian orthogonality condition.
- 5.Section 9.6: We generalise to the case where an external magnetic field breaks time-reversal invariance, yielding $L_{ij}(\mathbf{B}) = \epsilon_i \epsilon_j L_{ji}(-\mathbf{B})$.

Throughout, we work classically $(\hbar \to 0)$ except where the quantum Kubo formula is quoted explicitly. We set $\beta = 1/k_{\mathrm{B}}T$.

9.2 Classical FDT from Liouville Dynamics

9.2.1 Setup and definitions

Consider a classical system with phase-space coordinates $\Gamma = (\mathbf{q}, \mathbf{p})$ and unperturbed Hamiltonian H_0. Let $A(\Gamma)$ be an observable of interest. The equilibrium auto-correlation function is

$$C(t) = \langle A(t)A(0)\rangle_0, \tag{9.1}$$

where $\langle\cdots\rangle_0$ denotes the canonical ensemble average with respect to $\rho_0 = e^{-\beta H_0}/Z_{\text{part}}$.

When a small external force $h(t)$ is applied through the perturbation $\Delta H = -A(\Gamma)h(t)$, the response of A is linear for small h :

$$\langle \Delta A(t)\rangle = \int_{-\infty}^{t} \chi\left(t-t'\right) h\left(t'\right) dt', \tag{9.2}$$

where causality is encoded by the upper limit t.

Rate of average decay. Differentiating Equation 9.2 with respect to t gives

$$\frac{d}{dt}\langle \Delta A(t)\rangle = \chi(0)h(t) + \int_{-\infty}^{t} \dot{\chi}\left(t-t'\right) h\left(t'\right) dt'. \tag{9.3}$$

The first term is the instantaneous kick from the current force; the second encodes the memory of all past forcing weighted by the decay rate of χ. For a spontaneous fluctuation there is no external force, so the relaxation rate is governed entirely by $\dot{\chi}(t)$. Since the FDT will identify $\chi(t) = -\beta\dot{C}(t)\theta(t)$, equation Equation 9.3 tells us directly that the rate of average decay of a fluctuation is proportional to $\ddot{C}(t)$-the curvature of the correlation function.

The goal of this section is to prove:

$$\chi(t) = -\beta\dot{C}(t)\theta(t). \tag{9.4}$$

9.2.2 Poisson brackets and the Liouville equation

The Poisson bracket of two phase-space functions f and g is

$$\{f,g\} = \sum_i \left(\frac{\partial f}{\partial q_i}\frac{\partial g}{\partial p_i} - \frac{\partial f}{\partial p_i}\frac{\partial g}{\partial q_i}\right). \tag{9.5}$$

The Liouville equation governing $\rho(\Gamma,t)$ is

$$\frac{\partial \rho}{\partial t} = \{H,\rho\} \equiv -\mathcal{L}\rho, \tag{9.6}$$

where $\mathcal{L} \equiv -\{H,\cdot\}$ is the Liouville operator. Hamilton's equations give $\dot{A} = \{A, H_0\}$ for any observable.

9.2.3 A key thermal identity

Theorem 9.1 (Thermal identity). For the canonical equilibrium density $\rho_0 = e^{-\beta H_0}/Z_{\text{part}}$,

$$\{A,\rho_0\} = -\beta\rho_0\dot{A}. \tag{9.7}$$

Proof. Using the chain rule $\{A, f(g)\} = f'(g)\{A,g\}$ with $f = e^{-\beta H_0}/Z_{\text{part}}$ and $g = H_0$:

$$\{A,\rho_0\} = \frac{1}{Z_{\text{part}}}\frac{d\left(e^{-\beta H_0}\right)}{dH_0}\{A,H_0\} = -\beta\rho_0\{A,H_0\} = -\beta\rho_0\dot{A}. \tag{9.8}$$

□

Physical meaning. Equation 9.7 is the classical analogue of the quantum identity $[A,\rho_0] = -i\beta\rho_0\dot{A}$ (with $\{,\} \to -i[,]/\hbar$ as $\hbar \to 0$). It encodes how the equilibrium distribution "knows about" dynamical quantities through β.

9.2.4 First-order perturbation of the density

Write $\rho(t) = \rho_0 + \Delta\rho(t)$ and insert into the Liouville equation with $H = H_0 - Ah(t)$. Keeping only terms linear in $h(t)$:

$$\frac{\partial \Delta\rho}{\partial t} = \{H_0, \Delta\rho\} - h(t)\{A, \rho_0\}. \tag{9.9}$$

Applying the thermal identity Equation 9.7 converts the second term: $-h(t)\{A,\rho_0\} = \beta h(t)\rho_0\dot{A}$. The formal solution via the unperturbed propagator $e^{\mathcal{L}_0(t-t')}$ is:

$$\Delta\rho(t) = \beta \int_{-\infty}^{t} e^{\mathcal{L}_0(t-t')}\left[\rho_0 \dot{A}(\Gamma)\right] h(t')\, dt'. \tag{9.10}$$

9.2.5 Computing the response and identifying $\chi(t)$

The observable response is $\langle \Delta A(t)\rangle = \int A(\Gamma)\Delta\rho(t)d\Gamma$. Shifting the time evolution from the density to the observable and using stationarity of the equilibrium ensemble:

$$\langle \Delta A(t)\rangle = \beta \int_{-\infty}^{t} h(t') \left\langle \dot{A}(0) A(t-t')\right\rangle_0 dt' \tag{9.11}$$

By time-translation invariance, $\left\langle \dot{A}(0)A(t-t')\right\rangle_0 = \left\langle \dot{A}(t'-t)A(0)\right\rangle_0$. Differentiating Equation 9.1 gives $\dot{C}(s) = \langle A(0)\dot{A}(s)\rangle_0$. Under time-reversal symmetry for an even-parity observable [1] $\langle A(0)\dot{A}(s)\rangle_0 = -\langle \dot{A}(0)A(s)\rangle_0$, so $\left\langle \dot{A}(0)A(t-t')\right\rangle_0 = -\dot{C}(t-t')$. Comparing with Equation 9.2 and invoking causality:

$$\chi(t) = -\beta \dot{C}(t)\theta(t). \tag{9.12}$$

This is the classical FDT. The response function is completely determined by the equilibrium correlation function; no separate knowledge of the out-of-equilibrium dynamics is needed.

9.3 Proof of the Regression Hypothesis

9.3.1 Protocol: abrupt removal of a static force

Consider a static force f_0 applied for all $t \le 0$ and then suddenly removed:

$$f(t) = f_0\theta(-t) = \begin{cases} f_0 & t \le 0 \\ 0 & t > 0 \end{cases} \tag{9.13}$$

At $t = 0^-$the system is in a shifted equilibrium with mean $\langle \delta A(0)\rangle = \beta f_0 C(0)$, obtained by integrating Equation 9.12 against a constant force.

9.3.2 Relaxation for $t > 0$

For $t > 0$ there is no applied force, but the system was perturbed for all $t' \le 0$. Inserting $f(t') = f_0\theta(-t')$ into Equation 9.2 and using Equation 9.12:

$$\begin{aligned} \langle \delta A(t)\rangle &= \int_{-\infty}^{0} \chi(t-t')\, f_0 dt' = -\beta f_0 \int_{-\infty}^{0} \dot{C}(t-t')\, dt' \\ &= -\beta f_0 \left[C(t-t')\right]_{t'=-\infty}^{t'=0} = -\beta f_0 [C(t) - C(\infty)] \end{aligned} \tag{9.14}$$

Since $C(\infty) = 0$ for any ergodic system (decorrelation at long times):

$$\langle \delta A(t)\rangle = \beta f_0 C(t), \quad t > 0. \tag{9.15}$$

9.3.3 The hypothesis as a ratio

Dividing the relaxation at time t by the initial displacement:

$$\frac{\langle \delta A(t) \rangle}{\langle \delta A(0) \rangle} = \frac{\beta f_0 C(t)}{\beta f_0 C(0)} = \frac{C(t)}{C(0)}. \tag{9.16}$$

Regression Hypothesis (proved). The normalised macroscopic relaxation (left-hand side) is identical to the normalised equilibrium auto-correlation function (right-hand side). The decay of a forced deviation from equilibrium follows the same temporal law as the spontaneous regression of a thermal fluctuation.

Physical interpretation. Equation 9.16 says the system cannot "tell the difference" between relaxing from a forced displacement and regressing from a rare spontaneous fluctuation. This is a consequence of the linearity of the response and the time-reversal symmetry of the microscopic equations of motion [7].

9.4 Connection to the Power Spectral Density

Fourier-transforming Equation 9.12 with the convention $\chi(\omega) = \int_0^\infty \chi(t) e^{i\omega t} dt$ gives the dissipative (imaginary) part of the susceptibility directly in terms of the equilibrium fluctuation spectrum.

9.4.1 Derivation

$$\begin{aligned} \chi(\omega) &= -\beta \int_0^\infty \dot{C}(t) e^{i\omega t} dt \\ &= -\beta \left[C(t) e^{i\omega t} \right]_0^\infty + i\omega\beta \int_0^\infty C(t) e^{i\omega t} dt \\ &= \beta C(0) + i\omega\beta \int_0^\infty C(t) e^{i\omega t} dt, \end{aligned} \tag{9.17}$$

where $C(t)e^{i\omega t} \to 0$ as $t \to \infty$ by decorrelation. Since $C(t)$ is real and even ($C(t) = C(-t)$ from time-reversal symmetry of equilibrium dynamics), the integral in Equation 9.17 contributes purely real and imaginary parts. Taking the imaginary part:

$$\chi''(\omega) \equiv \operatorname{Im} \chi(\omega) = \omega\beta \int_0^\infty C(t) \cos(\omega t) dt \tag{9.18}$$

Defining the two-sided power spectral density via the Wiener-Khinchin theorem,

$$S(\omega) = \int_{-\infty}^\infty C(t) e^{i\omega t} dt = 2 \int_0^\infty C(t) \cos(\omega t) dt \tag{9.19}$$

we obtain the classical FDT in the frequency domain:

$$\chi''(\omega) = \frac{\beta\omega}{2} S(\omega). \tag{9.20}$$

Remark 9.1. The factor of ω reflects that χ'' describes dissipation (energy absorbed per cycle scales as frequency), while $S(\omega)$ is the fluctuation spectrum. At low frequencies both vanish, but their ratio approaches a finite constant controlled by the zero-frequency diffusion coefficient (Einstein relation).

9.4.2 Generalisation to cross-correlations

When the driving force $f(t)$ couples to observable B while we monitor observable A, the same Liouville calculation yields the cross-susceptibility

$$\chi_{AB}(t) = -\beta \dot{C}_{AB}(t) \theta(t), \quad C_{AB}(t) \equiv \langle A(t) B(0) \rangle_0, \tag{9.21}$$

which is the natural generalisation of Equation 9.12. In the frequency domain:

$$\chi''_{AB}(\omega) = \frac{\beta\omega}{2} S_{AB}(\omega), \quad S_{AB}(\omega) = \int_{-\infty}^\infty C_{AB}(t) e^{i\omega t} dt. \tag{9.22}$$

Note that C_{AB} is generically not symmetric, i.e. $C_{AB}(t) \neq C_{BA}(t)$ in general. This asymmetry is the classical seed of the Onsager

reciprocal relations derived in the next section.

9.5 Onsager-Casimir Reciprocal Relations

9.5.1 Phenomenological setup

Consider a system near equilibrium characterised by thermodynamic variables $\{A_i\}$ with thermodynamic forces

$$X_i = \frac{\partial S}{\partial A_i}, \quad J_i = \frac{dA_i}{dt}, \tag{9.23}$$

where S is the total entropy. The fluxes are assumed to depend linearly on the forces:

$$J_i = \sum_j L_{ij} X_j. \tag{9.24}$$

The entropy production rate is therefore

$$\dot{S} = \sum_i J_i X_i = \sum_{i,j} L_{ij} X_i X_j, \tag{9.25}$$

so the second law of thermodynamics ($\dot{S} \geq 0$) requires only that the symmetric part of $\mathbf{L}$ be positive semidefinite. The reciprocity $L_{ij} = L_{ji}$ is an additional, stronger statement that follows from microscopic reversibility-not from thermodynamics alone.

The Onsager matrix L encodes all transport phenomena: thermal conductivity, electrical conductivity, thermoelectric coefficients, diffusion, and their cross-effects.

We now present two independent proofs of the reciprocal relations, each illuminating a different facet of the underlying physics.

9.5.2 Proof A: Green-Kubo formula and time-reversal parity

Green-Kubo formula for L_{ij}

Let the perturbation Hamiltonian be $H'(t) = -\sum_j X_j(t) B_j$, where B_j are observables conjugate to the forces. The Kubo formula for the quantum retarded response function is

$$\chi_{ij}(t) = \frac{1}{\hbar} \theta(t) \left\langle [J_i(t), B_j(0)] \right\rangle_0, \tag{9.26}$$

where $[\cdot, \cdot]$ is the commutator. In the classical (low-frequency) limit, via $[,]/i\hbar \to \{,\}$, and using the cross-FDT Equation 9.21, the dc transport coefficients become

$$L_{ij} = \int_0^\infty \left\langle J_i(t) J_j(0) \right\rangle_0 dt \tag{9.27}$$

Time-reversal parity of fluxes

Let Θ denote the antiunitary time-reversal operator. The equilibrium state is Θ-invariant:

$$\left\langle \Theta \mathcal{O} \Theta^{-1} \right\rangle_0 = \langle \mathcal{O} \rangle_0 \quad \text{for any observable } \mathcal{O}. \tag{9.28}$$

We assign each flux a definite parity under time reversal:

$$\Theta J_i \Theta^{-1} = \epsilon_i J_i, \quad \epsilon_i = \pm 1, \tag{9.29}$$

which gives the dynamical relation

$$\Theta J_i(t) \Theta^{-1} = \epsilon_i J_i(-t). \tag{9.30}$$

Position-like quantities (density, concentration) have $\epsilon = +1$; velocity-like quantities (heat or charge currents) have $\epsilon = -1$.

Symmetry of the current correlator

Define $C_{ij}(t) = \langle J_i(t) J_j(0) \rangle_0$. Applying time-reversal invariance Equation 9.28-Equation 9.30:

$$\begin{aligned} C_{ij}(t) &= \left\langle \Theta J_i(t) J_j(0) \Theta^{-1} \right\rangle_0 \\ &= \left\langle \left(\Theta J_i(t) \Theta^{-1}\right) \left(\Theta J_j(0) \Theta^{-1}\right) \right\rangle_0 \\ &= \epsilon_i \epsilon_j \left\langle J_i(-t) J_j(0) \right\rangle_0 . \end{aligned} \tag{9.31}$$

Applying stationarity, $\langle J_i(-t) J_j(0) \rangle_0 = \langle J_j(t) J_i(0) \rangle_0 = C_{ji}(t)$:

$$C_{ij}(t) = \epsilon_i \epsilon_j C_{ji}(t). \tag{9.32}$$

Deriving the reciprocal relations

Substituting Equation 9.32 into the Green-Kubo formula Equation 9.27:

$$L_{ij} = \int_0^\infty C_{ij}(t) dt = \epsilon_i \epsilon_j \int_0^\infty C_{ji}(t) dt = \epsilon_i \epsilon_j L_{ji} \tag{9.33}$$

Hence the Onsager-Casimir reciprocal relations:

$$L_{ij} = \epsilon_i \epsilon_j L_{ji}. \tag{9.34}$$

When all relevant fluxes share the same time-reversal parity ($\epsilon_i \epsilon_j = 1$), this reduces to the original Onsager symmetry $L_{ij} = L_{ji}$. The mixed-parity case ($\epsilon_i \epsilon_j = -1$) yields the Casimir antisymmetry $L_{ij} = -L_{ji}$ [8], relevant for cross-effects between charge and heat currents in a magnetic field.

9.5.3 Proof B: Entropy-production and Gaussian fluctuations

This alternative proof works entirely at the level of fluctuation statistics, without invoking the Green-Kubo integral explicitly. It follows closely the original reasoning of Onsager [1, 3].

Equilibrium fluctuation measure

Near equilibrium, the joint distribution of the variables $\{A_i\}$ (each with zero mean) is approximately Gaussian:

$$P(\{A_i\}) \propto \exp\left(\frac{S}{k_B}\right), \quad S \approx S_{\text{eq}} - \frac{1}{2} \sum_{i,j} g_{ij} A_i A_j, \tag{9.35}$$

where g_{ij} is a symmetric positive-definite matrix (the inverse of the fluctuation covariance matrix, $g = \langle AA \rangle^{-1}$). The thermodynamic forces Equation 9.23 are therefore linear in the A_i :

$$X_k = \frac{\partial S}{\partial A_k} = -\sum_j g_{kj} A_j. \tag{9.36}$$

Orthogonality relation

Lemma 9.2 (Gaussian orthogonality). Under the distribution Equation 9.35,

$$\langle A_i X_j \rangle = -k_B \delta_{ij}. \tag{9.37}$$

Proof. $\langle A_i X_j \rangle = -\sum_k g_{jk} \langle A_i A_k \rangle = -\sum_k g_{jk} \left(g^{-1}\right)_{ki} = -\delta_{ji}$. □

Connecting time derivatives of correlators to L_{ij}

By the Regression Hypothesis (Section 9.3), the decay of $\langle A_k \rangle$ conditioned on an initial fluctuation $\{A_i\}$ follows the same linear

law as a macroscopic relaxation:

$$\frac{d}{dt}\langle A_k(t)A_i(0)\rangle = \sum_j L_{kj}\langle X_j(t)A_i(0)\rangle\,. \tag{9.38}$$

Setting $t = 0$ and using the orthogonality relation Equation 9.37:

$$\frac{d}{dt}C_{ki}(t)\Big|_{t=0} = \sum_j L_{kj}\langle X_j A_i\rangle = -k_{\mathrm{B}}L_{ki}. \tag{9.39}$$

Time-reversal symmetry of the correlator

The three-step argument exploiting microscopic reversibility:

- 1.Time-reversal invariance. Under microscopic reversibility, for even-parity variables:

$$\langle A_i(t)A_k(t+\tau)\rangle = \langle A_i(t)A_k(t-\tau)\rangle\,. \tag{9.40}$$

- 2.Stationarity. Shifting the time origin by τ :

$$\langle A_i(t)A_k(t-\tau)\rangle = \langle A_i(t+\tau)A_k(t)\rangle\,. \tag{9.41}$$

- 3.Commutativity. Classical phase-space functions commute:

$$\langle A_i(t+\tau)A_k(t)\rangle = \langle A_k(t)A_i(t+\tau)\rangle\,. \tag{9.42}$$

Combining these three steps:

$$C_{ik}(\tau) \equiv \langle A_i(t)A_k(t+\tau)\rangle = \langle A_k(t)A_i(t+\tau)\rangle \equiv C_{ki}(\tau). \tag{9.43}$$

Hence for even-parity variables the cross-correlator is symmetric: $C_{ik}(\tau) = C_{ki}(\tau)$.

Concluding reciprocity

Differentiating both sides at $\tau = 0$ and applying Equation 9.39:

$$-k_{\mathrm{B}}L_{ik} = -k_{\mathrm{B}}L_{ki}, \tag{9.44}$$

and therefore

$$L_{ij} = L_{ji}. \tag{9.45}$$

The analogous argument for odd-parity variables (which pick up a sign under time reversal) yields the Casimir extension $L_{ij} = -L_{ji}$ in the mixed case, consistent with Equation 9.34.

Remark 9.2. Proofs A and B are complementary, not redundant. Proof A makes the role of the current-current Green-Kubo correlator explicit and extends immediately to quantum systems via Equation 9.26. Proof B is closer to Onsager's original argument and makes the Gaussian fluctuation assumption and the orthogonality relation Equation 9.37 explicit-ingredients that are sometimes hidden in the Green-Kubo approach.

9.6 Modification by an External Magnetic Field

A static magnetic field B is odd under time reversal: $\Theta\mathbf{B}\Theta^{-1} = -\mathbf{B}$. Therefore, microscopic reversibility at field B maps trajectories to those of the system at -B. The equilibrium correlation identity becomes

$$\langle J_i(t)J_j(0)\rangle_{\mathbf{B}} = \epsilon_i\epsilon_j\langle J_j(t)J_i(0)\rangle_{-\mathbf{B}}\,. \tag{9.46}$$

After integration via the Green-Kubo formula:

$$L_{ij}(\mathbf{B}) = \epsilon_i\epsilon_j L_{ji}(-\mathbf{B}). \tag{9.47}$$

At $\mathbf{B} = 0$, strict symmetry $L_{ij} = \epsilon_i \epsilon_j L_{ji}$ is recovered. At nonzero $\mathbf{B}$, the symmetry is between the matrix at field +B and the transposed matrix at field -B. This is the full Onsager-Casimir generalisation [8].

Physical example. In thermoelectric transport, the Seebeck coefficient S_{AB} (voltage per temperature gradient) and the Peltier coefficient Π_{BA} (heat flux per current) are related by $\Pi_{BA}(\mathbf{B}) = TS_{AB}(-\mathbf{B})$, a consequence of Equation 9.47.

9.7 Summary and Logical Chain

Step-by-step proof outline:

1. Start from microscopic dynamics that are time-reversal invariant at $\mathbf{B} = 0$.

2. The thermal identity $\{A, \rho_0\} = -\beta \rho_0 \dot{A}$ (Theorem 15.2.1) converts the first-order Liouville perturbation into an equilibrium correlator.

3. Integration over the forcing history yields the classical FDT, $\chi(t) = -\beta \dot{C}(t)\theta(t)$.

4. Applying the FDT to a suddenly removed static force proves Onsager's Regression Hypothesis: macroscopic relaxation and microscopic regression are both governed by $C(t)/C(0)$.

5. Fourier-transforming the FDT yields $\chi''(\omega) = \frac{1}{2}\beta\omega S(\omega)$, linking dissipation to the equilibrium fluctuation spectrum.

6. Route A: The Green-Kubo formula expresses L_{ij} as $\int_0^\infty \langle J_i(t) J_j(0) \rangle_0 \, dt$. Time-reversal parity gives $C_{ij}(t) = \epsilon_i \epsilon_j C_{ji}(t)$, and hence $L_{ij} = \epsilon_i \epsilon_j L_{ji}$.

7. Route B: The Regression Hypothesis applied to equilibrium fluctuation correlators, combined with the Gaussian orthogonality relation $\langle A_i X_j \rangle = -k_B \delta_{ij}$ and the symmetry $C_{ij}(\tau) = C_{ji}(\tau)$ from microscopic reversibility, directly gives $L_{ij} = L_{ji}$.

8. If a magnetic field B is present, time reversal maps $\mathbf{B} \to -\mathbf{B}$, yielding $L_{ij}(\mathbf{B}) = \epsilon_i \epsilon_j L_{ji}(-\mathbf{B})$.

The entire argument uses only three inputs: (i) canonical equilibrium statistics, (ii) linearity of the response, (iii) time-reversal invariance of the Hamiltonian dynamics. No phenomenological assumptions are needed.

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11: From Microscopic Reversibility to Macroscopic Irreversibility

Every student of physics encounters, at some point, a striking contradiction. The microscopic laws that govern the constituents of matter-Newton's equations, the Schrödinger equation, the Hamilton-Jacobi formalism-are time-reversal invariant. If a sequence of molecular collisions is a valid solution, then running that sequence backwards in time is equally valid. Yet when a drop of ink disperses in a glass of water, it never spontaneously reconcentrates. When two gases mix, they do not unmix. Heat flows from hot to cold, never the reverse. Macroscopic processes have a definite arrow of time, while microscopic processes do not. This is the reversibility paradox, and resolving it is one of the deepest problems in theoretical physics.

Historical Background

The paradox has a precise formulation in Boltzmann's kinetic theory. In 1872, Boltzmann introduced the H-function,

$$H(t) = \int f(\mathbf{v}, t) \ln f(\mathbf{v}, t) d^3v$$

where $f(\mathbf{v}, t)$ is the single-particle velocity distribution, and proved his celebrated H-theorem: $dH/dt \leq 0$ for any gas evolving under his kinetic equation. Since H is (up to sign and a factor of $k_B N$) the thermodynamic entropy, the H-theorem appears to derive the second law of thermodynamics from mechanics.

The response was immediate and sharp. In 1876, Loschmidt raised what is now called Loschmidt's objection: if at any instant one reverses all molecular velocities, the H-theorem demands that H decrease in both time directions from that point, which is a contradiction. More precisely, for every microstate in which H decreases, there exists a time-reversed microstate in which H increases-yet the H-theorem forbids the latter. Loschmidt concluded that no purely mechanical derivation can imply irreversibility.

Boltzmann's response introduced a crucial new element: probability. The time-reversed, entropy-decreasing trajectories exist, he conceded, but they form a set of overwhelmingly small measure in the space of all initial conditions. Macroscopic irreversibility is not a consequence of the dynamics alone; it is a consequence of the dynamics combined with the strong probabilistic bias toward initial conditions of low entropy. This insight was sharpened by Zermelo's recurrence objection (1896), based on Poincaré's recurrence theorem: any finite Hamiltonian system will, with probability one, return arbitrarily close to its initial state. Boltzmann acknowledged the point but noted that recurrence times for macroscopic systems are astronomically large-many orders of magnitude beyond the age of the universe.

These nineteenth-century debates established the conceptual landscape that the twentieth century would have to navigate. Three lessons emerged:

- 1.Irreversibility cannot be derived from mechanics alone; an element of coarse-graining or probabilistic reasoning is unavoidable.
- 2.The second law is statistical, not absolute: entropy-decreasing fluctuations are possible, merely improbable.
- 3.A satisfactory theory must explain not just that irreversibility arises, but how and on what timescale.

The Modern Resolution: Projection and Contraction

The modern answer to the reversibility paradox is not a single theorem but a framework: the systematic elimination of irrelevant degrees of freedom. Any realistic system consists of a small number of slowly-varying, macroscopically observable variables-a colloidal particle's position, a spin's magnetization, a reaction coordinate-embedded in an enormous bath of fast microscopic degrees of freedom. The full dynamics of the combined system is exactly reversible. But when one contracts the description to the relevant variables alone, integrating out or projecting away the bath, memory of the detailed initial conditions of the bath is irretrievably lost. This loss of information is the statistical counterpart of thermodynamic irreversibility.

The contraction is not an approximation in the usual sense. The projection-operator formalism of Nakajima, Zwanzig, and Mori shows that the resulting equation for the relevant variable is exact-but it takes the form of a generalized Langevin equation containing a memory kernel (encoding the retarded influence of the bath) and a fluctuating force (encoding our ignorance of

the bath's initial state). The noise is not postulated, as in the original Langevin equation, but derived from deterministic bath dynamics. What appears random is so only because we have discarded the bath's degrees of freedom. The noise is given by deterministic motion of the bath oscillators, the randomness arises from our ignorance of initial conditions. In other words, the fluctuating force arises from the thermalized initial conditions of the bath oscillators. This is precisely the sense in which the Mori-Zwanzig formalism resolves the reversibility paradox: irreversibility is not a property of the fundamental laws but of the reduced description we choose to work with.

Plan of the Following Four Chapters

The next four chapters develop this program in increasing depth and generality.

Chapter 12 - Magalinski's Derivation of the Memory Function. We begin with the most transparent and instructive example: a single harmonic oscillator (the "system") bilinearly coupled to a bath of N independent harmonic oscillators (the Caldeira-Leggett Hamiltonian). Magalinski (1959) showed that this model can be solved exactly by integrating out each bath oscillator using its causal Green's function. The result is a generalized Langevin equation with an explicit memory kernel and fluctuating force, both derived analytically rather than postulated. This chapter makes the mechanism of irreversibility maximally concrete: the memory kernel is the bath's retarded mechanical response, and the fluctuating force is the driven oscillation of each bath mode evaluated at the initial bath conditions.

Chapter 13 — The Mori-Zwanzig Formulation. We then develop the abstract projection-operator framework in its full generality. Zwanzig's projection operator $\mathcal{P}$, which maps any phase-space function onto the relevant subspace, and its complement $\mathcal{Q} = 1 - \mathcal{P}$ split the Liouville equation into coupled equations for the relevant and irrelevant sectors. Formally integrating the

irrelevant sector and substituting back yields the exact Mori-Zwanzig identity: a generalized Langevin equation with a frequency matrix, a memory kernel, and a projected noise term, all expressed as equilibrium correlation functions. The chapter emphasizes both the mathematical structure and the physical interpretation: the memory kernel represents the bath's "echo," the delayed mechanical back-reaction on the system.

Chapter 14 - The Magalinski Model as a Physical Realization of Mori-Zwanzig. Having presented the Magalinski model concretely and the Mori-Zwanzig formalism abstractly, we close the loop by applying the projection-operator technique directly to the Magalinski Hamiltonian. This exercise serves two purposes. First, it verifies that the abstract formalism reproduces the exact Magalinski result, confirming internal consistency. Second, and more importantly, it reveals the physical identity of every abstract object in the Mori-Zwanzig equation: the "orthogonal dynamics" governed by $e^{\mathcal{Q}\mathcal{L}t}$ is precisely the free (uncoupled) motion of the bath oscillators; the projected noise is the bath displacement driven by its initial conditions alone; and the memory kernel is the force autocorrelation of the free bath. The formalism is thereby stripped of its abstractness and grounded in mechanical intuition.

Chapter 15 - Derivation of the Nakajima-Zwanzig and Mori-Zwanzig Formalisms. The final chapter of this part provides a rigorous and self-contained derivation of both the Nakajima-Zwanzig equation for the reduced density matrix and the Mori-Zwanzig generalized Langevin equation, following the original operator algebraic route. The Nakajima-Zwanzig equation governs the reduced description of an open quantum system and is the formal ancestor of master equations and Lindblad dynamics. The Mori-Zwanzig equation governs dynamical variables in classical statistical mechanics and is the formal ancestor of the generalized Langevin equation and mode-coupling theory. Presenting both derivations side by side illuminates their common structure while making explicit the distinctions between quantum and classical reduced dynamics.

Together, these four chapters carry a single argument: the appearance of irreversibility, noise, and dissipation in macroscopic physics is not in conflict with the time-reversal invariance of the underlying laws. It is the inevitable consequence of contracting an exact, reversible description onto a small set of relevant variables, with the information content of the discarded degrees of freedom repackaged into memory kernels and fluctuating forces.

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12: Magalinski's Derivation of the Memory Function and the Generalized Langevin Equation for a System Coupled to a Bath of Harmonic Oscillators

This chapter gives a detailed, step-by-step derivation of the memory function (damping kernel) and the generalized Langevin equation (GLE) for a single "system" harmonic coordinate coupled bilinearly to a bath of harmonic oscillators. The bath is integrated out exactly using the causal Green's function of each oscillator. The resulting equation of motion for the system contains a convolution (memory) term and a fluctuating force.

12.1 Introduction

An overarching goal of statistical physics is to derive macroscopic irreversible equations starting with microscopic reversible equations of motion. A direct model was provided by Magalinski in 1959, solving a mechanical model of an oscillator coupled to N bath oscillators to derive the generalized Langevin equation (GLE). This stands in contrast to heuristic derivations where stochastic forces are merely postulated; here, they are derived analytically.

12.2 Model and Hamiltonian

Consider a system coordinate X with mass M and frequency Ω, bilinearly coupled to a bath of n oscillators. We use the Caldeira-Leggett Hamiltonian:

$$H = \frac{P^2}{2M} + \frac{1}{2}M\Omega^2 X^2 + \sum_n \left[\frac{p_n^2}{2m_n} + \frac{1}{2}m_n\omega_n^2 \left(q_n - \frac{c_n}{m_n\omega_n^2}X \right)^2 \right]. \tag{12.1}$$

Physical Role of the Counterterm: The expansion of the bath potential includes a term $\sum_n \frac{c_n^2}{2m_n\omega_n^2}X^2$. This is the "counterterm," which ensures that the coupling does not shift the equilibrium position of the system. Without it, the bath would exert a static pinning force on X, making it impossible to recover free Brownian motion in the limit where the bare potential vanishes.

12.3 The Green's Function Method

The evolution of the bath coordinates q_n is governed by a linear inhomogeneous differential equation representing a driven harmonic oscillator:

$$\ddot{q}_n(t) + \omega_n^2 q_n(t) = \frac{c_n}{m_n}X(t). \tag{12.2}$$

The Green's function method is the mathematical engine of this derivation. We define the causal (retarded) Green's function $g_n(t)$, which satisfies:

$$\left(\frac{d^2}{dt^2} + \omega_n^2 \right) g_n(t) = \delta(t). \tag{12.3}$$

Derivation of the Impulse Response

To solve for $g_n(t)$, we apply the following physical and mathematical constraints:

- 1.Causality: As the response to an impulse at $t = 0$, we require $g_n(t) = 0$ for $t < 0$. This implies $g_n(0) = 0$.
- 2.Homogeneous Solution ($t > 0$): For $t > 0$, the equation reduces to $\ddot{g}_n + \omega_n^2 g_n = 0$. The general solution is $g_n(t) = A\cos(\omega_n t) + B\sin(\omega_n t)$. Applying $g_n(0) = 0$ forces $A = 0$.
- 3.The Jump Condition: Integrating the governing equation over an infinitesimal interval $[-\epsilon, +\epsilon]$ yields:

$$\int_{-\epsilon}^{+\epsilon}\left(\frac{d^2g_n}{dt^2}+\omega_n^2 g_n\right)dt=\int_{-\epsilon}^{+\epsilon}\delta(t)dt\Longrightarrow \dot{g}_n\left(0^+\right)-\dot{g}_n\left(0^-\right)=1. \tag{12.4}$$

Since $\dot{g}_n(t)=0$ for $t<0$, we find $\dot{g}_n\left(0^+\right)=1$. Differentiating $g_n(t)=B\sin\left(\omega_n t\right)$ gives $\dot{g}_n(t)=B\omega_n\cos\left(\omega_n t\right)$. At $t=0, B\omega_n=1$, so $B=1/\omega_n$.

Thus, the impulse response is $g_n(t)=\frac{\sin(\omega_n t)}{\omega_n}\Theta(t)$. By convolving this response with the driving force $c_nX(t)$, we obtain the exact solution:

$$q_n(t)=q_n(0)\cos\left(\omega_n t\right)+\frac{\dot{q}_n(0)}{\omega_n}\sin\left(\omega_n t\right)+\frac{c_n}{m_n}\int_0^t\frac{\sin\left(\omega_n(t-s)\right)}{\omega_n}X(s)ds. \tag{12.5}$$

12.4 Generalized Langevin Equation

Substituting the solution for $q_n(t)$ back into the system equation of motion and performing integration by parts, we arrive at the GLE:

$$M\ddot{X}(t)+M\Omega^2X(t)+M\int_0^t\gamma(t-s)\dot{X}(s)ds=\xi(t) \tag{12.6}$$

The memory kernel $\gamma(t)$ represents the dissipative drag exerted by the bath:

$$\gamma(t):=\frac{1}{M}\sum_n\frac{c_n^2}{m_n\omega_n^2}\cos\left(\omega_n t\right). \tag{12.7}$$

The fluctuating force $\xi(t)$ arises from the thermalized initial conditions of the bath oscillators.

12.5 Spectral Density and the Continuum Limit

To describe a macroscopic environment, we take the limit where the number of bath oscillators $N\to\infty$. In this continuum limit, the properties of the bath are summarized by the spectral density $J(\omega)$:

$$J(\omega)=\frac{\pi}{2}\sum_n\frac{c_n^2}{m_n\omega_n}\delta\left(\omega-\omega_n\right). \tag{12.8}$$

The memory kernel $\gamma(t)$ can then be expressed as an integral over the spectral density:

$$\gamma(t)=\frac{2}{M\pi}\int_0^\infty\frac{J(\omega)}{\omega}\cos(\omega t)d\omega. \tag{12.9}$$

12.5.1 Physical Models and the Drude Model

The choice of $J(\omega)$ determines the physical nature of the dissipation.

- η (Friction Coefficient): Represents the magnitude of the coupling between the system and the bath.
- ω_c (Cut-off Frequency): The frequency scale above which the bath oscillators can no longer follow the system motion efficiently.

The Drude Model is defined by the spectral density:

$$J(\omega)=\eta\omega\frac{\omega_c^2}{\omega^2+\omega_c^2}. \tag{12.10}$$

Physically, the Drude model accounts for the finite response time of a realistic bath. While the simple Ohmic model implies an instantaneous response, the Drude model leads to a memory kernel that decays exponentially:

$$\gamma(t)=\eta\omega_c e^{-\omega_c|t|}. \tag{12.11}$$

This indicates that the influence of the system's past velocity on its current acceleration persists for a characteristic time scale $\tau = 1/\omega_c$.

Table 12.1: Common Spectral Densities and their Physical Kernels

Model	$J(\omega)$	$\gamma(t)$	Physical Context
Ohmic	$\eta\omega$	$2\eta\delta(t)$	Markovian friction
Ohmic (Cutoff)	$\eta\omega e^{-\omega/\omega_c}$	$\frac{2\eta}{\pi}\frac{\omega_c}{1+(\omega_c t)^2}$	Finite response time
Drude	$\eta\omega\frac{\omega_c^2}{\omega^2+\omega_c^2}$	$\eta\omega_c e^{-\omega_c\lvert t\rvert}$	Exponential memory

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13: Mori-Zwanzig Formulation

An overarching goal of statistical physics is to derive macroscopic irreversible equations starting with microscopic reversible equations of motion. The Mori-Zwanzig Projection Operator Method achieves this by projecting out the motions of irrelevant variables and studying the equations of the relevant variables. While the Mori-Zwanzig identity provides an exact rearrangement of the Liouville deterministic equation, it is often critiqued as a mathematical identity without immediate physical meaning. The noise is given by deterministic motion of the bath oscillators, where randomness arises from our ignorance of initial conditions. The "memory" physically is the bath's "echo": the system pushes the bath, and the bath pushes back later.

13.1 Introduction

The transition from microscopic, time-reversible processes to macroscopic, irreversible behavior is a central problem in statistical physics, often known as the reversibility paradox. The Mori-Zwanzig Projection Operator Method achieves this by projecting out the motions of irrelevant variables to obtain the generalized Langevin equation (GLE). The GLE is a cornerstone of nonequilibrium statistical mechanics, yet its derivation is often presented in a highly formal manner.

13.2 The Mori-Zwanzig Method

A careful and pedagogic derivation involves using the initial vectors at $t = 0$ in phase space as the basis onto which subsequent vectors are projected. The main ideas include the separation of dynamics into "relevant" and "irrelevant" parts, the use of projection operators, and the resulting GLE which describes coarse-grained dynamics with memory and noise.

13.3 Liouville Dynamics and Decomposition

The dynamics of a vector in phase space is studied using the Liouville Operator $\mathcal{L}$ defined in terms of the Hamiltonian H. For a system of $N + 1$ degrees of freedom, the state is specified by $\Gamma = (q_0, \dots, q_N, p_0, \dots, p_N)$.

13.3.1 Explicit Form and Evolution

The Liouville operator $\mathcal{L}$ generates time evolution via the Poisson bracket:

$$\mathcal{L}A = \{A, H\} = \sum_{\alpha} \left(\frac{\partial A}{\partial q_\alpha} \frac{\partial H}{\partial p_\alpha} - \frac{\partial A}{\partial p_\alpha} \frac{\partial H}{\partial q_\alpha} \right). \tag{13.1}$$

The equation of motion for $A(t)$ is given formally by:

$$\frac{d}{dt} A(t) = \mathcal{L}A(t), \quad A(t) = e^{\mathcal{L}t} A(0). \tag{13.2}$$

13.3.2 Projection Operators

The projector $\mathcal{P}$ projects an arbitrary vector B onto the relevant variable A :

$$\mathcal{P}B = \langle B, A \rangle \mathbb{C}^{-1} A(0), \tag{13.3}$$

where $\mathbb{C} = \langle A, A \rangle$ is the correlation matrix. The complementary projector $\mathcal{Q} = 1 - \mathcal{P}$ projects onto the orthogonal subspace. These operators satisfy $\mathcal{P}^2 = \mathcal{P}$, $\mathcal{Q}^2 = \mathcal{Q}$, and $\mathcal{Q}\mathcal{P} = 0$.

13.4 Proof of the Mori-Zwanzig Identity

To derive the operator identity required for the formalism, consider two non-commuting operators $\mathcal{A}$ and $\mathcal{B}$. We define an operator-valued function:

$$F(s) = e^{\mathcal{A}(t-s)}e^{\mathcal{B}s}. \tag{13.4}$$

Differentiating $F(s)$ with respect to s using the product rule:

$$\frac{d}{ds}F(s) = -\mathcal{A}e^{\mathcal{A}(t-s)}e^{\mathcal{B}s} + e^{\mathcal{A}(t-s)}\mathcal{B}e^{\mathcal{B}s} = e^{\mathcal{A}(t-s)}(\mathcal{B}-\mathcal{A})e^{\mathcal{B}s} \tag{13.5}$$

Integrating from $s = 0$ to $s = t$:

$$F(t) - F(0) = \int_0^t e^{\mathcal{A}(t-s)}(\mathcal{B}-\mathcal{A})e^{\mathcal{B}s}ds \tag{13.6}$$

Substituting the boundary values $F(t) = e^{\mathcal{B}t}$ and $F(0) = e^{\mathcal{A}t}$:

$$e^{\mathcal{B}t} - e^{\mathcal{A}t} = \int_0^t e^{\mathcal{A}(t-s)}(\mathcal{B}-\mathcal{A})e^{\mathcal{B}s}ds \tag{13.7}$$

Rearranging to solve for $e^{\mathcal{A}t}$ and setting $\mathcal{A} = \mathcal{L}$ and $\mathcal{B} = \mathcal{Q}\mathcal{L}$:

$$e^{\mathcal{L}t} = e^{\mathcal{Q}\mathcal{L}t} + \int_0^t dse^{\mathcal{L}(t-s)}\mathcal{P}\mathcal{L}e^{\mathcal{Q}\mathcal{L}s} \tag{13.8}$$

This is the Mori-Zwanzig identity, splitting the propagator into orthogonal dynamics and a projection-weighted integral.

13.4.1 Alternate Derivation of the Mori-Zwanzig Identity

Show the identity

$$e^{\mathcal{L}t} = e^{O_1\mathcal{L}t} + \int_0^t dse^{\mathcal{L}(t-s)}O_2\mathcal{L}e^{O_1\mathcal{L}s} \tag{13.9}$$

holds for any two operators which have properties $O_1 + O_2 = 1$. Hint: Use the operator identity

$$\frac{1}{s-\mathcal{L}} = \frac{1}{s-O_1\mathcal{L}} + \frac{1}{s-\mathcal{L}}(1-O_1)\mathcal{L}\frac{1}{s-O_1\mathcal{L}} \tag{13.10}$$

Now because $O_1 + O_2 = 1$, the Laplace inversion yields the Mori-Zwanzig Identity. Note that $e^{\mathcal{Q}\mathcal{L}t}\mathcal{Q} = \mathcal{Q}e^{\mathcal{Q}\mathcal{L}t}\mathcal{Q}$. Hint: Expand the exponential and the left hand side and use $\mathcal{Q}^2 = \mathcal{Q}$.

13.5 Derivation of the Generalized Langevin Equation

Starting with the microscopic definition of motion from Equation 13.2:

$$\frac{d}{dt}A(t) = e^{\mathcal{L}t}\mathcal{L}A(0) \tag{13.11}$$

We insert the identity $1 = \mathcal{P} + \mathcal{Q}$ to separate the initial force:

$$\frac{d}{dt}A(t) = e^{\mathcal{L}t}\mathcal{P}\mathcal{L}A(0) + e^{\mathcal{L}t}\mathcal{Q}\mathcal{L}A(0) \tag{13.12}$$

13.5.1 The Systematic Term

The first term in Equation 13.12 uses the definition of $\mathcal{P}$:

$$e^{\mathcal{L}t}\mathcal{P}\mathcal{L}A(0) = e^{\mathcal{L}t}\left(\langle\mathcal{L}A, A\rangle\mathbb{C}^{-1}A(0)\right) = \Omega e^{\mathcal{L}t}A(0) = \Omega A(t), \tag{13.13}$$

where $\Omega = \langle\mathcal{L}A, A\rangle\mathbb{C}^{-1}$ is the frequency matrix.

13.5.2 The Memory and Noise Terms

For the second term in Equation 13.12, we substitute the identity derived in Equation 13.8:

$$e^{\mathcal{L}t}\mathcal{Q}\mathcal{L}A(0) = e^{\mathcal{Q}\mathcal{L}t}\mathcal{Q}\mathcal{L}A(0) + \int_0^t ds e^{\mathcal{L}(t-s)}\mathcal{P}\mathcal{L}e^{\mathcal{Q}\mathcal{L}s}\mathcal{Q}\mathcal{L}A(0) \tag{13.14}$$

We define the fluctuating force (noise) as:

$$F(t) = e^{\mathcal{Q}\mathcal{L}t}\mathcal{Q}\mathcal{L}A(0). \tag{13.15}$$

The integral term then becomes:

$$\int_0^t ds e^{\mathcal{L}(t-s)}\mathcal{P}\mathcal{L}F(s) \tag{13.16}$$

Applying the projector $\mathcal{P}$ and using the adjoint property $\langle \mathcal{L}O_1, O_2\rangle = -\langle O_1, \mathcal{L}O_2\rangle$:

$$\mathcal{P}\mathcal{L}F(s) = \langle \mathcal{L}F(s), A\rangle \mathbb{C}^{-1}A(0) = -\langle F(s), \mathcal{L}A\rangle \mathbb{C}^{-1}A(0). \tag{13.17}$$

Since $F(s)$ is in the $\mathcal{Q}$-subspace, we note $\langle F(s), \mathcal{P}\mathcal{L}A\rangle = 0$, thus:

$$-\langle F(s), \mathcal{L}A\rangle = -\langle F(s), \mathcal{Q}\mathcal{L}A\rangle = -\langle F(s), F(0)\rangle. \tag{13.18}$$

Substituting this into the integral and moving the propagator $e^{\mathcal{L}(t-s)}$ onto $A(0)$ to obtain $A(t-s)$:

$$\int_0^t ds e^{\mathcal{L}(t-s)}\left(-\langle F(s), F(0)\rangle \mathbb{C}^{-1}A(0)\right) = -\int_0^t ds K(s)A(t-s) \tag{13.19}$$

Combining these results yields the Generalized Langevin Equation:

$$\frac{d}{dt}A(t) = \Omega A(t) - \int_0^t ds K(s)A(t-s) + F(t) \tag{13.20}$$

Fluctuating force $F(t)$: This represents the effect of all the degrees of freedom orthogonal to A. It captures the random, microscopic fluctuations.

13.5.3 Properties of the Fluctuating Force

13.6 Properties and Relations of the Fluctuating Force

The fluctuating force $F(t)$, defined as $e^{\mathcal{Q}\mathcal{L}t}\mathcal{Q}\mathcal{L}A(0)$, represents the projection of the dynamics onto the irrelevant subspace. We now provide the formal proofs for its statistical properties and its relationship to the memory kernel.

13.6.1 Proof of Zero Mean: $\langle F(t)\rangle = 0$

By definition, the fluctuating force at any time t is given by $F(t) = e^{\mathcal{Q}\mathcal{L}t}F(0)$, where $F(0) = \mathcal{Q}\mathcal{L}A(0)$. Taking the equilibrium average:

$$\langle F(t)\rangle = \int d\Gamma \rho(\Gamma) e^{\mathcal{Q}\mathcal{L}t}\mathcal{Q}\mathcal{L}A(0) \tag{13.21}$$

Using the property that the projector $\mathcal{Q}$ ensures orthogonality to the relevant subspace, and assuming the identity vector 1 is part of the relevant subspace (or noting that $\mathcal{Q}1 = 0$), we observe that the projection $\mathcal{Q}$ acting on any vector results in a vector with zero mean in the equilibrium ensemble:

$$\langle \mathcal{Q}B\rangle = \langle B\rangle - \langle \mathcal{P}B\rangle = \langle B\rangle - \langle B, A\rangle \mathbb{C}^{-1}\langle A\rangle = 0. \tag{13.22}$$

Since $F(t)$ remains in the $\mathcal{Q}$-subspace for all t, its equilibrium average vanishes.

13.6.2 Proof of Orthogonality: $\langle F(t)A(0)\rangle = 0$

The fluctuating force is constructed to be orthogonal to the initial state of the relevant variables. To see this for all t :

$$\langle F(t), A(0)\rangle = \left\langle e^{\mathcal{Q}\mathcal{L}t}\mathcal{Q}\mathcal{L}A(0), A(0)\right\rangle . \tag{13.23}$$

Because the Liouville operator is anti-Hermitian ($\langle \mathcal{L}O_1, O_2\rangle = -\langle O_1, \mathcal{L}O_2\rangle$), and by extension its projection $\mathcal{Q}\mathcal{L}$ preserves this orthogonality within the subspace:

$$\left\langle e^{\mathcal{Q}\mathcal{L}t}\mathcal{Q}\mathcal{L}A(0), A(0)\right\rangle = \left\langle \mathcal{Q}\left(e^{\mathcal{Q}\mathcal{L}t}\mathcal{L}A(0)\right), A(0)\right\rangle . \tag{13.24}$$

By the definition of the projection operator $\mathcal{Q} = 1 - \mathcal{P}$, the vector $\mathcal{Q}B$ is orthogonal to $A(0)$ for any B :

$$\langle \mathcal{Q}B, A(0)\rangle = \langle B, A(0)\rangle - \langle \mathcal{P}B, A(0)\rangle = \langle B, A(0)\rangle - \langle B, A(0)\rangle = 0. \tag{13.25}$$

Thus, $\langle F(t)A(0)\rangle = 0$ for all t.

13.6.3 The Fluctuation-Dissipation Relation: $\langle F(t)F(0)\rangle = k_BTK(t)$

The second fluctuation-dissipation theorem relates the correlation of the fluctuating forces to the memory kernel $K(t)$. From the derivation of the GLE, we found the memory kernel to be:

$$K(t) = \langle F(t), F(0)\rangle \mathbb{C}^{-1}. \tag{13.26}$$

For a single variable A in a canonical ensemble, the correlation matrix $\mathbb{C} = \langle A, A\rangle$ is related to the thermal energy. In many physical representations (such as velocity or momentum), equipartition implies $\langle A, A\rangle = k_BT/m$. Substituting the definition of the inner product as an equilibrium correlation, we obtain:

$$K(t) = \frac{\langle F(t)F(0)\rangle}{\langle A^2\rangle}. \tag{13.27}$$

13.6.4 Summary of properties of the fluctuating forces

The fluctuating force has the following properties:

- 1.$\langle F(t)\rangle = 0$ (zero mean)
- 2.$\langle F(t)A(0)\rangle = 0$ (orthogonality)

13.6.5 Fluctuation-Dissipation Relation

The memory kernel and fluctuating force are related:

$$\langle f(t)f(0)\rangle = k_BTK(t) \tag{13.28}$$

This is a manifestation of the second fluctuation-dissipation theorem.[4]

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14: The Magalinski Model- A Physical Realization of Mori-Zwanzig Dynamics

While the Mori-Zwanzig (M-Z) formalism provides an exact framework for deriving irreversible macroscopic equations from reversible microscopic dynamics, it is often viewed as a formal mathematical identity. In this chapter, we apply the M-Z projection operator technique to the Magalinski model-a system oscillator coupled to a harmonic bath. We demonstrate that the abstract "orthogonal evolution" corresponds precisely to the free dynamics of the bath. This concrete example serves to ground the formal identities of the previous chapter in physical intuition, explicitly deriving the memory kernel and the fluctuation-dissipation relation.

14.1 Introduction: From Formalism to Physics

As developed in the preceding chapter, the Mori-Zwanzig identity rearranges the Liouville equation into a form resembling the Langevin equation. However, the physical nature of the memory kernel $K(t)$ and the noise $F(t)$ often remains opaque.

To bridge this gap, we apply the method to the Magalinski model [1]. This system is uniquely instructive because it allows for an exact evaluation of the projection operators, revealing that the "orthogonal space" is not merely a mathematical construct, but represents the physical degrees of freedom of the environment that we choose to "project out."

14.2 The Coupled Oscillator Hamiltonian

We consider a system oscillator (coordinate q_0, momentum p_0) bilinearly coupled to N bath oscillators (q_i, p_i). The total Hamiltonian is:

$$H = \frac{p_0^2}{2m_0} + \frac{1}{2}m_0\omega_0^2 q_0^2 + \sum_{i=1}^{N}\left(\frac{p_i^2}{2m_i} + \frac{1}{2}m_i\omega_i^2 q_i^2\right) + \sum_{i=1}^{N} c_i q_0 q_i, \tag{14.1}$$

where c_i are the coupling constants. Recalling the Liouville operator $\mathcal{L}A = \{A, H\}$, we decompose it into system, bath, and interaction components:

$$\begin{aligned}
\mathcal{L}_0 &= \frac{p_0}{m_0}\frac{\partial}{\partial q_0} - m_0\omega_0^2 q_0 \frac{\partial}{\partial p_0} \\
\mathcal{L}_B &= \sum_{i=1}^{N}\left(\frac{p_i}{m_i}\frac{\partial}{\partial q_i} - m_i\omega_i^2 q_i \frac{\partial}{\partial p_i}\right), \\
\mathcal{L}_{\text{int}} &= -\sum_{i=1}^{N} c_i q_i \frac{\partial}{\partial p_0} - \sum_{i=1}^{N} c_i q_0 \frac{\partial}{\partial p_i}.
\end{aligned} \tag{14.2}$$

14.3 Choosing Relevant Variables

A natural choice of relevant (slow) variables for the system oscillator is the vector

$$A(t) = \begin{pmatrix} q_0(t) \\ p_0(t) \end{pmatrix}. \tag{14.3}$$

The equation of motion for $A(t)$ is given formally by

$$\frac{d}{dt}A(t) = \mathcal{L}A(t), \quad A(t) = e^{\mathcal{L}t}A(0). \tag{14.4}$$

The action of $\mathcal{L}$ on A, using the above Hamiltonian, Equation 14.20 is

$$\mathcal{L}A = \begin{pmatrix} \mathcal{L}q_0 \\ \mathcal{L}p_0 \end{pmatrix} = \begin{pmatrix} p_0/m_0 \\ -m_0\omega_0^2 q_0 - \sum_j c_j q_j \end{pmatrix}. \tag{14.5}$$

(Repeat: Some authors include a factor i by convention common in projection-operator literature; here we work without it.)

$$\mathcal{P}B = (B, A)(A, A)^{-1}A = \sum_{j,k=0}^{1} \langle A_j B \rangle_{eq} \left(\mathbb{C}^{-1}\right)_{jk} A_k, \tag{14.6}$$

where $\mathbb{C}_{jk} = \langle A_j(0) A_k(0) \rangle_{eq}$ is the correlation matrix.

With the identification of the relevant vector A is a 2-component vector, Equation 14.3,

$$\mathbb{C} = \begin{pmatrix} \langle q_0^2 \rangle_{eq} & \langle q_0 p_0 \rangle_{eq} \\ \langle p_0 q_0 \rangle_{eq} & \langle p_0^2 \rangle_{eq} \end{pmatrix} \tag{14.7}$$

The equipartition theorem [4], remarkably, is independent of the precise form of the function H. An elegant proof is given in the book by Pathria and Beale [4], page 62. Using the equipartition theorem we have,

$$\mathbb{C} = \begin{pmatrix} \langle q_0^2 \rangle_{eq} & 0 \\ 0 & \langle p_0^2 \rangle_{eq} \end{pmatrix} = \begin{pmatrix} \frac{k_B T}{m_0 \omega_0^2} & 0 \\ 0 & m_0 k_B T \end{pmatrix}. \tag{14.8}$$

14.3.1 Frequency Matrix:The Systematic Term

Recall that the frequency matrix Ω is defined as

$$\Omega = \langle \mathcal{L}A, A \rangle \mathbb{C}^{-1} \tag{14.9}$$

First consider the first factor on the right hand side, i. e., the matrix $\langle \mathcal{L}A, A \rangle$

$$\begin{pmatrix} \langle q_0 \mathcal{L} q_0 \rangle_{eq} & \langle p_0 \mathcal{L} q_0 \rangle_{eq} \\ \langle q_0 \mathcal{L} p_0 \rangle_{eq} & \langle p_0 \mathcal{L} p_0 \rangle_{eq}. \end{pmatrix} \tag{14.10}$$

Now use Eq. 14.5 and note that the diagonal terms involve cross-terms between $\sim q_0 p_0$, i. e., the 11 term involves $\langle q_0 \mathcal{L} q_0 \rangle_{eq}$ $\sim \langle q_0 p_0 \rangle_{eq}$ and the 22 term involves $\langle p_0 \mathcal{L} p_0 \rangle_{eq} \sim \langle p_0 q_0 \rangle_{eq}$ and, therefore, they Vanish. Similarly, the off-diagonal term12 is $\langle p_0 \mathcal{L} q_0 \rangle_{eq}$ $= \langle p_0^2 / (m_0) \rangle_{eq} = k_B T$ and the off-diagonal term 21 is $\langle q_0 \mathcal{L} p_0 \rangle_{eq} = \left\langle q_0 \left(-m_0 \omega_0^2 q_0\right)\right\rangle_{eq} = -k_B T$

$$\begin{pmatrix} \langle q_0 \mathcal{L} q_0 \rangle_{eq} & \langle p_0 \mathcal{L} q_0 \rangle_{eq} \\ \langle q_0 \mathcal{L} p_0 \rangle_{eq} & \langle p_0 \mathcal{L} p_0 \rangle_{eq} \end{pmatrix} = \begin{pmatrix} 0 & k_B T \\ -k_B T & 0 \end{pmatrix}. \tag{14.11}$$

Using $\mathbb{C}^{-1} = \mathrm{diag}\left(\frac{m_0 \omega_0^2}{k_B T}, \frac{1}{m_0 k_B T}\right)$ one obtains the expected structure for $\mathbf{\Omega}$

$$\Omega = \begin{pmatrix} \langle q_0 \mathcal{L} q_0 \rangle_{eq} & \langle p_0 \mathcal{L} q_0 \rangle_{eq} \\ \langle q_0 \mathcal{L} p_0 \rangle_{eq} & \langle p_0 \mathcal{L} p_0 \rangle_{eq} \end{pmatrix} \mathbb{C}^{-1} = \begin{pmatrix} 0 & \frac{1}{m_0} \\ -m_0 \omega_0^2 & 0 \end{pmatrix} \tag{14.12}$$

14.3.2 Noise Vector

We have seen above, Equation ???, that the noise vector is given by $F(t) = e^{\mathcal{Q}\mathcal{L}t}\mathcal{Q}\mathcal{L}A(0)$. But from Equation 14.5 for $\mathcal{L}A$ upon further projection by the $\mathcal{Q}$ yields:

$$\mathcal{Q}\mathcal{L}A = \mathcal{Q}\begin{pmatrix} p_0/m_0 \\ -m_0\omega_0^2 q_0 - \sum_j c_j q_j \end{pmatrix} = \begin{pmatrix} 0 \\ -\sum_j c_j q_j \end{pmatrix} = \begin{pmatrix} 0 \\ f(0) \end{pmatrix}. \tag{14.13}$$

Since $\mathcal{L}q_0 = p_0/m_0$ lies in the span of the relevant variables, $\mathcal{Q}\mathcal{L}q_0 = 0$. For the momentum component,

$$\mathcal{Q}\mathcal{L}p_0 = -\sum_{i=1}^{N} c_i q_i \equiv f(0).$$

14.4 On the projected subspace $\mathcal{Q}$ the bath evolves freely

For the linear coupling $H_{\text{int}} = \sum_{i=1}^{N} c_i q_0 q_i$, we show

$$\mathcal{Q}\mathcal{L}f(0) = \mathcal{L}_B f(0),$$

where $f(0) = -\sum_j c_j q_j(0)$ and $\mathcal{L}_B$ is the bath Liouville operator generated by H_B. Consequently,

$$F_2(t) = e^{\mathcal{Q}\mathcal{L}t} f(0) = e^{\mathcal{L}_B t} f(0),$$

i.e. the orthogonal evolution of $f(0)$ is identical to the free bath evolution.

This result is the 'Rosetta Stone' of the derivation, translating the abstract orthogonal dynamics of Mori-Zwanzig into the familiar language of free Newtonian oscillations.

14.4.1 Algebraic proof

First compute

$$\mathcal{L}f(0) = -\sum_j c_j \{q_j, H\} = -\sum_j c_j \frac{p_j}{m_j}.$$

Since the right hand side involves only the vectors in the B space, the further projection by $\mathcal{Q}$ does not affect it, i.e., $\mathcal{Q}\mathcal{L}f(0) = -\sum_j c_j \frac{p_j}{m_j}$. But this equals $\mathcal{L}_B f(0)$, since from the above definition of $\mathcal{L}_B$, we have, $\mathcal{L}_B q_j = p_j/m_j$. Therefore

$$\mathcal{Q}\mathcal{L}f(0) = \mathcal{L}_B f(0),$$

and exponentiation yields $e^{\mathcal{Q}\mathcal{L}t} f(0) = e^{\mathcal{L}_B t} f(0)$.

14.5 Explicit expression for $F_2(t) = e^{\mathcal{Q}\mathcal{L}t} f(0)$

For the harmonic bath, the homogeneous solution is given by, $q_j^{\text{hom}}(t)$,

$$e^{\mathcal{L}_B t} q_j(0) = q_j(0)\cos(\omega_j t) + \frac{p_j(0)}{m_j \omega_j}\sin(\omega_j t) = q_j^{\text{hom}}(t).$$

Thus,

$$F_2(t) = -\sum_{j=1}^{N} c_j \left[q_j(0)\cos(\omega_j t) + \frac{p_j(0)}{m_j \omega_j}\sin(\omega_j t) \right]. \tag{14.14}$$

i.e. the noise vector is

$$F(t) = \begin{pmatrix} 0 \\ F_2(t) \end{pmatrix} = \begin{pmatrix} 0 \\ e^{\mathcal{Q}\mathcal{L}t} f(0) \end{pmatrix}.$$

From now on we will designate the non-zero component of the above vector as $F(t) = F_2(t)$, i. e. drop the subscript 2.

14.6 Difference between $f(t) = e^{\mathcal{L}t} f(0)$ and $F(t) = F_2(t) = e^{\mathcal{Q}\mathcal{L}t} f(0)$

- Full evolution $f(t)$. Contains both homogeneous bath evolution and driven contributions from the system degrees of freedom because $\mathcal{L}$ includes interactions.
- Orthogonal evolution $F(t) = F_2(t)$. Evolution under the dynamics constrained to the subspace orthogonal to the relevant

variables. For the linear harmonic model it reduces to the free bath evolution of the same initial combination and contains no driven/system-coupling pieces.

We re-emphasize that $F(t)$ is "random" only in the sense of being orthogonal to the system variables, but its underlying dynamics are still deterministic.

14.7 Memory Kernel

Next evaluate the general formula

$$K(t) = \langle F(0), F(t)\rangle_{eq}\mathbb{C}^{-1} \tag{14.15}$$

for the problem of the coupled oscillator. The non-zero component of the memory kernel is

$$K_{22}(t) = K_{pp}(t) = \frac{1}{m_0 k_B T}\langle F(0)F(t)\rangle_{eq}, \tag{14.16}$$

and using Equation 14.14 one obtains

$$\langle F(0)F(t)\rangle_{eq} = \sum_{i=1}^{N} c_i^2 \left\langle q_i(0)q_i(t)\right\rangle_{eq} = \sum_{i=1}^{N} \frac{c_i^2 k_B T}{m_i\omega_i^2}\cos\left(\omega_i t\right).$$

Thus, redefining non-zero component of the memory kernel K as a scalar, for convenience,

$$K(t) = K_{22}(t) = K_{pp}(t) = \frac{1}{m_0}\sum_{i=1}^{N} \frac{c_i^2}{m_i\omega_i^2}\cos\left(\omega_i t\right). \tag{14.17}$$

14.8 Complete Generalized Langevin Equation[4]

By combing the results above for the system oscillator, the frequency matrix, Equation 14.12, the Kernel Equation 14.17 and the noise Equation 14.14, with the M-Z formalism Equation (B.10) gives us

$$\frac{dq_0}{dt} = \frac{p_0}{m_0}, \tag{14.18}$$

$$\frac{dp_0}{dt} = -m_0\omega_0^2 q_0 - \int_0^t K(t-s)\frac{p_0(s)}{m_0}ds + F(t), \tag{14.19}$$

with the fluctuation-dissipation relation[4]

$$\langle F(t)F(s)\rangle_{eq} = k_B T m_0 K(|t-s|).$$

(Note: $\mathbb{C}_{pp}^{-1} = \frac{1}{m_0 k_B T}$ was used in $K_{22} = K_{pp} = K$ which leads to a factor of m_0 here compared to some other conventions.)

14.9 Continuum limit

With the spectral density

$$J(\omega) = \frac{\pi}{2}\sum_{i=1}^{N} \frac{c_i^2}{m_i\omega_i^2}\delta\left(\omega-\omega_i\right),$$

the continuum limit gives

$$K(t) = K_{22}(t) = \frac{2}{m_0\pi}\int_0^\infty d\omega J(\omega)\cos(\omega t)$$

14.9.1 Ohmic damping

For an Ohmic spectral density $J(\omega) = m_0\gamma\omega$ (with appropriate high-frequency cutoff), one finds in the Markov limit

$$K(t) \approx 2\gamma\delta(t),$$

leading to the classical damped oscillator

$$\ddot{q}_0 + 2\gamma\dot{q}_0 + \omega_0^2 q_0 = \frac{F(t)}{m_0}.$$

This example demonstrates how memory kernels reduce to simple friction in the Markovian limit.

14.10 Relation to the generalized Langevin equation of Magalinski[1]

The final results agree with the solution obtained by Magalinski [1] by direct integration (Green's function) solution of coupled harmonic oscillators. We leave Magalinski's [1] derivation as an exercise below. In particular, the noise time evolution is governed by free bath oscillators, exactly the same way.

14.11 Numerical Illustration of "Deterministic" Noise

Even with a finite N, the superposition of sines and cosines in Equation 14.14 produces a "noisy" trajectory. Figure 14.1 illustrates $F(t)$ for $N = 10$, and its Fourier spectrum is shown in Figure 14.2. Though the underlying equations are deterministic, the ignorance of initial bath conditions $\rho(\Gamma)$ provides the statistical randomness required for the Langevin description.

14.12 Bilinear Coupling

Here we have assumed a bilinear coupling between the central oscillator and the bath oscillators,

$$H = \underbrace{\frac{p_0^2}{2m_0} + \frac{1}{2}m_0\omega_0^2 q_0^2}_{H_0} + \underbrace{\sum_{i=1}^{N}\left(\frac{p_i^2}{2m_i} + \frac{1}{2}m_i\omega_i^2 q_i^2\right)}_{H_B} + \underbrace{\sum_{i=1}^{N} c_i q_0 q_i}_{H_{\text{int}}}. \tag{14.20}$$

It is crucial at this stage to alert the reader to a major mathematical specialty of bilinear systems. In general, $f(0) = \mathcal{Q}\mathcal{L}p_0(0)$ is the initial unprojected force generated by the interaction. For linear coupling, $f(0)$ happens to depend only on the bath coordinates $\{q_j\}$, containing no primary system coordinates q_0 or p_0. Because $f(0)$ resides exclusively in the linear subspace of bath degrees of freedom, applying $\mathcal{Q}\mathcal{L}$ repeatedly generates operations that stay entirely within the bath subspace.

CHAPTER 14. THE MAGALINSKI MODEL: A PHYSICAL REALIZATION OF MORI-ZWANZIG DYNAM

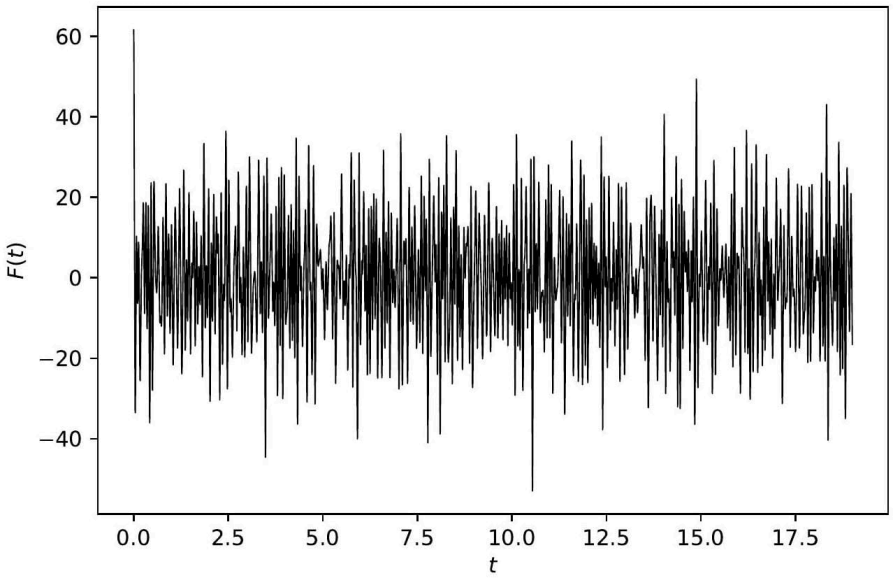


Figure 14.1: Time evolution of the fluctuating force $F(t) = -\sum_{j=1}^{N} c_j \left[q_j(0)\cos(\omega_j t) + \frac{p_j(0)}{m_j\omega_j}\sin(\omega_j t)\right]$ for $N = 10$ bath oscillators with random initial conditions. Despite being generated by fully deterministic equations of motion, the superposition of incommensurate frequencies produces a trajectory that is effectively random.

However, if $f(0)$ contains higher-order non-linear terms in q_0 or cross-terms (such as quadratic/cubic system terms arising from non-linear coupling H_{int} or non-linear system potentials), additional terms generated in $f(0)$ will fail to remain orthogonal to the projection subspace under further applications of $\mathcal{L}$. Projection operator $\mathcal{Q} = 1 - \mathcal{P}$ will then continually strip off non-zero projections back onto q_0 and p_0, creating an infinite hierarchy of non-linear operator couplings. Thus, the identity $\mathcal{Q}\mathcal{L}f(0) = \mathcal{L}_B f(0)$ is a unique, remarkable closure property of linear bath systems, allowing $e^{\mathcal{Q}\mathcal{L}t}$ to be replaced by the free bath operator $e^{\mathcal{L}_B t}$.

It is essential to separate two distinct claims. The Mori-Zwanzig identity is an exact operator rearrangement of the Liouville equation: it holds for any Hamiltonian, linear or non-linear, and does not rely on the harmonic bath model at all. What is special to the harmonic bath is not the identity itself but the fact that it can be evaluated in closed form - the exact evaluation $\mathcal{Q}\mathcal{L}f(0) = \mathcal{L}_B f(0)$ used throughout relies crucially on the linear nature of the harmonic interactions between the oscillator and the bath variables. When non-linearities are introduced, either through an anharmonic system potential $V(q_0)$ or non-linear coupling $H_{\text{int}}(q_0, q_i)$, the identity remains exact but its evaluation becomes intractable in closed form. Students should not read this section as a failure of the Mori-Zwanzig method, but as a statement about which systems admit an explicit solution.

The mechanism is concrete. Suppose the coupling contains a cubic term, $H_{\text{int}} = cq_0q_j + \lambda q_0^2 q_j$. Acting with $\mathcal{Q}\mathcal{L}$ on $f(0) = q_j(0)$ now produces, alongside the linear term $\propto q_0$, a term $\propto q_0^2$. Because q_0^2 does not lie in the linear span of the bath coordinates $\{q_j, p_j\}$ that $\mathcal{Q}$ projects onto, this term is not annihilated and does not close back into $\mathcal{L}_B f(0)$: the orthogonal dynamics generates an ever-growing hierarchy of higher powers of q_0 under repeated application of $\mathcal{Q}\mathcal{L}$. Consequently: 1. The orthogonal propagator $e^{\mathcal{Q}\mathcal{L}t}$ no longer reduces to uncoupled bath dynamics $\mathcal{L}_B$. 2. The fluctuating force $F(t)$ and memory kernel $K(t)$ become state-dependent, leading to non-Gaussian noise statistics and non-linear memory structures. 3. Closed-form analytic evaluation of $K(t)$ is generally impossible, requiring mode-coupling approximations.

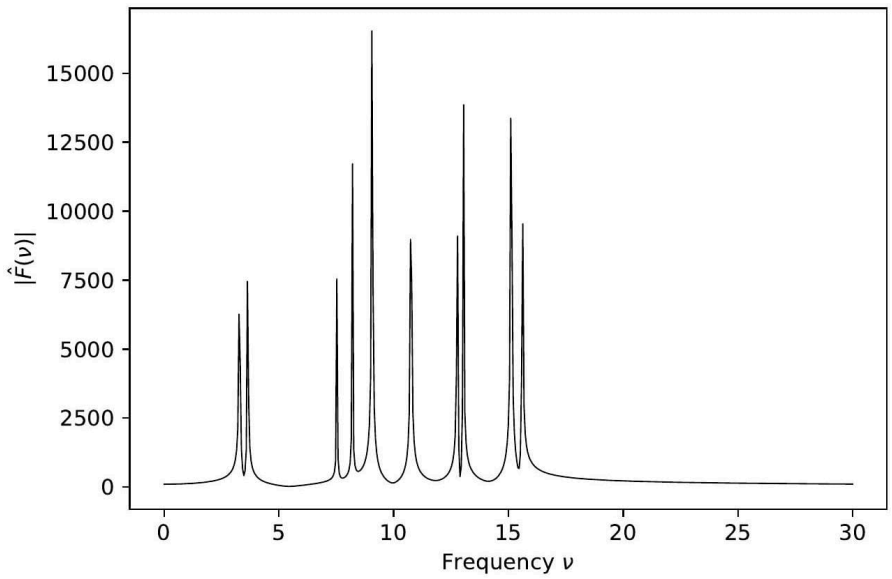


Figure 14.2: Fourier spectrum of $F(t)$ (frequencies up to $\omega = 30$) for the same $N = 10$ realisation shown in Figure 14.1. Each spike corresponds to a bath oscillator frequency ω_j. In the continuum limit $N \to \infty$ the discrete spikes merge into the smooth spectral density $J(\omega)$, recovering the memory kernel $\gamma(t)$ via $\gamma(t) = \frac{2}{M\pi} \int_0^\infty \frac{J(\omega)}{\omega} \cos(\omega t) d\omega$.

Highlighting this limitation helps students appreciate why the harmonic bath model is a unique paradigm where Mori-Zwanzig projection yields fully analytic closed-form solutions, while the identity itself remains available as an exact starting point for perturbative or numerical treatments of the general case.

14.13 Conclusion

The Magalinski model demonstrates that the "memory" in the Generalized Langevin Equation is physically the "echo" of the bath. After the system pushes the bath, and the bath, evolving through its own dynamics, pushes back at a later time. The formal M-Z identity thus finds a concrete, intuitive home in the dynamics of coupled oscillators.

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15: Derivation of the Nakajima-Zwanzig and Mori-Zwanzig Formalisms

The Nakajima-Zwanzig projection operator technique is a powerful formal method in non-equilibrium statistical mechanics that is used to derive the equation of motion for a "system of interest" that is interacting with a larger "reservoir" or "bath". At its core, the method allows you to "reduce" the full density matrix of the universe (system + bath) into a reduced density matrix for just the system by formally integrating out the bath degrees of freedom. The projection-operator formalism, developed independently by Nakajima (1958) and Zwanzig (1960) and later refined by Mori (1965), constitutes a cornerstone of modern non-equilibrium statistical mechanics. Starting from the exact Liouville equation, the formalism provides a systematic procedure to eliminate microscopic degrees of freedom while retaining exact, closed equations of motion for macroscopic observables of interest. The price paid is the appearance of memory kernels and fluctuating forces - objects that encode the influence of the discarded modes on the relevant ones.

This chapter provides a self-contained, step-by-step derivation of (i) the Nakajima-Zwanzig (NZ) equation for the reduced density matrix $\rho_s(t)$, and (ii) the Mori-Zwanzig Generalized Langevin Equation (GLE) for dynamical variables $\mathbf{A}(t)$. We follow the Zwanzig convention, in which the Liouville operator is defined through the classical Poisson bracket, so that no explicit factor of i appears. Derivations are given in full detail, with physical interpretation after each key step.

15.1 Motivation and Physical Setting

A generic physical system of interest - a spin coupled to a phonon bath, a colloidal particle suspended in a solvent, a molecule undergoing chemical reactions in a heat reservoir - can be divided conceptually into two parts:

- A relevant (or "system") sector S, described by a small number of slowly-varying degrees of freedom.
- An irrelevant (or "bath") sector B, comprising a large number of fast, microscopic degrees of freedom.

The full microscopic dynamics of $S + B$ is governed by a Hamiltonian

$$H = H_S + H_B + H_{SB}, \tag{15.1}$$

where H_{SB} is the coupling. In principle, Liouville's equation determines the time evolution of the full phase-space distribution (or density matrix) exactly. In practice, we neither know the precise initial state of B nor care about its detailed dynamics. The challenge is to derive exact, closed equations for the relevant sector alone.

Naive perturbation theory in H_{SB} is inadequate for strong coupling or long times. The projection-operator approach [1, 2, 3] achieves the elimination exactly, at the cost of introducing an equation with a memory integral and an inhomogeneous noise term. These are not approximations - they are exact reformulations. Approximations are made only afterwards (e.g., Markov approximation, Born approximation), and the formalism keeps track of what is being discarded.

15.2 The Liouville Operator and Zwanzig Convention

15.2.1 Classical mechanics setting

Let the full system have coordinates $(q_j, p_j), j = 1, \ldots, N$, and Hamiltonian H. The time evolution of any observable $A(q, p)$ along a Hamiltonian trajectory obeys

$$\dot{A} = \{H, A\} \equiv \sum_j \left(\frac{\partial H}{\partial p_j} \frac{\partial A}{\partial q_j} - \frac{\partial H}{\partial q_j} \frac{\partial A}{\partial p_j} \right). \tag{15.2}$$

Following Zwanzig [3], we define the Liouville operator L by

$$LA \equiv \{H, A\}, \tag{15.3}$$

so that $\dot{A} = LA$. The formal solution is $A(t) = e^{Lt}A(0)$.

15.2.2 Evolution of the phase-space density

The phase-space distribution function $\rho(q, p, t)$ satisfies the Liouville equation, which expresses conservation of probability along Hamiltonian trajectories:

$$\frac{\partial \rho}{\partial t} = -L\rho. \tag{15.4}$$

The minus sign arises because ρ transforms contravariantly: if observables are pushed forward in time by e^{Lt}, then the distribution is pulled back by e^{-Lt}. Equation 15.4 is the starting point for everything that follows.

15.3 Projection Operators: Setup and Algebra

15.3.1 Definition and basic properties

The key idea is to split any phase-space distribution ρ into two orthogonal parts: a relevant part $\mathcal{P}\rho$ and an irrelevant part $\mathcal{Q}\rho$. This is accomplished by a projection operator $\mathcal{P}$ satisfying

$$\mathcal{P}^2 = \mathcal{P} \quad \text{(idempotency)}. \tag{15.5}$$

Its complement is

$$\mathcal{Q} \equiv \mathcal{I} - \mathcal{P}, \quad \mathcal{Q}^2 = \mathcal{Q}, \quad \mathcal{P}\mathcal{Q} = \mathcal{Q}\mathcal{P} = 0. \tag{15.6}$$

Every distribution decomposes uniquely as $\rho = \mathcal{P}\rho + \mathcal{Q}\rho$.

15.3.2 A concrete choice of $\mathcal{P}$

A standard and physically transparent choice is

$$\mathcal{P}\rho(t) \equiv \rho_B^{\mathrm{eq}} \,\mathrm{Tr}_B[\rho(t)] = \rho_B^{\mathrm{eq}} \otimes \rho_S(t), \tag{15.7}$$

where ρ_B^{eq} is the equilibrium distribution of the bath and $\rho_S(t) = \mathrm{Tr}_B[\rho(t)]$ is the reduced density of the system. One readily verifies $\mathcal{P}^2 = \mathcal{P}$: applying $\mathcal{P}$ twice simply traces out the bath again, recovering the same $\rho_S(t)$.

Physical picture. The projection $\mathcal{P}\rho$ retains only the information about the system degrees of freedom, discarding all correlations between system and bath. The irrelevant part $\mathcal{Q}\rho$ encodes precisely those system-bath correlations that build up over time due to the interaction H_{SB}. The NZ equation will show how $\mathcal{Q}\rho$ feeds back into the evolution of $\mathcal{P}\rho$ through a memory integral.

15.4 The Nakajima-Zwanzig Equation

15.4.1 Splitting the Liouville equation

Apply $\mathcal{P}$ and $\mathcal{Q}$ to both sides of Equation 15.4. Since $\rho = \mathcal{P}\rho + \mathcal{Q}\rho$ and $\mathcal{P} + \mathcal{Q} = \mathcal{I}$, we obtain two coupled equations:

$$\frac{\partial}{\partial t}\mathcal{P}\rho(t) = -\mathcal{P}L\mathcal{P}\rho(t) - \mathcal{P}L\mathcal{Q}\rho(t), \tag{15.8}$$

$$\frac{\partial}{\partial t}\mathcal{Q}\rho(t) = -\mathcal{Q}L\mathcal{P}\rho(t) - \mathcal{Q}L\mathcal{Q}\rho(t). \tag{15.9}$$

These are exact. Equation 15.8 governs the relevant part but is not closed: it is driven by the irrelevant part $\mathcal{Q}\rho$ through the coupling term $-\mathcal{P}L\mathcal{Q}\rho$. Our strategy is to solve Equation ??? for $\mathcal{Q}\rho(t)$ in terms of $\mathcal{P}\rho$ and substitute back.

15.4.2 Formal solution for the irrelevant part

Equation ??? is a first-order linear ODE in $\mathcal{Q}\rho$:

$$\frac{\partial}{\partial t}\mathcal{Q}\rho(t) = -\mathcal{Q}L\mathcal{Q}\rho(t) - \mathcal{Q}L\mathcal{P}\rho(t) \tag{15.10}$$

The homogeneous propagator is $e^{-\mathcal{Q}Lt}$, which generates dynamics entirely within the irrelevant subspace (since $\mathcal{Q}L\mathcal{Q}$ appears, not the full L). Using the method of integrating factors (variation of constants), the solution is

$$\mathcal{Q}\rho(t) = e^{-\mathcal{Q}Lt}\mathcal{Q}\rho(0) - \int_0^t d\tau e^{-\mathcal{Q}L(t-\tau)}\mathcal{Q}L\mathcal{P}\rho(\tau) \tag{15.11}$$

Let us examine each term:

- First term $e^{-\mathcal{Q}Lt}\mathcal{Q}\rho(0)$: the irrelevant part of the initial distribution, propagated forward by the projected dynamics. If $\mathcal{Q}\rho(0) = 0$ (the common choice of initially uncorrelated system and bath), this term vanishes.
- Second term: the irrelevant correlations generated at all previous times $\tau < t$ by the coupling of $\mathcal{P}\rho(\tau)$ to $\mathcal{Q}$, each subsequently propagated to time t by $e^{-\mathcal{Q}L(t-\tau)}$.

15.4.3 Derivation of the closed equation for $\mathcal{P}\rho$

Substitute Equation 15.11 into Equation 15.8:

$$\begin{aligned}\frac{\partial}{\partial t}\mathcal{P}\rho(t) =& -\mathcal{P}L\mathcal{P}\rho(t) - \mathcal{P}L\left[e^{-\mathcal{Q}Lt}\mathcal{Q}\rho(0)\right] \\ &+ \int_0^t d\tau \underbrace{\mathcal{P}Le^{-\mathcal{Q}L(t-\tau)}\mathcal{Q}L\mathcal{P}}_{\mathcal{K}(t-\tau)}\rho(\tau)\end{aligned}$$

Collecting terms, the Nakajima-Zwanzig equation reads:

$$\frac{\partial}{\partial t}\mathcal{P}\rho(t) = -\mathcal{P}L\mathcal{P}\rho(t) + \int_0^t d\tau\mathcal{K}(t-\tau)\mathcal{P}\rho(\tau) + \mathcal{I}(t), \tag{15.12}$$

with

$$\mathcal{K}(t) \equiv \mathcal{P}Le^{-\mathcal{Q}Lt}\mathcal{Q}L\mathcal{P} \quad \text{(memory kernel)}\ , \tag{15.13}$$

$$\mathcal{I}(t) \equiv -\mathcal{P}Le^{-\mathcal{Q}Lt}\mathcal{Q}\rho(0) \quad \text{(inhomogeneous/noise term)} \tag{15.14}$$

15.4.4 Physical interpretation of each term

- 1.Streaming term $-\mathcal{P}L\mathcal{P}\rho(t)$: the instantaneous, Markovian evolution of the relevant sector due to the projected Liouvillian. In the spin-boson picture, this term would describe the precession of the spin under its own field, ignoring the bath.
- 2.Memory integral $\int_0^t d\tau\mathcal{K}(t-\tau)\mathcal{P}\rho(\tau)$: the cumulative non-Markovian feedback of the bath on the system. The kernel $\mathcal{K}(t-\tau)$ encodes how correlations generated at time τ influence the relevant sector at time t. The memory decays on a timescale τ_B characteristic of the bath. In the limit $\tau_B \to 0$, the kernel collapses to a delta function and one recovers a Markovian (GKSL-type) master equation.
- 3.Inhomogeneous term $\mathcal{I}(t)$: a noise contribution from the initial system-bath correlations. Under the assumption $\mathcal{Q}\rho(0) = 0$ (the system and bath are initially uncorrelated), this term vanishes exactly, which is the standard initial condition in open quantum systems.

15.5 The Mori-Zwanzig Generalized Langevin Equation

15.5.1 Change of perspective: observables instead of distributions

While the NZ equation acts on density matrices (distributions over phase space), Mori's formulation [2] focuses on the

Heisenberg-picture evolution of a chosen set of slow variables (observables) $\mathbf{A} = (A_1, A_2, \dots, A_n)$. These might be the total momentum, magnetization, or energy of a subsystem - whatever quantities are expected to evolve slowly relative to the bath.

The time evolution is:

$$\mathbf{A}(t) = e^{Lt}\mathbf{A}, \quad \frac{d\mathbf{A}(t)}{dt} = L\mathbf{A}(t) = e^{Lt}L\mathbf{A}. \tag{15.15}$$

The projection operator now acts on observables: given an inner product $(\cdot, \cdot)$ on the space of observables (see below), we define

$$\mathcal{P}B \equiv (B, \mathbf{A})(\mathbf{A}, \mathbf{A})^{-1}\mathbf{A}, \tag{15.16}$$

which projects any observable B onto the subspace spanned by $\mathbf{A}$.

15.5.2 Key operator identity

The derivation of the GLE rests on a single operator identity known as the Dyson decomposition (or Dyson identity):

$$e^{Lt} = e^{\mathcal{Q}Lt} + \int_0^t d\tau e^{L(t-\tau)}\mathcal{P}Le^{\mathcal{Q}L\tau} \tag{15.17}$$

Proof. Differentiate the right-hand side with respect to t and verify it satisfies the same ODE $\frac{d}{dt}e^{Lt} = Le^{Lt}$ with the same initial condition $e^{L\cdot 0} = \mathcal{I}$. Alternatively, write $e^{Lt} - e^{\mathcal{Q}Lt}$ and differentiate to obtain the desired integral equation.

15.5.3 Derivation of the GLE

We apply the Dyson identity Equation 15.17 to act on $L\mathbf{A}$:

$$e^{Lt}L\mathbf{A} = e^{\mathcal{Q}Lt}L\mathbf{A} + \int_0^t d\tau e^{L(t-\tau)}\mathcal{P}Le^{\mathcal{Q}L\tau}L\mathbf{A} \tag{15.18}$$

Now decompose $L\mathbf{A}$ using the projection:

$$L\mathbf{A} = \mathcal{P}L\mathbf{A} + \mathcal{Q}L\mathbf{A}. \tag{15.19}$$

Substituting the definitions of $\Omega, \mathbf{F}(t)$, and $\Gamma(t)$ (given below), one arrives at the Mori-Zwanzig Generalized Langevin Equation:

$$\frac{d\mathbf{A}(t)}{dt} = \Omega\mathbf{A}(t) - \int_0^t d\tau\Gamma(\tau)\mathbf{A}(t-\tau) + \mathbf{F}(t), \tag{15.20}$$

with

$$\Omega \equiv (L\mathbf{A}, \mathbf{A})(\mathbf{A}, \mathbf{A})^{-1} \quad \text{(frequency/drift matrix)} \tag{15.21}$$

$$\mathbf{F}(t) \equiv e^{\mathcal{Q}Lt}\mathcal{Q}L\mathbf{A} \quad \text{(fluctuating force)}, \tag{15.22}$$

$$\Gamma(t) \equiv (\mathbf{F}(t), \mathbf{F}(0))(\mathbf{A}, \mathbf{A})^{-1} \quad \text{(memory/friction kernel)}. \tag{15.23}$$

15.5.4 Physical interpretation of each term

- 1.Frequency matrix $\Omega\mathbf{A}(t)$: the instantaneous "precession" of the slow variables due to the projected streaming. For a harmonic oscillator it becomes $-\omega_0^2 x$; for a spin it gives the Larmor precession term.
- 2.Memory integral $\int_0^t d\tau\Gamma(\tau)\mathbf{A}(t-\tau)$: the dissipative (friction) contribution. The kernel $\Gamma(\tau)$ is the autocorrelation of the fluctuating force, evaluated in the projected subspace. It encodes how much "drag" the bath exerts on the slow variables at lag τ.
- 3.Fluctuating force $\mathbf{F}(t) = e^{\mathcal{Q}Lt}\mathcal{Q}L\mathbf{A}$: the noise driving the slow variables. It lives entirely in the irrelevant subspace (since $\mathcal{Q}L\mathbf{A}$ is acted on by $e^{\mathcal{Q}Lt}$, which never leaves $\operatorname{ran}\mathcal{Q}$). Consequently, $\mathbf{F}(t)$ is orthogonal to $\mathbf{A}(t')$ for all $t' \le t$:

$$(\mathbf{F}(t), \mathbf{A}) = 0 \quad \forall t \ge 0. \tag{15.24}$$

This orthogonality is the algebraic statement of the fluctuation-dissipation theorem.

15.5.5 The fluctuation-dissipation theorem

A key consequence of the Mori-Zwanzig construction is the second fluctuation-dissipation theorem:

$$\Gamma(t) = (\mathbf{F}(t), \mathbf{F}(0))(\mathbf{A}, \mathbf{A})^{-1}. \tag{15.25}$$

This is not an approximation but an exact identity within the formalism. It states that the friction kernel $\Gamma(t)$ governing dissipation is completely determined by the time correlations of the fluctuating force $\mathbf{F}(t)$. In the classical scalar case, with $\Gamma(t) = \gamma\delta(t)$ (white noise, Markov limit), one recovers the familiar Einstein relation $\gamma = k_B T/D$.

15.6 Connections and Limiting Cases

15.6.1 The Markov approximation

If the bath correlation time τ_B is much shorter than the system relaxation time τ_S (i.e., $\tau_B \ll \tau_S$), the memory kernel decays rapidly and we may replace $\mathbf{A}(t-\tau)$ by $\mathbf{A}(t)$ in the GLE:

$$\int_0^t d\tau \Gamma(\tau)\mathbf{A}(t-\tau) \approx \left(\int_0^\infty d\tau \Gamma(\tau)\right)\mathbf{A}(t) \equiv \gamma\mathbf{A}(t). \tag{15.26}$$

The GLE reduces to an ordinary Langevin equation:

$$\dot{\mathbf{A}}(t) = (\Omega - \gamma)\mathbf{A}(t) + \mathbf{F}(t), \tag{15.27}$$

with white noise. The Markov approximation is thus clearly identified as the assumption of a vanishing bath correlation time, and its validity can be assessed by examining the decay of $\Gamma(\tau)$. Together, NZ and MZ provide a complete, exact framework for coarse-graining microscopic dynamics. The key physical content - memory, fluctuations, and dissipation - emerges naturally and is related by exact identities that transcend any perturbative approximation.

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16: Quantum Linear Response Theory

This chapter presents a self-contained derivation of linear response theory, emphasizing the role of commutators, the Kubo-Martin-Schwinger (KMS) condition, and their connection to dissipation and transport. Starting from the von Neumann equation in the interaction picture, we derive the Kubo formula for the retarded susceptibility and show that energy absorption is governed by its imaginary part. A detailed derivation of the fluctuation-dissipation theorem (FDT) is given, tracing its origin to the KMS condition and detailed balance. These results are illustrated through the damped harmonic oscillator and used to derive the Kubo-Greenwood formula for electrical conductivity. The space-dependent formalism and the dynamic structure factor are also discussed.

Keywords: linear response, Kubo formula, fluctuation-dissipation theorem, KMS condition, electrical conductivity, dynamic structure factor.

Logical structure of the presentation:

KMS ⮚ detailed balance ⮚ commutator ⮚ susceptibility ⮚ dissipation ⮚ FDT ⮚ transport

A. 1 Introduction

Linear response theory provides a fundamental bridge between equilibrium statistical mechanics and non-equilibrium phenomena. The central insight, due to Kubo [1], is that the response of a system to a weak perturbation is determined entirely by equilibrium fluctuations of the unperturbed system. This is not an approximation: it is an exact consequence of quantum mechanics and thermodynamics, valid to first order in the perturbation strength[2].

The theory is important both conceptually and practically. Conceptually, it unifies phenomena as different as electrical conductivity, magnetic susceptibility, viscosity, and dielectric response within a single framework. Practically, it provides microscopically exact formulae (Kubo formulae) for transport coefficients in terms of equilibrium correlation functions.

Here we follow closely Tong's [3] unsurpassable notes.

A. 2 Setup: Hamiltonian and Objectives

Consider a system described by the Hamiltonian

$$H(t) = H_0 - f(t)B, \tag{A.1}$$

where H_0 is the time-independent unperturbed Hamiltonian, B is a Hermitian observable (the coupling operator), and $f(t)$ is a real, time-dependent external driving force that is turned on adiabatically from $t = -\infty$.

The system is prepared at $t = -\infty$ in thermal equilibrium:

$$\rho_0 = \frac{e^{-\beta H_0}}{Z_0}, \quad Z_0 = \mathrm{Tr}\left(e^{-\beta H_0}\right), \quad \beta = \frac{1}{k_B T}. \tag{A.2}$$

Before stating the objective we fix notation precisely. Let $\rho(t)$ denote the full density matrix of the system at time t, evolving under $H(t)$. We define two expectation values:

In the interaction picture (Section A.3.1) the density matrix $\rho_I(t)$ satisfies $\rho_I(-\infty) = \rho_0$, and the full average is equivalently

$$\langle A(t)\rangle = \frac{\mathrm{Tr}\left(\rho_I(t) A_I(t)\right)}{\mathrm{Tr}\,\rho_I(t)}. \tag{A.3}$$

Our goal is the linear change induced by the perturbation:

$$\delta\langle A(t)\rangle \equiv \langle A(t)\rangle - \langle A\rangle_0. \tag{A.4}$$

A. 3 Derivation of the Kubo Formula

A.3.1 Interaction picture

We work in the interaction picture, in which operators evolve with H_0 and the density matrix evolves with the perturbation. The interaction-picture counterpart of any Schrödinger-picture operator O is

$$O_I(t) = e^{iH_0 t/\hbar} O e^{-iH_0 t/\hbar}. \tag{A.5}$$

The perturbation Hamiltonian in the interaction picture is therefore

$$H_I(t) = -f(t) B_I(t), \quad B_I(t) = e^{iH_0 t/\hbar} B e^{-iH_0 t/\hbar}. \tag{A.6}$$

The interaction-picture density matrix obeys the von Neumann equation:

$$\frac{d\rho_I}{dt} = -\frac{i}{\hbar}\left[H_I(t), \rho_I(t)\right]. \tag{A.7}$$

A.3.2 First-order perturbation theory

Integrating Eq. (A.7) from $t = -\infty$ with initial condition $\rho_I(-\infty) = \rho_0$, and retaining only the first-order term in f :

$$\rho_I(t) \approx \rho_0 + \delta\rho_I(t), \quad \delta\rho_I(t) = -\frac{i}{\hbar}\int_{-\infty}^{t} dt' \left[H_I\left(t'\right), \rho_0\right]. \tag{A.8}$$

The change in the expectation value of A is

$$\begin{aligned} \delta\langle A(t)\rangle &= \mathrm{Tr}\left[\delta\rho_I(t) A_I(t)\right] \\ &= -\frac{i}{\hbar}\int_{-\infty}^{t} dt' f\left(t'\right) \mathrm{Tr}\left[\rho_0 \left[A_I(t), B_I\left(t'\right)\right]\right] \end{aligned} \tag{A.9}$$

where we used the cyclic property of the trace: $\mathrm{Tr}\left(\left[H_I\left(t'\right), \rho_0\right] A_I(t)\right) = \mathrm{Tr}\left(\rho_0 \left[A_I(t), B_I\left(t'\right)\right]\right)$.

The cyclic property $\mathrm{Tr}(XYZ) = \mathrm{Tr}(ZXY)$ gives

$$\mathrm{Tr}\left(\left[H_I\left(t'\right), \rho_0\right] A_I(t)\right) = \mathrm{Tr}\left(H_I\left(t'\right) \rho_0 A_I(t)\right) - \mathrm{Tr}\left(\rho_0 H_I\left(t'\right) A_I(t)\right) = f\left(t'\right) \mathrm{Tr}\left(\rho_0 \left[A_I(t), B_I\left(t'\right)\right]\right).$$

Since H_0 is time-independent, the commutator depends only on $t - t'$, and we may write $\left[A_I(t), B_I\left(t'\right)\right] = \left[A\left(t - t'\right), B(0)\right]$ (using translational invariance of the equilibrium average). Extending the upper limit to ∞ with a Heaviside function, we define the retarded susceptibility:

$$\chi_{AB}\left(t - t'\right) = \frac{i}{\hbar}\theta\left(t - t'\right) \left\langle\left[A\left(t - t'\right), B(0)\right]\right\rangle_0 \tag{A.10}$$

so that $\delta\langle A(t)\rangle = \int_{-\infty}^{\infty} dt' \chi_{AB}\left(t - t'\right) f\left(t'\right)$.

The $\theta\left(t - t'\right)$ factor enforces causality: the response at time t can only depend on the perturbation at earlier times $t' < t$.

A. 4 Frequency Domain and Energy Absorption

In the frequency domain, the convolution in the Kubo formula becomes a product:

$$\delta\langle A(\omega)\rangle = \chi_{AB}(\omega) f(\omega), \tag{A.11}$$

where $\chi_{AB}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \chi_{AB}(t)$ is the Fourier transform of the retarded susceptibility. Being retarded (causal), $\chi_{AB}(\omega)$ is analytic in the upper half of the complex ω-plane. We decompose it into real and imaginary parts:

$$\chi(\omega) = \chi'(\omega) + i\chi''(\omega). \tag{A.12}$$

A.4.1 Derivation of mean power dissipation

Consider a real, monochromatic driving force (written as a sum to keep $f(t)$ real):

$$f(t) = f_0 \cos(\omega t) = \frac{f_0}{2}\left(e^{-i\omega t} + e^{i\omega t}\right), \quad f_0 \in \mathbb{R}. \tag{A.13}$$

The instantaneous power delivered to the system by the perturbation $H' = -f(t)B$ is

$$P(t) = \frac{d\langle H'\rangle}{dt} = -\dot{f}(t)\langle B(t)\rangle, \tag{A.14}$$

where we used $\frac{d}{dt}\langle H'\rangle = \langle \partial H'/\partial t\rangle = -\dot{f}(t)\langle B(t)\rangle$ (the Hellmann-Feynman theorem applied to the time derivative of the perturbation).

Because $H' = -f(t)B$, we have $\partial H'/\partial t = -\dot{f}(t)B$, so $P = \langle \partial H/\partial t\rangle = -\dot{f}(t)\langle B\rangle$. The minus sign is consistent with the convention that work done on the system is positive when $\dot{f}$ and $\langle B\rangle$ have opposite signs.

The linear response gives $\langle B(t)\rangle = \chi(\omega)\frac{f_0}{2}e^{-i\omega t} +$ c.c., and $\dot{f}(t) = -i\omega\frac{f_0}{2}e^{-i\omega t} +$ c.c. Multiplying and time-averaging over one period (the cross terms at $\pm 2\omega$ vanish):

$$\begin{aligned}\langle P\rangle &= -\frac{f_0^2}{4}\left[(-i\omega)\chi(\omega) + (i\omega)\chi^*(\omega)\right] \\ &= \frac{f_0^2}{4}\cdot i\omega\left[\chi(\omega) - \chi^*(\omega)\right] = \frac{f_0^2}{4}\cdot i\omega\cdot 2i\chi''(\omega).\end{aligned} \tag{A.15}$$

$$\langle P\rangle = \frac{\omega f_0^2}{2}\chi''(\omega). \tag{A.16}$$

The passivity condition (energy is absorbed from the drive, not emitted) requires $\langle P\rangle \geq 0$ for $\omega > 0$, which implies $\chi''(\omega) \geq 0$ for $\omega > 0$.

Comparison with the complex-amplitude convention: Some texts write $f(t) = f_0 e^{-i\omega t} +$ c.c. (with $|f_0|^2$ replacing $f_0^2/4$). In that convention, the mean power is $\langle P\rangle = 2\omega|f_0|^2\chi''(\omega)$. Here we use the real cosine drive (A.13); the result (A.16) follows directly.

A.4.2 Physical interpretation

- $\chi'(\omega)$: the dispersive (reactive) part of the response - describes energy storage, analogous to the elastic modulus or inductance.
- $\chi''(\omega)$: the absorptive (dissipative) part - describes irreversible energy transfer from the field to the system (viscosity, resistance, damping). This is the directly measurable part in spectroscopy.

A. 5 Kramers-Kronig Relations

Since $\chi(t)$ is real and causal ($\chi(t) = 0$ for $t < 0$), its Fourier transform $\chi(\omega)$ is analytic in the upper half plane and satisfies $\chi(-\omega) = \chi^*(\omega)$. By a contour-integral argument (closing in the upper half-plane), the real and imaginary parts are related by the Kramers-Kronig (dispersion) relations:

$$\chi'(\omega) = +\frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty}\frac{\chi''(\omega')}{\omega' - \omega}d\omega', \tag{A.17}$$

$$\chi''(\omega) = -\frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty}\frac{\chi'(\omega')}{\omega' - \omega}d\omega'. \tag{A.18}$$

Here $\mathcal{P}$ denotes the Cauchy principal value. These relations are exact consequences of causality alone, independent of any microscopic model. They are fundamental consistency checks for experimental susceptibility data.

A. 6 The KMS Condition and Detailed Balance

A.6.1 Derivation of the KMS condition

Define the two-time correlation function $C_{AB}(t) = \langle A(t)B(0)\rangle_0 = \mathrm{Tr}\,(\rho_0 A(t)B)$. Using $\rho_0 = e^{-\beta H_0}/Z_0$ and the cyclic property of the trace:

$$\begin{aligned}\mathrm{Tr}\left(e^{-\beta H_0}A(t)B\right) &= \mathrm{Tr}\left(e^{-\beta H_0}e^{iH_0t/\hbar}Ae^{-iH_0t/\hbar}B\right)\\ &= \mathrm{Tr}\left(Be^{-\beta H_0}e^{iH_0t/\hbar}Ae^{-iH_0t/\hbar}\right)\\ &= \mathrm{Tr}\left(e^{-\beta H_0}e^{iH_0(t+i\hbar\beta)/\hbar}Ae^{-iH_0(t+i\hbar\beta)/\hbar}B\right).\end{aligned} \tag{A.19}$$

The third line follows because $e^{\beta H_0}Be^{-\beta H_0}$ can be absorbed by shifting the time argument $t \to t + i\hbar\beta$ in the evolution operator. This gives the KMS condition:

$$\langle A(t)B(0)\rangle_0 = \langle B(0)A(t+i\hbar\beta)\rangle_0. \tag{A.20}$$

The KMS condition states that a thermal state can be distinguished from an arbitrary state by a universal periodicity in imaginary time of period $\hbar\beta$. It serves as the rigorous mathematical definition of thermal equilibrium in both quantum mechanics and quantum field theory, even in situations (e.g., infinite-volume limits) where a density matrix may not exist.

A.6.2 Role of the KMS condition

The KMS condition is the algebraic engine of the entire formalism:

- 1.Operator reordering. It allows the two orderings $\langle A(t)B\rangle_0$ and $\langle BA(t)\rangle_0$ to be related via an imaginary time shift, which in Fourier space becomes multiplication by $e^{\beta\hbar\omega}$.

- 2.Detailed balance. Fourier-transforming Eq. (A.20) gives the detailed balance relation (see next subsection).
- 3.Fluctuation-dissipation theorem. Combining detailed balance with the definition of the susceptibility yields the FDT (Section A.7).

A.6.3 Detailed balance

Define $C_{AB}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t}\langle A(t)B(0)\rangle_0$. Taking the Fourier transform of Eq. (A.20):

$$C_{AB}(\omega) = e^{\beta\hbar\omega}C_{BA}(\omega), \tag{A.21}$$

since the imaginary time shift $t \to t + i\hbar\beta$ generates a factor $e^{-\omega\cdot\hbar\beta} = e^{-\beta\hbar\omega}$ upon Fourier transformation, or equivalently:

$$C_{AB}(\omega) = e^{\beta\hbar\omega}C_{BA}(\omega). \tag{A.22}$$

This is the quantum detailed balance condition: the spectral weight for a transition that emits a quantum of energy $\hbar\omega$ is Boltzmann-enhanced relative to the reverse process, consistent with the system preferring lower-energy configurations at finite temperature.

A. 7 The Fluctuation-Dissipation Theorem

A.7.1 Connecting the commutator to the correlation functions

The retarded susceptibility (A.10) involves the commutator $\langle[A(t), B(0)]\rangle_0$. Decomposing into the two orderings:

$$\langle[A(t), B(0)]\rangle_0 = C_{AB}(t) - C_{BA}(-t). \tag{A.23}$$

Fourier-transforming:

$$\chi''_{AB}(\omega) = \frac{1}{2\hbar}\left[C_{AB}(\omega) - C_{BA}(-\omega)\right]. \tag{A.24}$$

(The factor $1/2\hbar$ comes from the definition (A.10) and the relation between the full susceptibility and its imaginary part via the Heaviside function.)

A.7.2 Applying detailed balance

Substituting $C_{BA}(-\omega) = e^{-\beta\hbar\omega}C_{AB}(\omega)$ (which follows from Eq. (A.21) applied with $\omega \to -\omega$ and swapped indices):

$$\chi''_{AB}(\omega) = \frac{1}{2\hbar}\left(1 - e^{-\beta\hbar\omega}\right)C_{AB}(\omega). \tag{A.25}$$

The symmetric (anticommutator) correlation function is:

$$S_{AB}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t}\left\langle \frac{1}{2}\{A(t), B(0)\}\right\rangle_0 = \frac{1}{2}\left[C_{AB}(\omega) + C_{BA}(-\omega)\right] = \frac{1}{2}\left(1 + e^{-\beta\hbar\omega}\right)C_{AB}(\omega). \tag{A.26}$$

Therefore the FDT can equivalently be written in terms of $S_{AB}(\omega)$, but the cleanest form directly connects χ'' to C_{AB} :

$$\chi''_{AB}(\omega) = \frac{1}{2\hbar}\left(1 - e^{-\beta\hbar\omega}\right)C_{AB}(\omega), \tag{A.27}$$

$$\text{equivalently: } C_{AB}(\omega) = \hbar\left[n_B(\omega) + 1\right]\cdot 2\chi''_{AB}(\omega), \tag{A.28}$$

where $n_B(\omega) = \left(e^{\beta\hbar\omega} - 1\right)^{-1}$ is the Bose-Einstein distribution.

The FDT equates a non-equilibrium quantity (χ'', measured by driving the system) to an equilibrium fluctuation (C_{AB}, measured without any drive). No perturbative assumptions are required; the result is exact. The Bose factor $n_B(\omega) + 1$ reflects stimulated plus spontaneous emission in the quantum language.

A.7.3 Classical limit

For $\hbar\omega \ll k_B T$ (high temperature / low frequency): $\left(1 - e^{-\beta\hbar\omega}\right) \approx \beta\hbar\omega$, so:

$$\chi''_{AB}(\omega) \approx \frac{\beta\omega}{2}S_{AB}(\omega), \tag{A.29}$$

where we used $S_{AB} \approx C_{AB}$ in the classical limit (the two orderings commute for $\hbar \to 0$). This is the classical FDT, equivalent to the Einstein-Nyquist relation.

A. 8 Worked Example: Damped Harmonic Oscillator

A.8.1 Response function

Consider a harmonic oscillator of mass m, spring constant k, and linear damping γ, driven by a force $f(t)$:

$$m\ddot{x} + \gamma\dot{x} + kx = f(t). \tag{A.30}$$

Taking the Fourier transform $\left(x(t) = \int \frac{d\omega}{2\pi}x(\omega)e^{-i\omega t}\right)$:

$$\left(-m\omega^2 - i\gamma\omega + k\right)x(\omega) = f(\omega). \tag{A.31}$$

The susceptibility $\chi(\omega) = x(\omega)/f(\omega)$ is:

$$\chi(\omega) = \frac{1}{k - m\omega^2 - i\gamma\omega}. \tag{A.32}$$

A.8.2 Dissipative part

Decomposing $\chi = \chi' + i\chi''$:

$$\chi'(\omega) = \frac{k - m\omega^2}{(k - m\omega^2)^2 + (\gamma\omega)^2}, \tag{A.33}$$

$$\chi''(\omega) = \frac{\gamma\omega}{(k - m\omega^2)^2 + (\gamma\omega)^2}. \tag{A.34}$$

Note $\chi''(\omega) > 0$ for $\omega > 0$, consistent with passivity (energy absorbed from the drive). At resonance $\omega = \omega_0 \equiv \sqrt{k/m}$, the response is purely dissipative: $\chi'(\omega_0) = 0, \chi''(\omega_0) = 1/(\gamma\omega_0)$.

A.8.3 Verification of the Kramers-Kronig relations

One can verify (A.17) directly using contour integration: the poles of $\chi(\omega) = [(k - m\omega^2) - i\gamma\omega]^{-1}$ lie at $\omega_\pm = -i\gamma/(2m) \pm \sqrt{k/m - \gamma^2/(4m^2)}$, both in the lower half-plane, confirming analyticity in the upper half-plane.

A. 9 Kubo-Greenwood Formula for Electrical Conductivity

A.9.1 Minimal coupling and the current operator

For a system of charges q coupled to an electromagnetic field, the minimal coupling Hamiltonian (to lowest order in the vector potential $\mathbf{A}$) is

$$H = \sum_n \frac{(\mathbf{p}_n - q\mathbf{A})^2}{2m} \approx H_0 - \frac{q}{m}\sum_n \mathbf{p}_n \cdot \mathbf{A} = H_0 - \mathbf{J} \cdot \mathbf{A}V, \tag{A.35}$$

where V is the volume and $\mathbf{J}$ is the current-density operator. The electric field is related to the vector potential in the temporal gauge by $\mathbf{E} = -\partial\mathbf{A}/\partial t$, so for a monochromatic field $\mathbf{E}(\omega)e^{-i\omega t}$:

$$\mathbf{A}(\omega) = \frac{i}{\omega}\mathbf{E}(\omega). \tag{A.36}$$

A.9.2 Kubo formula for conductivity

The Kubo formula gives the induced current as $J_i(\omega) = \chi_{J_iJ_j}(\omega)A_j(\omega)V$. Using Eq. (A.36) and $\sigma_{ij}(\omega) = J_i(\omega)/E_j(\omega)$:

$$\sigma_{ij}(\omega) = \frac{\chi_{J_iJ_j}(\omega)}{i\omega} + \sigma_{ij}^{\text{dia}}, \tag{A.37}$$

where $\sigma_{ij}^{\text{dia}} = nq^2/(im\omega)$ is the diamagnetic contribution from the $\mathbf{A}^2$ term. This term ensures that $\sigma_{ij}(\omega)$ is finite as $\omega \to 0$ (it cancels a spurious pole in $\chi/i\omega$).

Substituting the Kubo formula (A.10):

Kubo-Greenwood formula:

$$\sigma_{ij}(\omega) = \frac{1}{i\omega V}\int_0^\infty dt e^{i\omega t}\langle[J_i(t), J_j(0)]\rangle_0 + \sigma_{ij}^{\text{dia}} \tag{A.38}$$

Common omission. Many textbook presentations drop the diamagnetic term σ_{ij}^{dia} . This is only valid for insulators (where it cancels exactly with the $\omega \to 0$ limit of the paramagnetic term) or when the f-sum rule is invoked. For metals or when working at finite ω, the diamagnetic term must be retained to obtain gauge-invariant results.

A.9.3 DC conductivity and the Einstein relation

In the $\omega \to 0$ limit (DC conductivity), the real part of Eq. (A.38) gives:

$$\sigma_{ij}^{\text{DC}} = \frac{1}{V}\int_0^\infty dt \langle J_i(t)J_j(0)\rangle_0 \tag{A.39}$$

which is the standard Green-Kubo relation for conductivity: the DC conductance is the time integral of the equilibrium current-current correlation function.

A. 10 Space-Dependent Response and the Dynamic Structure Factor

A.10.1 Non-local susceptibility

When the external perturbation varies in space,

$$H(t) = H_0 - \int d^3r f(\mathbf{r}, t) B(\mathbf{r}) \tag{A.40}$$

the linear response is governed by a non-local susceptibility $\chi_{AB}(\mathbf{r} - \mathbf{r}', t - t')$ (assuming translational invariance). Transforming to momentum space:

$$\delta\langle A(\mathbf{k}, \omega)\rangle = \chi_{AB}(\mathbf{k}, \omega) f(\mathbf{k}, \omega), \tag{A.41}$$

with

$$\chi_{AB}(\mathbf{k}, t) = \frac{i}{\hbar}\theta(t)\langle[A(\mathbf{k}, t), B(-\mathbf{k}, 0)]\rangle_0, \tag{A.42}$$

where $A(\mathbf{k}, t) = \int d^3r e^{-i\mathbf{k}\cdot\mathbf{r}} A(\mathbf{r}, t)$.

A.10.2 The dynamic structure factor

The dynamic structure factor is the power spectrum of density fluctuations:

$$S(\mathbf{k}, \omega) = \int_{-\infty}^{\infty} dt e^{i\omega t}\langle\rho(\mathbf{k}, t)\rho(-\mathbf{k}, 0)\rangle_0 \tag{A.43}$$

where $\rho(\mathbf{k}) = \sum_n e^{-i\mathbf{k}\cdot\mathbf{r}_n}$ is the Fourier-transformed density. The FDT (A.27) applied to $A = B = \rho_{\mathbf{k}}$ gives:

$$\chi''_{\rho\rho}(\mathbf{k}, \omega) = \frac{1}{2\hbar}\left(1 - e^{-\beta\hbar\omega}\right) S(\mathbf{k}, \omega). \tag{A.44}$$

Physical significance of $S(\mathbf{k}, \omega)$.

- Scattering experiments: $S(\mathbf{k}, \omega)$ is directly measured in inelastic neutron and X-ray scattering, providing a microscopic probe of the system's dynamics at wavevector $|\mathbf{k}|$ and energy $\hbar\omega$.
- Hydrodynamic limit: As $\mathbf{k} \to 0$ and $\omega \to 0$, $S(\mathbf{k}, \omega)$ exhibits peaks corresponding to hydrodynamic modes (sound, diffusion), from which macroscopic transport coefficients can be extracted.
- Sum rules: Integrating $\chi''(\mathbf{k}, \omega)$ over ω yields the f-sum rule: $\int_{-\infty}^{\infty} \frac{d\omega}{\pi}\omega\chi''(\mathbf{k}, \omega) = \frac{\hbar k^2 n}{2m}$, where n is the particle number density. This is an exact, model-independent result.

A. 11 Summary

The table below collects the principal results and their logical connections.

Result	Key equation	Origin
Kubo formula	$\chi_{AB}(t) = \frac{i}{\hbar}\theta(t)\langle[A(t), B]\rangle_0$	1st-order perturbation theory
Energy absorption	$\langle P\rangle = \frac{\omega f_0^2}{2}\chi''(\omega)$	Linear response + time-average
KMS condition	$\langle A(t)B\rangle_0 = \langle BA(t + i\hbar\beta)\rangle_0$	Cyclicity of trace
Detailed balance	$C_{AB}(\omega) = e^{\beta\hbar\omega} C_{BA}(\omega)$	Fourier transform of KMS
FDT	$\chi''_{AB}(\omega) = \frac{1}{2\hbar}\left(1 - e^{-\beta\hbar\omega}\right) C_{AB}(\omega)$	KMS + commutator decomposition

Result	Key equation	Origin
Kramers-Kronig	Eqs. (A.17)-(A.18)	Causality (analyticity)
Kubo-Greenwood	Eq. (A.38)	Kubo formula + minimal coupling

The key conceptual message is that all dissipative and transport properties of a system at thermal equilibrium are encoded in equilibrium time-correlation functions. The KMS condition is the precise statement of what thermal equilibrium means at the quantum level, and the FDT is its most direct physical consequence.

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17: Generalized Langevin Dynamics for an Arbitrary Potential- Thermal Renormalization and Stability

The generalized Langevin equation (GLE) provides the exact equation of motion for a central coordinate coupled bilinearly to a harmonic bath, with the bath eliminated in favor of a memory kernel and a fluctuating force tied together by the fluctuation-dissipation theorem (FDT). While the standard textbook presentation specializes immediately to a harmonic central oscillator, the bath-elimination procedure itself never uses the harmonicity of the central potential-only its bilinear coupling to the bath. This appendix therefore derives the GLE for a completely general potential $V(X)$ from the outset, and then specializes the single general result to three cases of increasing physical interest: an arbitrary smooth potential, a quartic (Duffing) correction that arises generically from the Taylor expansion of any smooth, symmetric potential minimum, and a cosine (Josephson-junction/pendulum) potential whose own Taylor expansion is shown to reproduce the quartic case with a fixed, universal softening coefficient. Using the quantummechanical FDT, we derive the self-consistent (Hartree) equation for the thermally and quantummechanically renormalized frequency $\Omega_{\text{eff}}(T)$ of the quartic problem, and give a unified treatment of the two qualitatively different outcomes set by the sign of the quartic coefficient β_D : a hardening quartic $(\beta_D > 0)$ produces a frequency that rises and saturates smoothly $\left(\Omega_{\text{eff}} \propto T^{1/4}\right.$ at high T), while a softening quartic ($\beta_D < 0$, as realized exactly by the cosine potential) produces a frequency that falls and the self-consistent solution terminates altogether at a finite Hartree instability temperature. We show that this instability has a precise dynamical meaning already visible in the linear theory: it is exactly the point at which the self-consistency condition on the renormalized pole of the retarded Green's function loses its solution. Finally we extend the self-consistency to the driven response amplitude itself, recovering the cubic equation responsible for Duffing bistability, and discuss which of its roots are dynamically stable and why.

B. 1 Hamiltonian and equations of motion

Consider a central coordinate X with mass M, moving in an arbitrary potential $V(X)$, bilinearly coupled to a bath of N independent harmonic oscillators labeled $n = 1, \ldots, N$, with coordinates q_n, masses m_n, and frequencies ω_n. Following Magalinski [1] (in the form popularized by Caldeira and Leggett [6, 7]), it is convenient to write the bath term with a built-in counterterm that removes an otherwise unphysical, instantaneous renormalization of the curvature of V :

$$H = \frac{P^2}{2M} + V(X) + \sum_{n=1}^{N} \left[\frac{p_n^2}{2m_n} + \frac{1}{2} m_n \omega_n^2 \left(q_n - \frac{c_n}{m_n \omega_n^2} X \right)^2 \right], \tag{B.1}$$

where c_n are coupling constants (dimensions of force). Expanding the square shows this is equivalent to the more commonly written bilinear-coupling form,

$$H = \frac{P^2}{2M} + V(X) + \sum_n \left(\frac{p_n^2}{2m_n} + \frac{1}{2} m_n \omega_n^2 q_n^2 \right) - X \sum_n c_n q_n + X^2 \sum_n \frac{c_n^2}{2 m_n \omega_n^2}, \tag{B.2}$$

where the last term is exactly the counterterm needed to cancel the instantaneous frequency shift that the bath coupling would otherwise induce. Notice that $V(X)$ enters Eq. (B.1) as a completely separate additive term: it plays no role whatsoever in the structure of the bath part of the Hamiltonian. Hamilton's equations give

$$M\ddot{X}(t) + V'(X(t)) - \sum_n c_n q_n(t) + X(t) \sum_n \frac{c_n^2}{m_n \omega_n^2} = 0, \tag{B.3}$$

$$m_n \ddot{q}_n(t) + m_n \omega_n^2 q_n(t) = c_n X(t). \tag{B.4}$$

Equation (B.4)-a driven harmonic oscillator for every bath mode, forced by the central coordinate- does not contain $V(X)$ at all: the bath modes only ever see $X(t)$ itself, never the force X experiences. This one observation is the crux of the entire appendix and is what allows Sec. B. 7 to specialize the result derived below to three completely different potentials without repeating any of the algebra.

B. 2 Eliminating the bath: the causal Green's function

The scalar operator for mode n is $L_n = d^2/dt^2 + \omega_n^2$, whose causal (retarded) Green's function, $L_n g_n(t) = \delta(t)$ with $g_n(t) = 0$ for $t < 0$, is

$$g_n(t) = \frac{\sin(\omega_n t)}{\omega_n}\Theta(t). \tag{B.5}$$

The general solution of Eq. (B.4), given initial data $q_n(0), \dot{q}_n(0)$, is

$$q_n(t) = q_n(0)\cos(\omega_n t) + \frac{\dot{q}_n(0)}{\omega_n}\sin(\omega_n t) + \frac{c_n}{m_n}\int_0^t g_n(t-s)X(s)ds. \tag{B.6}$$

Substituting this into Eq. (B.3) and integrating the convolution piece by parts (using $u = X(s)$, $dv = [\sin\omega_n(t-s)/\omega_n]\,ds$) converts the memoryless convolution with $X(s)$ into a convolution with $\dot{X}(s)$; the resulting instantaneous term proportional to $X(t)/\omega_n^2$ is exactly canceled by the counterterm already built into Eq. (B.1). Because none of this manipulation ever touched $V(X)$-it is purely a statement about how the bath responds to a given trajectory $X(t)$-it goes through for any $V(X)$ exactly as it would for a harmonic potential. What survives is

$$M\ddot{X}(t) + V'(X(t)) + \sum_n \frac{c_n^2}{m_n\omega_n^2}\int_0^t \cos[\omega_n(t-s)]\,\dot{X}(s)ds = \xi(t) \tag{B.7}$$

with the fluctuating force collecting all the bath-initial-condition pieces,

$$\xi(t) \equiv -\sum_n c_n\left[q_n(0) - \frac{c_n}{m_n\omega_n^2}X(0)\right]\cos(\omega_n t) - \sum_n c_n\frac{\dot{q}_n(0)}{\omega_n}\sin(\omega_n t)\,. \tag{B.8}$$

B. 3 Memory kernel and the generalized Langevin equation

Defining the memory (damping) kernel, normalized by the system mass,

$$\gamma(t) \equiv \frac{1}{M}\sum_n \frac{c_n^2}{m_n\omega_n^2}\cos(\omega_n t)\,, \tag{B.9}$$

Eq. (B.7) becomes the central result of this appendix, the classical GLE for an arbitrary central-oscillator potential $V(X)$:

$$M\ddot{X}(t) + V'(X(t)) + M\int_0^t \gamma(t-s)\dot{X}(s)ds = \xi(t) \tag{B.10}$$

This equation is exact for the bilinear bath model, Eq. (B.1), for any central-oscillator potential $V(X)$ and any number of bath oscillators N (finite or, after the continuum limit below, infinite); it is causal, since the memory integral runs only over the system's own past; and, crucially, the memory kernel $\gamma(t)$ and the noise $\xi(t)$ depend only on the bath parameters $\{c_n, m_n, \omega_n\}$-not on $V(X)$ at all. Section B. 7 exploits exactly this fact.

B. 4 Continuum limit, spectral density, and the Markovian limit

For a dense bath one introduces the spectral density $J(\omega) \equiv \frac{\pi}{2}\sum_n (c_n^2/m_n\omega_n)\,\delta(\omega - \omega_n)$, in terms of which

$$\gamma(t) = \frac{2}{M\pi}\int_0^\infty \frac{J(\omega)}{\omega}\cos(\omega t)d\omega. \tag{B.11}$$

For an Ohmic bath with exponential cutoff, $J(\omega) = M\eta\omega e^{-\omega/\omega_c}$,

$$\gamma(t) = \frac{2\eta}{\pi}\int_0^\infty e^{-\omega/\omega_c}\cos(\omega t)d\omega = \frac{2\eta}{\pi}\frac{\omega_c}{1+(\omega_c t)^2}, \tag{B.12}$$

plotted in Fig. $17.B1$ for several cutoffs ω_c. As $\omega_c \to \infty$ this family of functions approaches $2\eta\delta(t)$, the memory becomes instantaneous, and Eq. (B.10) reduces to the ordinary (Markovian) Langevin equation for a general potential,

$$M\ddot{X}(t) + \gamma_0 M\dot{X}(t) + V'(X(t)) = \xi(t), \quad \gamma_0 \equiv 2\eta. \tag{B.13}$$

This Markovian limit is used throughout the rest of the appendix.

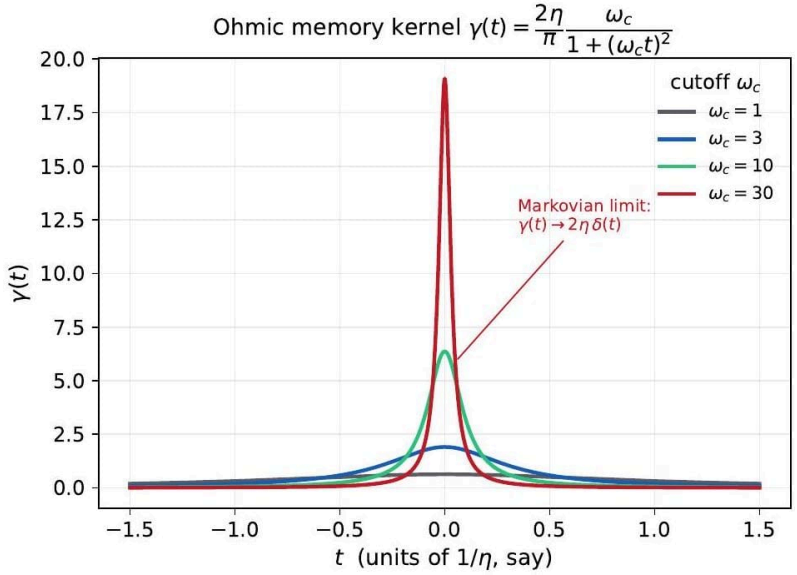


Figure $17.B1$: The Ohmic memory kernel, Eq. (B.12), for several bath cutoffs ω_c. As ω_c increases the kernel narrows and grows taller while its area stays fixed, converging to $2\eta\delta(t)$: the Markovian, memoryless limit used for the rest of this appendix. Nothing in this figure depends on the form of $V(X)$.

B. 5 Fluctuation-dissipation theorem

If the bath starts in thermal equilibrium at temperature T, independent of the system, the fluctuating force $\xi(t)$ of Eq. (B.8) has zero mean, and its correlator is fixed-not free to choose- by the very kernel $\gamma(t)$ that damps the system, since both descend from the same coupling constants c_n; this is Kubo's FDT [10, 11, 12]. Classically,

$$\langle \xi(t) \rangle_0 = 0, \quad \langle \xi(t)\xi(t') \rangle_0 = M k_{\mathrm{B}} T \gamma(t - t') . \tag{B.14}$$

Quantum-mechanically, the symmetrized correlator instead involves the full Bose-thermal factor,

$$S_\xi(\omega) = M\gamma(\omega)\hbar\omega \coth\left(\frac{\hbar\omega}{2k_{\mathrm{B}}T}\right), \tag{B.15}$$

where $\gamma(\omega)$ is the Fourier transform of the memory kernel (for the Markovian limit, $\gamma(\omega) \to \gamma_0$, a constant); the range of validity of this quantum Nyquist-type formula, and its relation to the Callen-Welton result, is discussed concisely by Ginzburg and Pitaevskiĭ [13] and at length by Weiss [9]. Equation (B.15) reduces to Eq. (B.14) whenever $\hbar\omega \ll k_{\mathrm{B}}T$ over the frequencies that matter, and to a temperature-independent zero-point plateau, $S_\xi(\omega) \to M\gamma_0\hbar|\omega|$, in the opposite limit. Like $\gamma(t)$ itself, neither Eq. (B.14) nor Eq. (B.15) makes any reference to $V(X)$: they are generic consequences of the bath model of Sec. B.1, independent of any particular physical embodiment of the bath or of the potential the central coordinate happens to sit in.

B. 6 Linear stability: the retarded Green's function and its poles

For a general $V(X)$, Eq. (B.10) is nonlinear and has no closed-form Laplace solution. However, linearizing about a stable equilibrium $X = 0$ of $V(X)$ (i.e. $V'(0) = 0, V''(0) \equiv M\Omega^2 > 0$) reduces Eq. (B.10) to the linear GLE

$$M\ddot{X}(t) + M\Omega^2 X(t) + M\int_0^t \gamma(t-s)\dot{X}(s)ds = \xi(t) \tag{B.16}$$

which is Magalinski's original problem, and is also exact for the strictly harmonic case of Sec. B.7.1 below. Equation (B.16) can be solved formally in the Laplace domain, $\tilde{f}(s) = \int_0^\infty e^{-st} f(t)dt$. Using the convolution theorem,

$$M\left[s^2\tilde{X}(s) - sX(0) - \dot{X}(0)\right] + M\Omega^2\tilde{X}(s) + M\tilde{\gamma}(s)[s\tilde{X}(s) - X(0)] = \tilde{\xi}(s), \tag{B.17}$$

which defines the retarded Green's function $\tilde{G}(s) = 1/\left\{M\left[s^2 + \Omega^2 + s\tilde{\gamma}(s)\right]\right\}$, satisfying $M\ddot{G} + M\Omega^2 G + M\int_0^t \gamma(t-s)\dot{G}(s)ds = \delta(t), G(t) = 0$ for $t < 0$. The system's response is then $X(t) = X_{\rm hom}(t) + \frac{1}{M}\int_0^t G(t-s)\xi(s)ds$, with $X_{\rm hom}$ the initial-condition transient.

The poles of $\tilde{G}(s)$-the roots, in s, of $s^2 + \Omega^2 + s\tilde{\gamma}(s) = 0$-are the normal-mode frequencies of the damped system, and their real parts determine stability: a physically sensible, damped, oscillatory system has all poles in $\Re(s) \leq 0$. In the Markovian limit this quadratic is elementary, $s = -\gamma_0/2 \pm \sqrt{\Omega^2 - \gamma_0^2/4}$, manifestly stable (damped) for any $\Omega^2 > 0$ and $\gamma_0 > 0$. This single fact-that the pole structure requires $\Omega^2 > 0$ for a bounded, oscillatory, causal response- is the thread that connects the purely linear theory of this section to the stability discussion of Sec. B.8.4 below: once thermal fluctuations renormalize $\Omega^2 \to \Omega^2_{\rm eff}(T)$ through the quartic nonlinearity of Sec.B.7.2, the identical pole criterion, applied now to the renormalized frequency, is what decides whether the mean-field, self-consistent description remains a stable, physically meaningful oscillator at all.

B. 7 Case studies: general potential, quartic, and cosine

Equation (B.16), together with the memory kernel (B.9) and the FDT of Sec. B.5, holds for any $V(X)$. We now specialize it to three choices of increasing physical richness, without repeating any bath-elimination algebra: only the force term $V'(X)$ changes from one case to the next.

B.7.1 General potential

The most general choice is an arbitrary smooth potential $V(X)$ with a nondegenerate minimum at $X = 0$ [Fig. B.2(a)], for which the force $V'(X)$ is left unspecified and Eq. (B.16) is the general nonlinear GLE

$$M\ddot{X}(t) + V'(X(t)) + M\int_0^t \gamma(t-s)\dot{X}(s)ds = \xi(t) \tag{B.18}$$

This is the master equation from which all subsequent cases follow by choosing $V(X)$. If $V(X)$ is harmonic, $V(X) = \frac{1}{2}M\Omega^2X^2$, then $V'(X) = M\Omega^2X$ and Eq. (B.18) reduces to the linear GLE (B.16) of Sec. B.6, with no approximation required: the Laplace/pole analysis given there is exact for this case. If $V(X)$ is quartic or cosine, the force is nonlinear and the analysis of Secs. B.7.2 B.7.3 applies. In every case the memory kernel $\gamma(t)$ and the noise $\xi(t)$ are identical to those of the harmonic problem: the bath does not know what potential the central coordinate sits in.

B.7.2 Quartic (Duffing) oscillator

Any smooth potential with a nondegenerate minimum at $X = 0$ can be Taylor expanded there; if the potential is symmetric enough that no cubic term appears (e.g. by an inversion symmetry $X \to -X$, as in both examples of this appendix), the leading anharmonic correction beyond the harmonic term is quartic,

$$V(X) = V(0) + \frac{1}{2}V''(0)X^2 + \frac{1}{24}V''''(0)X^4 + O\left(X^6\right). \tag{B.19}$$

Writing $M\Omega^2 \equiv V''(0)$ and $M\beta_D \equiv V''''(0)/6$ gives the Duffing potential

$$V(X) = \frac{1}{2}M\Omega^2X^2 + \frac{1}{4}M\beta_DX^4, \tag{B.20}$$

shown in Fig. B.2(b) for both signs of β_D : hardening $(\beta_D > 0)$ or softening $(\beta_D < 0)$, depending on the physical system. Since Eq. (B.16) depends on $V(X)$ only through the force $V'(X) = M\Omega^2X + M\beta_DX^3$-and, as emphasized in Sec. B.1, the bath elimination never touches this term at all-specializing Eq. (B.16) to the quartic potential is immediate, giving the noisy Duffing generalized Langevin equation,

$$M\ddot{X}(t) + M\Omega^2X(t) + M\beta_DX^3(t) + M\int_0^t \gamma(t-s)\dot{X}(s)ds = \xi(t) \tag{B.21}$$

with exactly the same memory kernel $\gamma(t)$, Eq. (B.9), and the exactly same fluctuating force $\xi(t)$, Eq. (B.8), obeying the exactly same

classical and quantum FDTs, Eqs. (B.14) and (B.15), as in the strictly harmonic case. Taking the Markovian limit of Sec. B. 4 reduces Eq. (B.21) to

$$\ddot{X}(t) + \gamma_0 \dot{X}(t) + \Omega^2 X(t) + \beta_D X^3(t) = \eta(t), \quad \eta(t) \equiv \xi(t)/M, \tag{B.22}$$

with $\langle \eta(t)\eta(t') \rangle_0 = 2D\delta(t-t')$ classically $(D = \gamma_0 k_B T/M)$, or the full quantum-mechanical noise spectrum of Eq. (B.15) divided by M^2 in general. Equation (B.22) is the noisy Duffing-Langevin equation whose thermal renormalization and stability occupy the rest of this appendix (Secs. B. 8 B. 9).

B.7.3 Cosine (Josephson-junction / pendulum) potential

A third, physically important case is the cosine (washboard/pendulum) potential,

$$V(X) = E_J[1 - \cos X], \tag{B.23}$$

shown in Fig. B.2(c), where E_J sets the energy scale (for a current-biased Josephson junction, E_J is the Josephson coupling energy and X is the gauge-invariant phase difference across the junction; for a simple pendulum, $E_J = MgL$ and X is the angular displacement). Here $V'(X) = E_J \sin X$, and Eq. (B.10) specializes immediately, again with no new derivation, to

$$M\ddot{X}(t) + E_J \sin X(t) + M\int_0^t \gamma(t-s)\dot{X}(s)ds = \xi(t) \tag{B.24}$$

the full noisy pendulum (or RCSJ-Josephson) generalized Langevin equation. Expanding $\sin X \approx X - X^3/6$ for small X recovers exactly the quartic case of Sec. B.7.2,

$$E_J \sin X \approx E_J X - \frac{E_J}{6}X^3 \quad \Longrightarrow \quad \Omega^2 = \frac{E_J}{M}, \quad \beta_D = -\frac{E_J}{6M} = -\frac{\Omega^2}{6}, \tag{B.25}$$

so that the cosine potential is not merely an example of a softening quartic oscillator: it fixes the softening coefficient to the specific, universal ratio $\beta_D = -\Omega^2/6$, independent of the overall energy scale E_J. Every result derived below for a general softening $\beta_D < 0$ therefore applies to the Josephson/pendulum problem with this particular substitution, and Fig. $17.B2c$ shows explicitly how good the quartic approximation is (and where it fails) by overlaying the truncated Taylor series on the exact cosine.

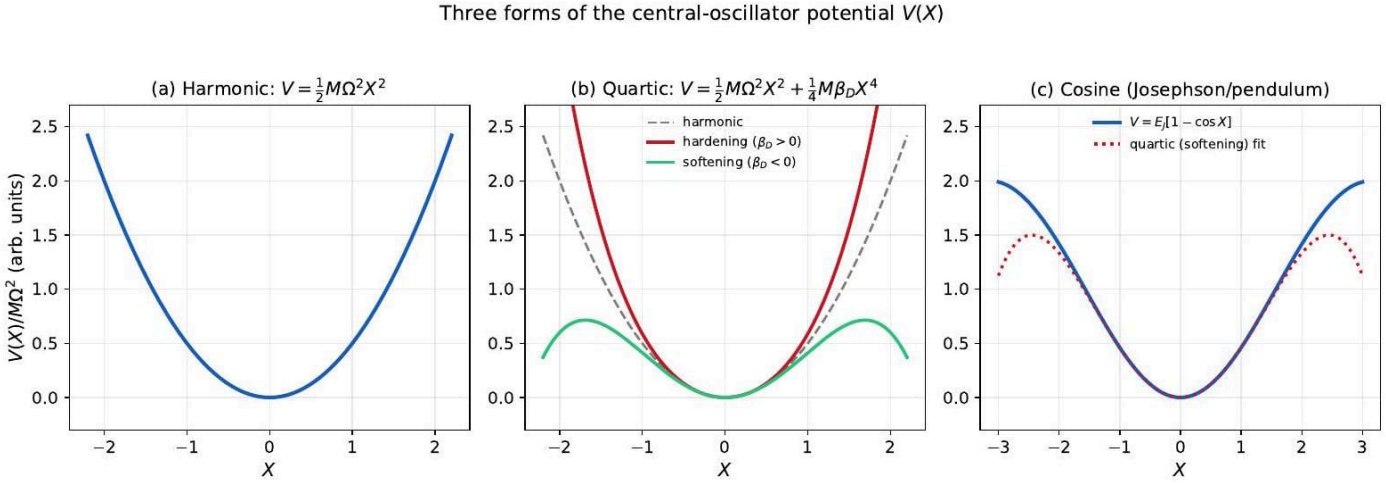


Figure $17.B2$: The three potentials of Sec. B.7. (a) General smooth potential with a nondegenerate minimum at $X = 0$, Sec. B.7.1. (b) Quartic (Duffing), Sec. B.7.2, for both signs of β_D; the softening curve $(\beta_D < 0)$ is the generic shape produced by truncating any cosine-like potential. (c) The cosine (Josephson/pendulum) potential of Sec. B.7.3, with its quartic (Taylor) approximation overlaid: the two agree closely near $X = 0$ and diverge once $|X|$ is no longer small, marking the boundary of validity of the Duffing approximation to the full problem.

B. 8 Thermal (Hartree) renormalization of the vibrational frequency

We now specialize to the quartic case of Sec. B.7.2-which, by Sec. B.7.3, includes the cosine potential's small-oscillation regime as the particular case $\beta_D = -\Omega^2/6$-and ask how the thermal bath renormalizes Ω.

B.8.1 Mean-field decoupling of the quartic term

Split $X = X_{\mathrm{coh}} + \delta X$ into a slowly varying coherent part and a rapidly fluctuating thermal part, and average the cubic restoring force over the noise at fixed X_{coh}. Since δX is a zero-mean Gaussian process to this order, its odd moments vanish and $\langle X^3 \rangle_\eta = X_{\mathrm{coh}}^3 + 3\sigma_{\mathrm{th}}^2 X_{\mathrm{coh}} + O(\beta_D^2)$, with $\sigma_{\mathrm{th}}^2 \equiv \langle \delta X^2 \rangle$. The coherent equation of motion therefore acquires a mean-field-shifted linear coefficient,

$$\ddot{X}_{\mathrm{coh}} + \gamma_0 \dot{X}_{\mathrm{coh}} + \Omega_{\mathrm{eff}}^2 X_{\mathrm{coh}} + \beta_D X_{\mathrm{coh}}^3 = f\cos(\omega_d t), \quad \Omega_{\mathrm{eff}}^2 \equiv \Omega^2 + 3\beta_D \sigma_{\mathrm{th}}^2. \tag{B.26}$$

The sign of β_D decides everything that follows: thermal and quantum fluctuations raise the vibrational frequency when the quartic term is hardening, and lower it when the quartic term is softening-which, by Eq. (B.25), is always the case for a cosine potential.

B.8.2 Quantum thermal variance from the FDT

For weak Markovian damping ($\gamma_0 \ll \Omega$), the narrow-resonance form of the quantum FDT (Sec. B.5) gives the standard result for the thermal variance of a weakly damped quantum oscillator [11, 9],

$$\sigma_{\mathrm{th}}^2 = \frac{\hbar}{2M\Omega} \coth\left(\frac{\hbar\Omega}{2k_{\mathrm{B}}T}\right), \tag{B.27}$$

with the familiar classical ($k_{\mathrm{B}}T \gg \hbar\Omega$) and zero-point ($k_{\mathrm{B}}T \ll \hbar\Omega$) limits,

$$\sigma_{\mathrm{th}}^2 \to \frac{k_{\mathrm{B}}T}{M\Omega^2} \quad (\text{ classical }), \quad \sigma_{\mathrm{th}}^2 \to \frac{\hbar}{2M\Omega} \quad (\text{ zero-point }). \tag{B.28}$$

B.8.3 Self-consistent gap equation; hardening vs. softening

Promoting Eq. (B.26) to self-consistency (evaluating σ_{th}^2 at Ω_{eff} rather than the bare Ω) gives the Hartree gap equation

$$\Omega_{\mathrm{eff}}^2 = \Omega^2 + \frac{3\beta_D \hbar}{2M\Omega_{\mathrm{eff}}} \coth\left(\frac{\hbar\Omega_{\mathrm{eff}}}{2k_{\mathrm{B}}T}\right). \tag{B.29}$$

In the classical regime this reduces to the algebraic equation $\Omega_{\mathrm{eff}}^4 - \Omega^2\Omega_{\mathrm{eff}}^2 - 3\beta_D k_{\mathrm{B}}T/M = 0$. Writing $y \equiv \Omega_{\mathrm{eff}}^2/\Omega^2$ and the dimensionless temperature $\tau \equiv 3|\beta_D| k_{\mathrm{B}}T/(M\Omega^4)$, the physical root is

$$\text{hardening } (\beta_D > 0): y(\tau) = \frac{1+\sqrt{1+4\tau}}{2}, \tag{B.30}$$

$$\text{softening } (\beta_D < 0): y(\tau) = \frac{1+\sqrt{1-4\tau}}{2}, \quad \tau \le \frac{1}{4}. \tag{B.31}$$

Figure B. 3 plots both branches side by side. The hardening branch grows without bound, saturating at high temperature as $y \sim \sqrt{\tau}$, i.e. $\Omega_{\mathrm{eff}} \propto T^{1/4}$: a smooth, physically unremarkable crossover. The softening branch, in stark contrast, terminates: the square root in Eq. (B.31) becomes imaginary beyond $\tau_{\max} = 1/4$, where $y \to 1/2$. Beyond this point no real, self-consistent solution of Eq. (B.29) exists at all-the Hartree instability already anticipated in the Introduction, and, via Eq. (B.25), a generic feature of every cosine-potential (Josephson or pendulum) problem once it is heated enough.

B.8.4 Connecting back to the linear theory: what the Hartree instability actually is

Section B. 6 showed that the Markovian GLE, linearized about $X = 0$, has stable, causal, oscillatory poles only when the coefficient

multiplying X is strictly positive: $\Omega^2 > 0$. Equation (B.26)

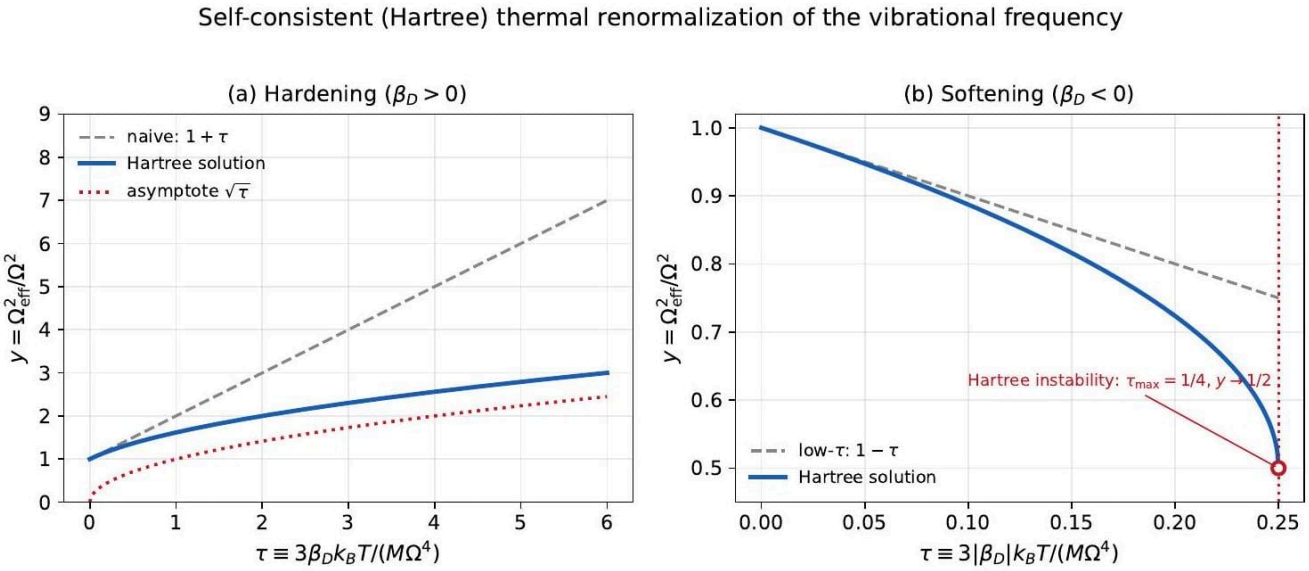


Figure $17.B1$: Self-consistent (classical-regime) thermal renormalization of the vibrational frequency, Eqs. (B.30)-(B.31). (a) Hardening quartic: the frequency rises and saturates smoothly, $\Omega_{\rm eff} \propto T^{1/4}$, with no upper bound on τ. (b) Softening quartic-including the cosine potential of Sec. B.7.3, for which $\beta_D = -\Omega^2/6$ exactly: the frequency falls and the self-consistent branch terminates cleanly at $\tau_{\rm max} = 1/4$, where $y = \Omega^2_{\rm eff}/\Omega^2 \to 1/2$-the Hartree instability discussed in Sec. B.8.4. shows that the Hartree-renormalized problem is, at the level of the coherent (mean-field) dynamics, an ordinary linear oscillator with Ω^2 replaced by $\Omega^2_{\rm eff}$; the pole criterion of Sec. B. 6 therefore applies verbatim, with $\Omega \to \Omega_{\rm eff}(T)$. As $\tau \to \tau^-_{\rm max}$ for a softening quartic, $\Omega^2_{\rm eff} \to \Omega^2/2 > 0$ still-the branch shown in Fig. B.3(b) never itself passes through zero frequency. What actually happens at $\tau_{\rm max}$ is that the self-consistency condition itself loses its solution: the equation $\Omega^2_{\rm eff} = \Omega^2 + 3\beta_D \sigma^2_{\rm th}(\Omega_{\rm eff})$, read as a fixed-point problem, has a solution branch that folds back on itself and disappears in exactly the same saddle-node (fold) sense as the disappearance of a root pair in the bistability cubic of Sec. B. 9 below. In plain terms: as the softening well is heated, each increment of thermal spread $\sigma^2_{\rm th}$ lowers $\Omega_{\rm eff}$, which itself raises $\sigma^2_{\rm th}$ further (since $\sigma^2_{\rm th} \propto 1/\Omega^2_{\rm eff}$ classically)-a positive feedback loop that a hardening quartic does not have (there, softening feeds back negatively: lower $\sigma^2_{\rm th}$ growth per unit $\Omega_{\rm eff}$ increase, which is why that branch saturates rather than runs away). Beyond $\tau_{\rm max}$ the feedback loop has no fixed point left to converge to, and the mean-field, small-oscillation description of the well breaks down-the physical system must be re-described either by the full cosine potential of Sec. B.7.3 or, physically, by thermally activated escape over the now-shallow barrier. The Hartree instability is thus not a failure of the linear stability criterion of Sec. B. 6 applied naively; it is a breakdown of the assumption, made in this section, that the quartic term can be treated as a small, self-consistently determined correction to an otherwise-good harmonic approximation-exactly the regime, visualized in Fig. B.2(c), in which the quartic curve has already begun to visibly depart from the true cosine.

B. 9 Stability of the driven, bistable response

The renormalization $\Omega \to \Omega_{\rm eff}(T)$ carries through into the driven problem unchanged, exactly as it did for the memory kernel and the FDT in Sec. B.7.2. Writing the driven, self-consistent fundamental-response amplitude as $u \equiv |A_1|^2$, gives the self-consistency condition

$$\left\{\left(\Omega^2_{\rm eff} - \omega_d^2 + 3\beta_D f^2 u\right)^2 + \gamma_0^2 \omega_d^2\right\} u = 1, \tag{B.32}$$

APPENDIX B. GENERALIZED LANGEVIN DYNAMICS FOR AN ARBITRARY POTENTIAL: THERMAL

an algebraic cubic equation in u (expand the square). A cubic with real coefficients has either three real roots or one real root together with a complex-conjugate pair; $u = |A_1|^2$ must be real and non-negative to describe an actual oscillation amplitude, so a complex pair, when present, simply plays no physical role, and the single real positive root left over is the unique, unambiguously monostable response. When three real positive roots occur, only the smallest and the largest are dynamically stable; the middle

root is the classic unstable branch of a folded (S-shaped) response curve, exactly as for the ordinary (non-thermally-renormalized) Duffing oscillator, and its presence is what produces hysteresis as the drive frequency or amplitude is swept back and forth. Because Eq. (B.32) depends on temperature only through $\Omega_{\text{eff}}(T)$, the entire bistable window-its location, its width, and (for a softening quartic) its eventual disappearance-is carried along rigidly by the same thermal renormalization derived in Sec. B.8, with the two qualitatively different outcomes of Fig. B. 3 now manifesting as a bistable window that either drifts smoothly to higher frequency without limit (hardening) or drifts to lower frequency and is extinguished altogether at a finite temperature (softening)- a purely thermal quenching of bistability with no counterpart in the zero-temperature theory.

B. 10 Summary

- 1.Eliminating a bath of N harmonic oscillators bilinearly coupled to a central coordinate of arbitrary potential $V(X)$, exactly following Magalinski's construction, gives the generalized Langevin equation (B.10): a memory kernel $\gamma(t)$ and a fluctuating force $\xi(t)$ tied together by the fluctuation-dissipation theorem, both fixed entirely by the bath's spectral density and completely independent of $V(X)$ (Sec. B.1).
- 2.Specializing this one general result-with no new bath-elimination algebra-produces the GLE for a general smooth potential, the noisy Duffing GLE for a quartic well, and the noisy pendulum/Josephson GLE for a cosine potential; the latter's own Taylor expansion fixes the quartic coefficient to the universal softening value $\beta_D = -\Omega^2/6$ (Sec. B.7).
- 3.The quantum-mechanical FDT gives the thermal variance $\sigma_{\text{th}}^2 = (\hbar/2M\Omega)\coth(\hbar\Omega/2k_{\text{B}}T)$, and Hartree self-consistency turns the frequency shift into a gap equation whose solution hardens smoothly $(\propto T^{1/4})$ for $\beta_D > 0$ but softens and terminates at a finite Hartree instability temperature for $\beta_D < 0$ (Sec. B.8, Fig. B.3).
- 4.That instability is not a violation of the linear stability criterion $\Omega_{\text{eff}}^2 > 0$ of Sec. B.6; it is the disappearance, via a saddle-node fold, of the self-consistency condition's own solution branch, driven by a positive feedback between frequency softening and thermal spread that has no counterpart in the hardening case (Sec. B.8.4).
- 5.The same renormalization propagates into the driven response, where a cubic self-consistency equation for the amplitude produces bistability with two stable and one unstable branch; the entire bistable window is carried along by $\Omega_{\text{eff}}(T)$, either advected indefinitely (hardening) or extinguished at finite temperature (softening) (Sec. B.9).

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18: Quantum Mori-Zwanzig Formulation of the Magalinski Model

Chapter 14 applied the Mori-Zwanzig (M-Z) projection technique to the Magalinski model purely classically: the Liouvillian was the Poisson-bracket generator, the projector $\mathcal{P}$ was built from the classical equilibrium average, and the equipartition theorem fixed the correlation matrix $\mathbb{C}$. Every one of those ingredients has a quantum-mechanical counterpart, and the purpose of this chapter is to carry the Magalinski-model calculation through operator by operator: the Liouvillian becomes the commutator generator of Heisenberg motion, the projector is built from Mori's canonical (Kubo-transform) inner product rather than the naive operator trace, and the equipartition theorem is replaced by its exact quantum generalization. We shall find that, once this dictionary is in place, the frequency matrix Ω and the memory kernel $K(t)$ obtained in Chapter 14 carry over unchanged, operator for operator, to all orders in the system-bath coupling. The genuinely new quantum content appears only when one asks what the noise operator $\hat{F}(t)$ actually is as a physical, non-commuting object: its Mori-transformed autocorrelation reproduces the classical fluctuation-dissipation relation exactly, while its symmetrized (measurable) autocorrelation carries the familiar thermal factor $\hbar\omega\coth\left(\hbar\omega/2k_{\mathrm{B}}T\right)$ derived independently, via the Kubo-Martin-Schwinger condition, in Appendix A.

A second, more subtle point concerns the Hamiltonian itself. Chapter 14 worked with the bare bilinear coupling $H_{\mathrm{int}}=\sum_j c_j q_0 q_j$ and implicitly set the system-bath position correlation $\langle q_0 q_j\rangle_0$ to zero when forming $\mathbb{C}$ and Ω. This is exact only to leading order in the coupling; at the operator level, making the Mori inner product well defined non-perturbatively requires the Ford-Kac-Mazur/Caldeira-Leggett renormalization counterterm discussed at length, for the single-oscillator system-plus-bath problem, in Appendix A ("Details of potential renormalization") of Ghosh et al. [6]. We include this counterterm from the outset below; doing so is what allows every statement in this chapter to hold exactly, not merely to leading order in c_j. This same counterterm construction - the Caldeira-Leggett Hamiltonian of Eq. (H-CL) - is already adopted, for a completely general central potential $V(X)$, in Appendix C ("Generalized Langevin Dynamics for an Arbitrary Potential"), which simply invokes "the quantum-mechanical FDT" at the point where it is needed; the present appendix supplies the missing first-principles derivation of that FDT, and of the underlying quantum generalized Langevin equation, for the exactly solvable harmonic case from which Appendix C's anharmonic analysis departs.

C. 1 The Quantum Hamiltonian and the Renormalization Counterterm

We promote the coordinates and momenta of Chapter 14 to Hermitian operators, $q_0\to\hat{q}_0$, $p_0\to\hat{p}_0$, $q_j\to\hat{q}_j$, $p_j\to\hat{p}_j$, satisfying the canonical commutation relations

$$[\hat{q}_0,\hat{p}_0]=i\hbar,\quad [\hat{q}_j,\hat{p}_k]=i\hbar\delta_{jk},\quad j,k=1,\ldots,N, \tag{C.1}$$

with all other commutators among $\{\hat{q}_0,\hat{p}_0,\hat{q}_j,\hat{p}_j\}$ vanishing. Rather than the bare Hamiltonian of Equation ??? of Chapter 14, we take, following Ford, Kac and Mazur and the independent-oscillator model reviewed in [6],

$$\hat{H}=\frac{\hat{p}_0^2}{2m_0}+\frac{m_0\omega_0^2}{2}\hat{q}_0^2+\sum_{j=1}^{N}\left[\frac{\hat{p}_j^2}{2m_j}+\frac{m_j\omega_j^2}{2}\left(\hat{q}_j+\frac{c_j}{m_j\omega_j^2}\hat{q}_0\right)^2\right]. \tag{C.2}$$

Expanding the square reproduces exactly the bilinear coupling of Chapter 14 together with one extra, j-summed, term quadratic in $\hat{q}_0$:

$$\hat{H}=\underbrace{\frac{\hat{p}_0^2}{2m_0}+\frac{m_0\omega_0^2}{2}\hat{q}_0^2}_{\hat{H}_S}+\underbrace{\sum_j\left[\frac{\hat{p}_j^2}{2m_j}+\frac{m_j\omega_j^2}{2}\hat{q}_j^2\right]}_{\hat{H}_B}+\underbrace{\sum_j c_j\hat{q}_0\hat{q}_j}_{\hat{H}_{\mathrm{int}}}+\underbrace{\frac{1}{2}\sum_j\frac{c_j^2}{m_j\omega_j^2}\hat{q}_0^2}_{V_r(\hat{q}_0)}. \tag{C.3}$$

The last piece, $V_r\left(\hat{q}_0\right)$, is the renormalization counterterm. It is not optional: without it, the bath-induced frequency shift $(\delta\omega)^2=(1/m_0)\sum_j c_j^2/\left(m_j\omega_j^2\right)$ pulls the true, measurable oscillation frequency of the system away from the parameter ω_0 appearing in $\hat{H}_S$ - indeed, for a strongly or continuously coupled bath $(\delta\omega)^2$ can exceed ω_0^2 and the potential in Equation ??? ceases to be bounded from below, exactly as explained in Appendix A of [6]. With V_r included, as we now show, ω_0 in Eq. (C.2) is the physical frequency, to all orders in $\{c_j\}$ and for any N, including $N\to\infty$.

It is convenient to introduce the shifted bath coordinate

$$\hat{Q}_j \equiv \hat{q}_j + \frac{c_j}{m_j\omega_j^2}\hat{q}_0, \tag{C.4}$$

which is simply the combination that is perfect-squared in Eq. (C.2). Because $\left[\hat{Q}_j, \hat{p}_j\right] = [\hat{q}_j, \hat{p}_j] = i\hbar$ and $\left[\hat{Q}_j, \hat{p}_k\right] = 0$ for $k \neq j$, the pair $\left(\hat{Q}_j, \hat{p}_j\right)$ remains canonically conjugate.

C. 2 The Quantum Liouvillian and Heisenberg Equations of Motion

Following the convention used throughout this book for the quantum case (and matching the "Key Foundations in Quantum Mechanics" used elsewhere), we define the quantum Liouvillian superoperator through the commutator,

$$i\mathcal{L}\hat{X} \equiv \frac{i}{\hbar}[\hat{H}, \hat{X}], \tag{C.5}$$

so that the Heisenberg equation of motion for any operator $\hat{X}(t) = e^{i\hat{H}t/\hbar}\hat{X}e^{-i\hat{H}t/\hbar}$ reads $d\hat{X}/dt = i\mathcal{L}\hat{X}$, in exact formal parallel with the classical $\dot{A} = \mathcal{L}A$ of Chapter 14 and of the general formalism of Chapter 15.

Using the canonical commutation relations (C.1) and the Hamiltonian (C.3), the Heisenberg equations of motion for the relevant vector $\hat{\mathbf{A}}(t) = (\hat{q}_0(t), \hat{p}_0(t))^T$ are obtained exactly as in

elementary quantum mechanics, $i\mathcal{L}\hat{q}_0 = (i/\hbar)\left[\hat{H}, \hat{q}_0\right] = \partial\hat{H}/\partial\hat{p}_0$ and $i\mathcal{L}\hat{p}_0 = -\partial\hat{H}/\partial\hat{q}_0$ (the operator ordering is unambiguous here because $\hat{H}$ is at most quadratic):

$$i\mathcal{L}\hat{q}_0 = \frac{\hat{p}_0}{m_0}, \quad i\mathcal{L}\hat{p}_0 = -m_0\omega_0^2\hat{q}_0 - \sum_j c_j\hat{q}_j - \hat{q}_0\sum_j \frac{c_j^2}{m_j\omega_j^2}. \tag{C.6}$$

Substituting $\hat{q}_j = \hat{Q}_j - c_j\hat{q}_0/\left(m_j\omega_j^2\right)$ from Eq. (C.4), the last two terms in $i\mathcal{L}\hat{p}_0$ combine as

$$-\sum_j c_j\hat{q}_j - \hat{q}_0\sum_j \frac{c_j^2}{m_j\omega_j^2} = -\sum_j c_j\hat{Q}_j + \hat{q}_0\sum_j \frac{c_j^2}{m_j\omega_j^2} - \hat{q}_0\sum_j \frac{c_j^2}{m_j\omega_j^2} = -\sum_j c_j\hat{Q}_j,$$

and the renormalizing pieces cancel exactly. We are left with

$$i\mathcal{L}\hat{q}_0 = \frac{\hat{p}_0}{m_0}, \quad i\mathcal{L}\hat{p}_0 = -m_0\omega_0^2\hat{q}_0 - \sum_j c_j\hat{Q}_j. \tag{C.7}$$

These are operator-identical in form to Equation ??? of Chapter 14, with the single replacement $q_j \to Q_j$: the renormalization counterterm's entire effect is to replace the bare bath coordinate by its recentred counterpart in the force law on the oscillator. This is the quantum-operator statement of the physics behind Appendix A of [6], and it is the technical fact that makes everything that follows exact rather than perturbative.

C. 3 The Mori (Kubo-Transform) Inner Product

For classical phase-space functions, Chapter 14 used the equilibrium average $(A, B) = \langle AB\rangle_0$ to build the projector $\mathcal{P}$. For non-commuting operators the naive choice $\left\langle \hat{X}^\dagger\hat{Y}\right\rangle_0$ is not symmetric and does not make $\mathcal{L}$ Hermitian with respect to it, so $\mathcal{P}$ built from it fails to be a genuine orthogonal projector. Mori's resolution [2] is to use instead the canonical (Kubo-transform) inner product,

$$(\hat{X}, \hat{Y}) \equiv \frac{1}{\beta}\int_0^\beta d\lambda \left\langle e^{\lambda\hat{H}}\hat{X}^\dagger e^{-\lambda\hat{H}}\hat{Y}\right\rangle_0, \quad \beta = \frac{1}{k_{\mathrm{B}}T} \tag{C.8}$$

where $\langle\cdot\rangle_0 = Z^{-1}\,\mathrm{Tr}\left[e^{-\beta\hat{H}}(\cdot)\right]$ is the canonical equilibrium average with respect to the full Hamiltonian (C.2). One verifies that $(i\mathcal{L}\hat{X}, \hat{Y}) = (\hat{X}, i\mathcal{L}\hat{Y})$, so that $\mathcal{L}$ is Hermitian with respect to $(\cdot,\cdot)$ and the Mori projector

$$\mathcal{P}\hat{B} \equiv (\hat{B}, \hat{\mathbf{A}})(\hat{\mathbf{A}}, \hat{\mathbf{A}})^{-1}\hat{\mathbf{A}}, \quad \mathcal{Q} \equiv 1 - \mathcal{P} \tag{C.9}$$

is a well-defined orthogonal projector onto the two-dimensional operator subspace spanned by $\hat{q}_0, \hat{p}_0$. Note that $(\hat{X}, \hat{Y})$ is bilinear in $\hat{X}, \hat{Y}$ (for Hermitian operators) and reduces to $\langle \hat{X}\hat{Y} \rangle_0$ whenever $\hat{X}$ and $\hat{Y}$ commute - in particular, it reduces to the classical equilibrium average in the limit $\hbar \to 0$.

Theorem C. 1 (Quantum / Kubo-canonical equipartition theorem). Let $\hat{x}_a$ denote any one of the canonical phase-space operators of a Hamiltonian system, $\{\hat{x}_a\} = \{\hat{q}_0, \hat{p}_0, \hat{q}_1, \hat{p}_1, \ldots, \hat{q}_N, \hat{p}_N\}$. Then

$$\left(\hat{x}_a, \frac{\partial \hat{H}}{\partial \hat{x}_b}\right) = k_\mathrm{B}T\delta_{ab} \tag{C.10}$$

for all a, b, exactly as in the classical equipartition theorem invoked in Chapter 14 (there citing Pathria and Beale [4]). This is a standard property of the Kubo-canonical correlation; see Kubo, Toda and Hashitsume [5].

We shall use Theorem C. 1 exactly as Chapter 14 used its classical counterpart - as a black box that fixes all equal-time correlations - without reproducing its (standard, and not especially illuminating) proof here.

C.3.1 The correlation matrix $\mathbb{C}$

Applying Theorem C. 1 with $a = b = q_0$ to the full Hamiltonian (C.3), and separately with $a = q_0, b = q_j$ (distinct canonical coordinates, so the right-hand side of Eq. (C.10) vanishes), one finds, after eliminating $(\hat{q}_0, \hat{q}_j)$ between the two resulting linear relations exactly as the classical renormalization identity of Appendix C of [6] does for the static susceptibility,

$$(\hat{q}_0, \hat{q}_0) = \frac{k_\mathrm{B}T}{m_0\omega_0^2}, \quad (\hat{q}_0, \hat{q}_j) = -\frac{c_j}{m_j\omega_j^2}(\hat{q}_0, \hat{q}_0) = -\frac{c_j k_\mathrm{B}T}{m_0\omega_0^2 m_j\omega_j^2}. \tag{C.11}$$

By bilinearity, the shifted bath coordinate is exactly uncorrelated with the system coordinate:

$$\left(\hat{q}_0, \hat{Q}_j\right) = (\hat{q}_0, \hat{q}_j) + \frac{c_j}{m_j\omega_j^2}(\hat{q}_0, \hat{q}_0) = 0. \tag{C.12}$$

Applying Theorem C. 1 with $a = q_0, b = p_0$ (distinct variables, $\partial\hat{H}/\partial\hat{p}_0 = \hat{p}_0/m_0$) gives $(\hat{q}_0, \hat{p}_0) = 0$; with $a = b = p_0$ it gives $(\hat{p}_0, \hat{p}_0) = m_0 k_\mathrm{B}T$; and with $a = p_0, b = q_j$ it gives $(\hat{p}_0, \hat{q}_j) = 0$ and hence, by the same bilinearity argument, $\left(\hat{p}_0, \hat{Q}_j\right) = 0$. Collecting these,

$$\mathbb{C} \equiv (\hat{\mathbf{A}}, \hat{\mathbf{A}}) = \begin{pmatrix} (\hat{q}_0, \hat{q}_0) & (\hat{q}_0, \hat{p}_0) \\ (\hat{p}_0, \hat{q}_0) & (\hat{p}_0, \hat{p}_0) \end{pmatrix} = \begin{pmatrix} \frac{k_\mathrm{B}T}{m_0\omega_0^2} & 0 \\ 0 & m_0 k_\mathrm{B}T \end{pmatrix}, \tag{C.13}$$

identical to Equation ??? of Chapter 14 - the quantum Mori-canonical correlation matrix coincides exactly with the classical equipartition matrix, with no $\hbar$-dependence whatsoever and no restriction to weak coupling. This is the single most important simplifying fact about Mori's inner product: it is constructed precisely so that static, equal-time quantum thermal averages reproduce their classical values.

For completeness we record, by the identical argument applied to $a = b = p_j$ and $a = p_j, b = p_k (j \neq k)$, that

$$(\hat{p}_j, \hat{p}_j) = m_j k_\mathrm{B}T, \quad (\hat{p}_j, \hat{p}_k) = 0 (j \neq k), \quad \left(\hat{Q}_j, \hat{Q}_j\right) = \frac{k_\mathrm{B}T}{m_j\omega_j^2}, \quad \left(\hat{Q}_j, \hat{p}_j\right) = 0 \tag{C.14}$$

the last two following from $\partial\hat{H}/\partial\hat{Q}_j = m_j\omega_j^2\hat{Q}_j$ and $\partial\hat{H}/\partial\hat{p}_j = \hat{p}_j/m_j$ evaluated at fixed $\hat{q}_0$. That is: in every Mori-canonical moment that matters below, the shifted operator pair $\left(\hat{Q}_j, \hat{p}_j\right)$ behaves exactly like an isolated quantum harmonic oscillator of mass m_j and frequency ω_j in thermal equilibrium at temperature T, decoupled from $\hat{q}_0, \hat{p}_0$ and from every other bath mode.

C. 4 The Frequency Matrix

With $\mathbb{C}$ in hand, the frequency matrix is defined, exactly as in Equation ??? of Chapter 14,

$$\Omega \equiv (i\mathcal{L}\hat{\mathbf{A}}, \hat{\mathbf{A}})\mathbb{C}^{-1}. \tag{C.15}$$

Using Eq. (C.7) and the vanishing of $\left(\hat{Q}_j, \hat{q}_0\right)$, $\left(\hat{Q}_j, \hat{p}_0\right)$ established in Eqs. (C.12)-(C.14):

$$(i\mathcal{L}\hat{q}_0, \hat{q}_0) = \frac{1}{m_0}(\hat{p}_0, \hat{q}_0) = 0, \quad (i\mathcal{L}\hat{p}_0, \hat{q}_0) = -m_0\omega_0^2(\hat{q}_0, \hat{q}_0) - \sum_j c_j\left(\hat{Q}_j, \hat{q}_0\right) = -k_{\mathrm{B}}T,$$

$$(i\mathcal{L}\hat{q}_0, \hat{p}_0) = \frac{1}{m_0}(\hat{p}_0, \hat{p}_0) = k_{\mathrm{B}}T, \quad (i\mathcal{L}\hat{p}_0, \hat{p}_0) = -m_0\omega_0^2(\hat{q}_0, \hat{p}_0) - \sum_j c_j\left(\hat{Q}_j, \hat{p}_0\right) = 0$$

so that, with $\mathbb{C}^{-1} = \mathrm{diag}\left(m_0\omega_0^2/k_{\mathrm{B}}T, 1/(m_0k_{\mathrm{B}}T)\right)$,

$$\Omega = \begin{pmatrix} 0 & 1/m_0 \\ -m_0\omega_0^2 & 0 \end{pmatrix}. \tag{C.16}$$

This is identical to the boxed result, Equation ???, of Chapter 14, and - unlike the classical derivation there, which quietly assumed the system-bath position correlation to vanish - it is here exact to all orders in $\{c_j\}$, a consequence of including the renormalization counterterm of Sec. C.1.

C. 5 Orthogonal Dynamics and the Quantum Random-Force Operator

Just as in Chapter 14, we must compute $i\mathcal{Q}\mathcal{L}\hat{p}_0 = i\mathcal{L}\hat{p}_0 - \mathcal{P}(i\mathcal{L}\hat{p}_0)$. From Eq. (C.7), $i\mathcal{L}\hat{p}_0 = -m_0\omega_0^2\hat{q}_0 - \sum_j c_j\hat{Q}_j$; since $\left(\hat{Q}_j, \hat{q}_0\right) = \left(\hat{Q}_j, \hat{p}_0\right) = 0$ for every j (Sec. C.3), the $\hat{Q}_j$ piece has no overlap at all with the relevant subspace, and projection removes only the first term:

$$\mathcal{P}(i\mathcal{L}\hat{p}_0) = -m_0\omega_0^2\hat{q}_0, \quad \hat{f} \equiv i\mathcal{Q}\mathcal{L}\hat{p}_0 = -\sum_j c_j\hat{Q}_j. \tag{C.17}$$

This matches Equation ??? of Chapter 14 with $q_j \to Q_j$.

To obtain the random-force operator $\hat{F}(t) = e^{i\mathcal{Q}\mathcal{L}t}\hat{f}$ we must know how $\hat{f}$ evolves under the orthogonal, projected dynamics. Compute first the unrestricted derivative,

$$i\mathcal{L}\hat{f} = -\sum_j c_j i\mathcal{L}\hat{Q}_j = -\sum_j c_j\left(\frac{\hat{p}_j}{m_j} - \frac{c_j}{m_j\omega_j^2}i\mathcal{L}\hat{q}_0\right) = -\sum_j \frac{c_j}{m_j}\hat{p}_j + \frac{\hat{p}_0}{m_0}\sum_j \frac{c_j^2}{m_j\omega_j^2},$$

using $i\mathcal{L}\hat{q}_0 = \hat{p}_0/m_0$ from Eq. (C.7). At first sight this leaks into the relevant subspace through the $\hat{p}_0$ term: $\hat{Q}_j$ itself "feels" $\hat{q}_0$ because its very definition, Eq. (C.4), involves $\hat{q}_0$. However, this leakage is projected straight back out again. Using $(\hat{p}_j, \hat{q}_0) = (\hat{p}_j, \hat{p}_0) = 0$ (Theorem C. 1 applied to $a = p_j, b = q_0$ or p_0) and $(\hat{p}_0, \hat{p}_0) = m_0k_{\mathrm{B}}T$,

$$\left(i\mathcal{L}\hat{f}, \hat{q}_0\right) = 0, \quad \left(i\mathcal{L}\hat{f}, \hat{p}_0\right) = \frac{k_{\mathrm{B}}T}{m_0}\sum_j \frac{c_j^2}{m_j\omega_j^2}\cdot m_0 = k_{\mathrm{B}}T\sum_j \frac{c_j^2}{m_j\omega_j^2},$$

so that $\mathcal{P}(i\mathcal{L}\hat{f}) = \left[\sum_j c_j^2/\left(m_j\omega_j^2\right)\right]\hat{p}_0/m_0$ - precisely the term that must be subtracted to cancel the leaked piece of $i\mathcal{L}\hat{f}$ itself:

$$i\mathcal{Q}\mathcal{L}\hat{f} = i\mathcal{L}\hat{f} - \mathcal{P}(i\mathcal{L}\hat{f}) = -\sum_j \frac{c_j}{m_j}\hat{p}_j = -\sum_j c_j i\mathcal{L}\hat{Q}_j\Big|_{\hat{q}_0\to 0}. \tag{C.18}$$

In other words, on the orthogonal subspace the generator $i\mathcal{Q}\mathcal{L}$ acting on $\hat{f}$ coincides exactly with the free-bath generator $i\mathcal{L}_B$, under which $\hat{Q}_j, \hat{p}_j$ evolve as an isolated oscillator, $i\mathcal{L}_B\hat{Q}_j = \hat{p}_j/m_j$, $i\mathcal{L}_B\hat{p}_j = -m_j\omega_j^2\hat{Q}_j$. This is the operator version of the "Rosetta Stone" identity of Chapter 14, $\mathcal{Q}\mathcal{L}f(0) = \mathcal{L}_Bf(0)$: the bilinear-coupling closure property survives quantization unchanged, provided one tracks the system-dependence hidden inside the shifted bath coordinate $\hat{Q}_j$, as we have just done explicitly. Exponentiating,

$$\hat{F}(t) = e^{i\mathcal{Q}\mathcal{L}t}\hat{f} = -\sum_{j=1}^{N} c_j\hat{Q}_j(t), \quad \hat{Q}_j(t) = \hat{Q}_j(0)\cos(\omega_j t) + \frac{\hat{p}_j(0)}{m_j\omega_j}\sin(\omega_j t), \tag{C.19}$$

exactly reproducing Equation ??? of Chapter 14 with $q_j \to Q_j$.

C. 6 Quantum Memory Kernel and the Mori-Form Fluctuation-Dissipation Theorem

We need the two-time Mori-canonical correlation of a single shifted bath mode, $\left(\hat{Q}_j(0), \hat{Q}_j(t)\right)$. Since $\left(\hat{Q}_j, \hat{p}_j\right)$ is, as established in Sec. C.3, in every relevant respect an isolated harmonic oscillator of mass m_j and frequency ω_j at temperature T, we may compute this directly from Eq. (C.8) using ladder operators $\hat{a}_j, \hat{a}_j^\dagger$ for that mode, $\hat{Q}_j = \sqrt{\hbar/2m_j\omega_j}\left(\hat{a}_j + \hat{a}_j^\dagger\right)$, with $\hat{Q}_j(t)$ as in Eq. (C.19) and thermal occupation $n_j \equiv \left\langle \hat{a}_j^\dagger \hat{a}_j \right\rangle_0 = \left(e^{\beta\hbar\omega_j} - 1\right)^{-1}$.

Lemma C. 2 (Two-time Mori correlation of a free quantum oscillator). For a free quantum harmonic oscillator of mass m, frequency ω, in thermal equilibrium at temperature T,

$$(\hat{q}(0), \hat{q}(t)) = \frac{k_\mathrm{B}T}{m\omega^2}\cos(\omega t). \tag{C.20}$$

Proof. With $\hat{q}(-i\hbar\lambda) = \sqrt{\hbar/2m\omega}\left(\hat{a}e^{-\omega\hbar\lambda} + \hat{a}^\dagger e^{\omega\hbar\lambda}\right)$ and $\hat{q}(t) = \sqrt{\hbar/2m\omega}\left(\hat{a}e^{-i\omega t} + \hat{a}^\dagger e^{i\omega t}\right)$,

$$\langle \hat{q}(-i\hbar\lambda)\hat{q}(t)\rangle_0 = \frac{\hbar}{2m\omega}\left[(n+1)e^{-\omega\hbar\lambda}e^{i\omega t} + ne^{\omega\hbar\lambda}e^{-i\omega t}\right].$$

Using $\frac{1}{\beta}\int_0^\beta d\lambda e^{\mp\omega\hbar\lambda} = \frac{1-e^{\mp\beta\hbar\omega}}{\pm\beta\hbar\omega}$ together with the Bose identities $(n+1)\left(1-e^{-\beta\hbar\omega}\right) = 1$ and $n\left(e^{\beta\hbar\omega}-1\right) = 1$, both integrals collapse to $1/(\beta\hbar\omega)$, giving

$$(\hat{q}(0), \hat{q}(t)) = \frac{\hbar}{2m\omega}\cdot\frac{1}{\beta\hbar\omega}\left(e^{i\omega t} + e^{-i\omega t}\right) = \frac{1}{\beta m\omega^2}\cos(\omega t) = \frac{k_\mathrm{B}T}{m\omega^2}\cos(\omega t).$$

□

Lemma C. 2 is the dynamical counterpart of Theorem C. 1 all explicit $\hbar$ - and temperature-dependence cancels, and the Mori-canonical two-time correlation of a harmonic coordinate is exactly the classical bath correlation $\langle q_i(0)q_i(t)\rangle_{eq} = k_\mathrm{B}T\cos(\omega_i t)/(m_i\omega_i^2)$ used in Chapter 14 immediately before its boxed result, Equation ???, at every temperature. Applying it to each shifted bath mode in Eq. (C.19),

$$(\hat{F}(0), \hat{F}(t)) = \sum_j c_j^2\left(\hat{Q}_j(0), \hat{Q}_j(t)\right) = k_\mathrm{B}T\sum_j \frac{c_j^2}{m_j\omega_j^2}\cos(\omega_j t), \tag{C.21}$$

and dividing by $\mathbb{C}_{pp} = m_0 k_\mathrm{B}T$ as in Chapter 14 (and Eq. (C.14) confirms $\mathcal{Q}$ does not mix the $\hat{Q}_j$-sector back into $\hat{p}_0$, so the pp -component is the only non-zero one), we obtain the quantum memory kernel

$$K(t) = \frac{(\hat{F}(0), \hat{F}(t))}{m_0 k_\mathrm{B}T} = \frac{1}{m_0}\sum_{j=1}^{N}\frac{c_j^2}{m_j\omega_j^2}\cos(\omega_j t), \tag{C.22}$$

identical to the boxed result, Equation ???, of Chapter 14. The complete quantum generalized Langevin equation for the Heisenberg operators $\hat{q}_0(t), \hat{p}_0(t)$ is therefore

$$\frac{d\hat{q}_0}{dt} = \frac{\hat{p}_0}{m_0}, \quad \frac{d\hat{p}_0}{dt} = -m_0\omega_0^2\hat{q}_0 - \int_0^t K(t-s)\frac{\hat{p}_0(s)}{m_0}ds + \hat{F}(t), \tag{C.23}$$

operator-identical to Equation ??? of Chapter 14, with the exact Mori-form ("second") fluctuation-dissipation theorem

$$(\hat{F}(t), \hat{F}(s)) = k_\mathrm{B}T m_0 K(|t-s|) \tag{C.24}$$

holding by construction, in exact parallel with Equation ??? of the general formalism of Chapter 15.

C. 7 From Mori Correlations to Physical Noise: the Thermal Factor and Operator Non-Commutativity

Equation (C.24) is an exact algebraic identity of the Mori formalism, but $(\hat{F}(t), \hat{F}(s))$ is not what an experiment measures: a measurement of the force operator at two times yields expectation values of the physical, symmetrized correlator $\frac{1}{2}\langle\{\hat{F}(t), \hat{F}(s)\}\rangle_0$, together with the (purely quantum, operator-ordering) commutator $\langle[\hat{F}(t), \hat{F}(s)]\rangle_0$. Both are obtained from the same mode expansion used in the proof of Lemma C.2.

Lemma C. 3 (Symmetrized correlator and commutator of a free quantum oscillator). For the same oscillator as in Lemma C.2,

$$\frac{1}{2}\langle\{\hat{q}(0), \hat{q}(t)\}\rangle_0 = \frac{\hbar}{2m\omega}\coth\left(\frac{\hbar\omega}{2k_{\mathrm{B}}T}\right)\cos(\omega t), \tag{C.25}$$

$$[\hat{q}(0), \hat{q}(t)] = \frac{i\hbar}{m\omega}\sin(\omega t), \tag{C.26}$$

with Eq. (C.26) a c-number, independent of temperature.

Proof. From $\hat{q}(0) = \sqrt{\hbar/2m\omega}\left(\hat{a} + \hat{a}^\dagger\right)$ and $\hat{q}(t) = \sqrt{\hbar/2m\omega}\left(\hat{a}e^{-i\omega t} + \hat{a}^\dagger e^{i\omega t}\right)$,

$$\langle\hat{q}(0)\hat{q}(t)\rangle_0 = \frac{\hbar}{2m\omega}\left[(n+1)e^{i\omega t} + ne^{-i\omega t}\right], \quad \langle\hat{q}(t)\hat{q}(0)\rangle_0 = \frac{\hbar}{2m\omega}\left[(n+1)e^{-i\omega t} + ne^{i\omega t}\right].$$

Adding and halving, and using $2n + 1 = \coth(\beta\hbar\omega/2)$, gives Eq. (C.25); subtracting gives $(\hbar/2m\omega)\cdot(2i\sin\omega t) = i\hbar\sin(\omega t)/(m\omega)$, which is Eq. (C.26) (and, being a c-number for this linear system, equals its own equilibrium average, consistent with evaluating it directly from the explicit solution $\hat{q}(t) = \hat{q}(0)\cos\omega t + \hat{p}(0)\sin\omega t/(m\omega)$ and $[\hat{q}(0), \hat{p}(0)] = i\hbar$). □

Applying Lemma C. 3 to each mode of $\hat{F}(t) = -\sum_j c_j\hat{Q}_j(t)$,

$$\frac{1}{2}\langle\{\hat{F}(0), \hat{F}(t)\}\rangle_0 = \sum_j c_j^2\frac{\hbar}{2m_j\omega_j}\coth\left(\frac{\hbar\omega_j}{2k_{\mathrm{B}}T}\right)\cos\left(\omega_j t\right), \tag{C.27}$$

$$[\hat{F}(0), \hat{F}(t)] = i\hbar\sum_j c_j^2\frac{1}{m_j\omega_j}\sin\left(\omega_j t\right). \tag{C.28}$$

Equation (C.27) is, in the continuum limit $\sum_j \to \int d\omega J(\omega)/(\ldots)$, exactly the Callen-Welton/KMS form of the fluctuation-dissipation theorem derived from scratch in Appendix A, Sec. "The KMS Condition and Detailed Balance," and, in particular, the boxed detailed-balance relation $\chi''_{AB}(\omega) = \frac{1}{2\hbar}\left(1 - e^{-\beta\hbar\omega}\right)C_{AB}(\omega)$, Eq. (A.26), of Sec. "The Fluctuation-Dissipation Theorem" there. Combining Eq. (A.26) with the symmetrized spectral density $S_{AB}(\omega)$ of Eq. (A.25) and the detailed-balance relation $C_{AB}(\omega) = e^{\beta\hbar\omega}C_{BA}(\omega)$, Eq. (A.21), yields precisely the familiar $\coth$ form $S_{AB}(\omega) = \hbar\coth(\beta\hbar\omega/2)\chi''_{AB}(\omega)$ of Eq. (C.27) above. This is, equivalently, the quantum noise correlator of the independent-oscillator model, Eq. (43) of Ghosh et al. [6]: the thermal weight $\hbar\omega\coth\left(\hbar\omega/2k_{\mathrm{B}}T\right)$ replaces the classical $2k_{\mathrm{B}}T$ exactly as expected from the KMS condition. Equation (C.28) has no classical analogue at all: classically $F(t)$ is a c-number trajectory and $[F\left(t_1\right), F\left(t_2\right)] \equiv 0$ trivially, whereas quantum mechanically the noise operator fails to commute with itself at unequal times - a direct consequence of the operator non-commutativity flagged as a defining feature of the quantum Mori-Zwanzig formalism. Notably, Eq. (C.28) is temperature-independent: it is a statement about the kinematic (causal) structure of the operator algebra, not about the thermal state, and it survives unchanged as $T \to 0$.

Remark C. 1 (Zero-point persistence). Setting $T \to 0$ in Eq. (C.27) gives $n_j \to 0$ but $\coth\left(\hbar\omega_j/2k_{\mathrm{B}}T\right) \to 1$, so $\frac{1}{2}\langle\{\hat{F}(0), \hat{F}(t)\}\rangle_0$ $\to \sum_j c_j^2\hbar\cos\left(\omega_j t\right)/\left(2m_j\omega_j\right) \neq 0$: the physical noise driving the oscillator, and hence the dissipative dynamics itself, does not switch off at absolute zero. This is the zero-point-fluctuation phenomenon noted for the general quantum Mori-Zwanzig formalism, and it has no counterpart in Chapter 14, where the classical force vanishes identically as $T \to 0$.

C. 8 The Classical Limit

As $\hbar \to 0$ at fixed $T, \coth\left(\hbar\omega/2k_{\mathrm{B}}T\right) \to 2k_{\mathrm{B}}T/(\hbar\omega)$, and Eq. (C.25) collapses to

$$\frac{1}{2}\langle\{\hat{q}(0), \hat{q}(t)\}\rangle_0 \longrightarrow \frac{k_{\mathrm{B}}T}{m\omega^2}\cos(\omega t),$$

which coincides with the Mori-canonical result of Lemma C.2: in the classical limit, the physical (symmetrized) and the Mori-canonical correlators merge into a single, $\hbar$-independent object, which is exactly the classical equal-ensemble correlation function used throughout Chapter 14. Simultaneously, the commutator (C.26), which carries an explicit overall factor of $\hbar$, vanishes. The entire apparatus of this chapter - the Hamiltonian (C.2), the equations of motion (C.7), the frequency matrix (C.16), the memory kernel (C.22), and the generalized Langevin equation (C.23) - therefore reduces smoothly, term by term, to the corresponding classical objects of Chapter 14 as $\hbar \to 0$, while the form of every one of those objects is already exact at any finite $\hbar$.

C. 9 Ohmic Bath and the Markovian Quantum Langevin Equation

In the continuum limit, with spectral density $J(\omega) = \frac{\pi}{2}\sum_j c_j^2/\left(m_j\omega_j^2\right)\delta\left(\omega-\omega_j\right)$ as in Chapter 14, Eq. (C.22) becomes $K(t) = (2/m_0\pi)\int_0^\infty d\omega J(\omega)\cos(\omega t)$, exactly as before; for an Ohmic spectrum, $J(\omega) = m_0\gamma\omega$, one again finds $K(t) \approx 2\gamma\delta(t)$ in the Markov limit, and Eq. (C.23) reduces to the quantum damped oscillator $\ddot{\hat{q}}_0 + 2\gamma\dot{\hat{q}}_0 + \omega_0^2\hat{q}_0 = \hat{F}(t)/m_0$. The genuinely quantum content is entirely in the noise strength: whereas the classical Markovian limit of Chapter 14 gives white noise of strength $2m_0\gamma k_{\mathrm{B}}T\delta(t-s)$, Eq. (C.27) gives, upon restricting to the resonant bath oscillators near ω_0 (the weak-coupling argument reviewed in Sec. 2.3 of [6]),

$$\frac{1}{2}\langle\{\hat{F}(t),\hat{F}(s)\}\rangle_0 \approx 2m_0\gamma\hbar\omega_0\coth\left(\frac{\hbar\omega_0}{2k_{\mathrm{B}}T}\right)\delta(t-s), \tag{C.29}$$

matching Eq. (47) of Ghosh et al. [6]. The classical white-noise strength $2m_0\gamma k_{\mathrm{B}}T$ is recovered from Eq. (C.29) only in the high-temperature regime $k_{\mathrm{B}}T \gg \hbar\omega_0$; at low temperature, $\coth\left(\hbar\omega_0/2k_{\mathrm{B}}T\right) \to 1$ and the noise strength saturates at the zero-point value $m_0\gamma\hbar\omega_0$, consistent with Remark C. 1 above.

C. 10 Summary: Structural Parallels and Genuine Quantum Differences

Table C. 1 collects the dictionary established in this chapter.

The overall moral is a clean one. Everything in the Mori-Zwanzig construction that is built from the canonical (Kubo-transform) inner product - the correlation matrix $\mathbb{C}$, the frequency matrix Ω, the memory kernel $K(t)$, and the Mori-form fluctuation-dissipation relation - is exactly classical in form, for any $\hbar$ and any temperature, once the renormalization counterterm of Sec. C. 1 is included; this is precisely the sense in which Mori's inner product was designed.

Table 18.1: Classical versus quantum Mori-Zwanzig treatment of the Magalinski model.

Ingredient	Classical (Ch. 14)	Quantum (this chapter)
Generator	$\mathcal{L}A = \{H, A\}$	$i\mathcal{L}\hat{X} = (i/\hbar)[\hat{H},\hat{X}]$
Inner product	$(A,B) = \langle AB\rangle_0$	Kubo transform, Eq. (C.8)
Equipartition	$\langle q_0^2\rangle_0 = k_{\mathrm{B}}T/\left(m_0\omega_0^2\right)$	$\left(\hat{q}_0,\hat{q}_0\right) = k_{\mathrm{B}}T/\left(m_0\omega_0^2\right)$, Thm. C. 1
Frequency matrix Ω	Equation ???	identical, Eq. (C.16)
Random force	$F(t) = -\sum_j c_j q_j(t)$	$\hat{F}(t) = -\sum_j c_j\hat{Q}_j(t)$ (shifted)
Memory kernel $K(t)$	Equation ???	identical, Eq. (C.22)
"Second FDT"	$\langle F(t)F(s)\rangle_0 = k_{\mathrm{B}}Tm_0K(\mid t-s\mid)$	$(\hat{F}(t),\hat{F}(s)) = k_{\mathrm{B}}Tm_0K(\mid t-s\mid)$
Physical noise strength	$2k_{\mathrm{B}}T$	$\hbar\omega\coth\left(\hbar\omega/2k_{\mathrm{B}}T\right)$
Noise at unequal times	commutes with itself	$[\hat{F}(t),\hat{F}(s)] \neq 0$, T -independent
Noise at $T=0$	vanishes	persists (zero-point)

Genuine quantum mechanics enters only when the formalism is asked to produce something measurable: the physical, symmetrized noise correlator, which carries the Bose thermal factor $\hbar\omega\coth\left(\hbar\omega/2k_{\mathrm{B}}T\right)$ derived independently in Appendix A from the Kubo-Martin-Schwinger condition, and the noise commutator, which has no classical counterpart and encodes the irreducibly operator-valued character of quantum noise.

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INDEX

B

Boltzmann's kinetic theory
11: From Microscopic Reversibility to Macroscopic Irreversibility

Brownian motion
5: Einstein and Markov Equations for Brownian Motion- Historical Foundations and Modern Perspective
6: Power Balance and the Necessity of Dissipation- Pedagogical Derivation of the Generalized Langevin Equation

C

canonical commutation relations
18: Quantum Mori-Zwanzig Formulation of the Magalinski Model

canonical distribution
2: Statistical Mechanical Fluctuations

canonical ensemble
4: Thermodynamics and Statistical Mechanics- From Static Response to Dynamic Fluctuations

Canonical Equilibrium
10: Electrokinetics in a Tube

chemical potential
1: Statistical Mechanical Fluctuations and Time-independent Linear Responser

classical mechanics
15: Derivation of the Nakajima-Zwanzig and Mori-Zwanzig Formalisms

classical statistical mechanics
11: From Microscopic Reversibility to Macroscopic Irreversibility

convolution integral
12: Magalinski's Derivation of the Memory Function and the Generalized Langevin Equation for a System Coupled to a Bath of Harmonic Oscillators

correlation functions
15: Derivation of the Nakajima-Zwanzig and Mori-Zwanzig Formalisms
7: Classical Linear Response Theory and the Kubo Formula

coupled oscillator
14: The Magalinski Model- A Physical Realization of Mori-Zwanzig Dynamics

critical point
1: Statistical Mechanical Fluctuations and Time-independent Linear Responser
3: Critical Opalescence- From Einstein's Theory to Correlation Functions

critical_exponent
3: Critical Opalescence- From Einstein's Theory to Correlation Functions

critical_value
3: Critical Opalescence- From Einstein's Theory to Correlation Functions

D

density matrix
15: Derivation of the Nakajima-Zwanzig and Mori-Zwanzig Formalisms

density of states
2: Statistical Mechanical Fluctuations

density_fluctuations
3: Critical Opalescence- From Einstein's Theory to Correlation Functions

diffusion equation
5: Einstein and Markov Equations for Brownian Motion- Historical Foundations and Modern Perspective

dynamic structure factor
16: Quantum Linear Response Theory

dynamical stability
17: Generalized Langevin Dynamics for an Arbitrary Potential- Thermal Renormalization and Stability

dynamical theory
7: Classical Linear Response Theory and the Kubo Formula

dynamical variables
15: Derivation of the Nakajima-Zwanzig and Mori-Zwanzig Formalisms

E

Einstein
5: Einstein and Markov Equations for Brownian Motion- Historical Foundations and Modern Perspective

electrical conductivity
16: Quantum Linear Response Theory

energy
2: Statistical Mechanical Fluctuations

energy conservation
13: Mori-Zwanzig Formulation

energy dissipation
6: Power Balance and the Necessity of Dissipation- Pedagogical Derivation of the Generalized Langevin Equation

entropy
11: From Microscopic Reversibility to Macroscopic Irreversibility

Entropy Production
10: Electrokinetics in a Tube

equations of motion
17: Generalized Langevin Dynamics for an Arbitrary Potential- Thermal Renormalization and Stability

equilibrium
1: Statistical Mechanical Fluctuations and Time-independent Linear Responser
4: Thermodynamics and Statistical Mechanics- From Static Response to Dynamic Fluctuations

equilibrium statistical mechanics
6: Power Balance and the Necessity of Dissipation- Pedagogical Derivation of the Generalized Langevin Equation

equipartition theorem
14: The Magalinski Model- A Physical Realization of Mori-Zwanzig Dynamics
18: Quantum Mori-Zwanzig Formulation of the Magalinski Model
6: Power Balance and the Necessity of Dissipation- Pedagogical Derivation of the Generalized Langevin Equation

F

fluctuation theorem
2: Statistical Mechanical Fluctuations

fluctuations
1: Statistical Mechanical Fluctuations and Time-independent Linear Responser
3: Critical Opalescence- From Einstein's Theory to Correlation Functions
4: Thermodynamics and Statistical Mechanics- From Static Response to Dynamic Fluctuations

friction coefficient
12: Magalinski's Derivation of the Memory Function and the Generalized Langevin Equation for a System Coupled to a Bath of Harmonic Oscillators

G

generalized Langevin equation
12: Magalinski's Derivation of the Memory Function and the Generalized Langevin Equation for a System Coupled to a Bath of Harmonic Oscillators
13: Mori-Zwanzig Formulation
15: Derivation of the Nakajima-Zwanzig and Mori-Zwanzig Formalisms
17: Generalized Langevin Dynamics for an Arbitrary Potential- Thermal Renormalization and Stability
6: Power Balance and the Necessity of Dissipation- Pedagogical Derivation of the Generalized Langevin Equation

Gibbs
2: Statistical Mechanical Fluctuations

Green's function
17: Generalized Langevin Dynamics for an Arbitrary Potential- Thermal Renormalization and Stability

H

Hamiltonian
14: The Magalinski Model- A Physical Realization of Mori-Zwanzig Dynamics
15: Derivation of the Nakajima-Zwanzig and Mori-Zwanzig Formalisms
16: Quantum Linear Response Theory
17: Generalized Langevin Dynamics for an Arbitrary Potential- Thermal Renormalization and Stability
18: Quantum Mori-Zwanzig Formulation of the Magalinski Model
4: Thermodynamics and Statistical Mechanics- From Static Response to Dynamic Fluctuations

Hamiltonian mechanics
13: Mori-Zwanzig Formulation

heat capacity
2: Statistical Mechanical Fluctuations

Heisenberg equations
18: Quantum Mori-Zwanzig Formulation of the Magalinski Model

I

impedance
8: Fluctuation-Dissipation Relations and Frequency-Dependent Johnson Nyquist Noise

impulse response
12: Magalinski's Derivation of the Memory Function and the Generalized Langevin Equation for a System Coupled to a Bath of Harmonic Oscillators
irreversibility
14: The Magalinski Model- A Physical Realization of Mori-Zwanzig Dynamics
irreversible equations
12: Magalinski's Derivation of the Memory Function and the Generalized Langevin Equation for a System Coupled to a Bath of Harmonic Oscillators
13: Mori-Zwanzig Formulation

J

Johnson noise
8: Fluctuation-Dissipation Relations and Frequency-Dependent Johnson Nyquist Noise

K

kinetic theory
5: Einstein and Markov Equations for Brownian Motion- Historical Foundations and Modern Perspective
Kubo formula
16: Quantum Linear Response Theory
7: Classical Linear Response Theory and the Kubo Formula

L

Langevin equation
14: The Magalinski Model- A Physical Realization of Mori-Zwanzig Dynamics
linear response
16: Quantum Linear Response Theory
Linear Response Theory
10: Electrokinetics in a Tube
6: Power Balance and the Necessity of Dissipation- Pedagogical Derivation of the Generalized Langevin Equation
Liouville equation
10: Electrokinetics in a Tube
14: The Magalinski Model- A Physical Realization of Mori-Zwanzig Dynamics
15: Derivation of the Nakajima-Zwanzig and Mori-Zwanzig Formalisms

M

macroscopic
4: Thermodynamics and Statistical Mechanics- From Static Response to Dynamic Fluctuations
macroscopic dynamics
12: Magalinski's Derivation of the Memory Function and the Generalized Langevin Equation for a System Coupled to a Bath of Harmonic Oscillators
macroscopic irreversibility
11: From Microscopic Reversibility to Macroscopic Irreversibility
Markov process
5: Einstein and Markov Equations for Brownian Motion- Historical Foundations and Modern Perspective
mechanical model
12: Magalinski's Derivation of the Memory Function and the Generalized Langevin Equation for a System Coupled to a Bath of Harmonic Oscillators
memory effects
13: Mori-Zwanzig Formulation
7: Classical Linear Response Theory and the Kubo Formula
memory function
12: Magalinski's Derivation of the Memory Function and the Generalized Langevin Equation for a System Coupled to a Bath of Harmonic Oscillators
memory kernel
17: Generalized Langevin Dynamics for an Arbitrary Potential- Thermal Renormalization and Stability
18: Quantum Mori-Zwanzig Formulation of the Magalinski Model
memory kernels
15: Derivation of the Nakajima-Zwanzig and Mori-Zwanzig Formalisms
microscopic
4: Thermodynamics and Statistical Mechanics- From Static Response to Dynamic Fluctuations

N

noise power spectral density
8: Fluctuation-Dissipation Relations and Frequency-Dependent Johnson Nyquist Noise
nonequilibrium statistical mechanics
13: Mori-Zwanzig Formulation

O

omega
8: Fluctuation-Dissipation Relations and Frequency-Dependent Johnson Nyquist Noise
Onsager
10: Electrokinetics in a Tube
open quantum systems
11: From Microscopic Reversibility to Macroscopic Irreversibility
operators
18: Quantum Mori-Zwanzig Formulation of the Magalinski Model

P

partition function
2: Statistical Mechanical Fluctuations
4: Thermodynamics and Statistical Mechanics- From Static Response to Dynamic Fluctuations
perturbation theory
16: Quantum Linear Response Theory
phase space
13: Mori-Zwanzig Formulation
7: Classical Linear Response Theory and the Kubo Formula
phase_transition
3: Critical Opalescence- From Einstein's Theory to Correlation Functions
power absorption
6: Power Balance and the Necessity of Dissipation- Pedagogical Derivation of the Generalized Langevin Equation
pressure
1: Statistical Mechanical Fluctuations and Time-independent Linear Responser
probability density
5: Einstein and Markov Equations for Brownian Motion- Historical Foundations and Modern Perspective

Q

quantum mechanics
1: Statistical Mechanical Fluctuations and Time-independent Linear Responser
16: Quantum Linear Response Theory
17: Generalized Langevin Dynamics for an Arbitrary Potential- Thermal Renormalization and Stability
18: Quantum Mori-Zwanzig Formulation of the Magalinski Model

R

Rayleigh_scattering
3: Critical Opalescence- From Einstein's Theory to Correlation Functions
RC circuit
8: Fluctuation-Dissipation Relations and Frequency-Dependent Johnson Nyquist Noise
recurrence theorem
11: From Microscopic Reversibility to Macroscopic Irreversibility
Regression Hypothesis
10: Electrokinetics in a Tube
renormalization
18: Quantum Mori-Zwanzig Formulation of the Magalinski Model
response functions
7: Classical Linear Response Theory and the Kubo Formula
reversibility paradox
11: From Microscopic Reversibility to Macroscopic Irreversibility
reversible equations
13: Mori-Zwanzig Formulation

S

scattering_angle
3: Critical Opalescence- From Einstein's Theory to Correlation Functions
spectral density
12: Magalinski's Derivation of the Memory Function and the Generalized Langevin Equation for a System Coupled to a Bath of Harmonic Oscillators
statistical
4: Thermodynamics and Statistical Mechanics- From Static Response to Dynamic Fluctuations
statistical mechanics
1: Statistical Mechanical Fluctuations and Time-independent Linear Responser
11: From Microscopic Reversibility to Macroscopic Irreversibility
14: The Magalinski Model- A Physical Realization of Mori-Zwanzig Dynamics
15: Derivation of the Nakajima-Zwanzig and Mori-Zwanzig Formalisms
16: Quantum Linear Response Theory
17: Generalized Langevin Dynamics for an Arbitrary Potential- Thermal Renormalization and Stability
18: Quantum Mori-Zwanzig Formulation of the Magalinski Model
2: Statistical Mechanical Fluctuations
5: Einstein and Markov Equations for Brownian Motion- Historical Foundations and Modern Perspective

statistical physics
12: Magalinski's Derivation of the Memory Function and the Generalized Langevin Equation for a System Coupled to a Bath of Harmonic Oscillators
13: Mori-Zwanzig Formulation
2: Statistical Mechanical Fluctuations
stochastic processes
5: Einstein and Markov Equations for Brownian Motion- Historical Foundations and Modern Perspective
susceptibility
3: Critical Opalescence- From Einstein's Theory to Correlation Functions
4: Thermodynamics and Statistical Mechanics- From Static Response to Dynamic Fluctuations
8: Fluctuation-Dissipation Relations and Frequency-Dependent Johnson Nyquist Noise

T

temperature
1: Statistical Mechanical Fluctuations and Time-independent Linear Responser
2: Statistical Mechanical Fluctuations
3: Critical Opalescence- From Einstein's Theory to Correlation Functions
thermal equilibrium
17: Generalized Langevin Dynamics for an Arbitrary Potential- Thermal Renormalization and Stability
6: Power Balance and the Necessity of Dissipation- Pedagogical Derivation of the Generalized Langevin Equation
thermal noise
8: Fluctuation-Dissipation Relations and Frequency-Dependent Johnson Nyquist Noise
thermodynamic
1: Statistical Mechanical Fluctuations and Time-independent Linear Responser
thermodynamic entropy
11: From Microscopic Reversibility to Macroscopic Irreversibility
thermodynamics
10: Electrokinetics in a Tube
14: The Magalinski Model- A Physical Realization of Mori-Zwanzig Dynamics
4: Thermodynamics and Statistical Mechanics- From Static Response to Dynamic Fluctuations
5: Einstein and Markov Equations for Brownian Motion- Historical Foundations and Modern Perspective
transport coefficients
7: Classical Linear Response Theory and the Kubo Formula
transport properties
16: Quantum Linear Response Theory

V

voltage fluctuation
8: Fluctuation-Dissipation Relations and Frequency-Dependent Johnson Nyquist Noise
voltage spectral density
8: Fluctuation-Dissipation Relations and Frequency-Dependent Johnson Nyquist Noise

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S

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    - Licensing - *CC BY-NC-SA 4.0*
  - 1: Statistical Mechanical Fluctuations and Time-independent Linear Responser - *CC BY-NC-SA 4.0*
  - 2: Statistical Mechanical Fluctuations - *CC BY-NC-SA 4.0*
    - 2.1: Gibbs's Derivation (1902) - *CC BY-NC-SA 4.0*
    - 2.2: Einstein's Independent Derivation (1904) - *CC BY-NC-SA 4.0*
    - 2.3: Keesom's Experiment and Opalescence - *CC BY-NC-SA 4.0*
    - 2.4: Ornstein-Zernike Correction - *CC BY-NC-SA 4.0*
    - 2.5: Bibliography - *CC BY-NC-SA 4.0*
  - 3: Critical Opalescence- From Einstein's Theory to Correlation Functions - *CC BY-NC-SA 4.0*
    - 3.1: Introduction - *CC BY-NC-SA 4.0*
    - 3.2: Local Fluctuations and the Dipole Picture - *CC BY-NC-SA 4.0*
    - 3.3: Wave Equation in an Inhomogeneous Medium - *CC BY-NC-SA 4.0*
    - 3.4: Green Function Solution - *CC BY-NC-SA 4.0*
    - 3.5: Born Approximation - *CC BY-NC-SA 4.0*
    - 3.6: Far-Field Limit - *CC BY-NC-SA 4.0*
    - 3.7: Scattered Intensity - *CC BY-NC-SA 4.0*
    - 3.8: Connection to Density Fluctuations - *CC BY-NC-SA 4.0*
    - 3.9: Structure Factor - *CC BY-NC-SA 4.0*
    - 3.10: Thermodynamic Limit and Critical Opalescence - *CC BY-NC-SA 4.0*
    - 3.11: Beyond Einstein- The Ornstein-Zernike Correction - *CC BY-NC-SA 4.0*
    - 3.12: The Wilson-Fisher Correction and Anomalous Scaling - *CC BY-NC-SA 4.0*
    - 3.13: Other examples - *CC BY-NC-SA 4.0*
    - 3.14: Comparison of Neutron Scattering at the Curie Point and Critical Opalescence - *CC BY-NC-SA 4.0*
    - 3.15: The Physical Mechanism - *CC BY-NC-SA 4.0*
    - 3.16: Technical Comparison - *CC BY-NC-SA 4.0*
    - 3.17: The Scattering Law - *CC BY-NC-SA 4.0*
    - 3.18: The Uniqueness of Neutrons - *CC BY-NC-SA 4.0*
    - 3.19: Summary of the Analogy - *CC BY-NC-SA 4.0*
    - 3.20: Bibliography - *CC BY-NC-SA 4.0*
  - 4: Thermodynamics and Statistical Mechanics- From Static Response to Dynamic Fluctuations - *CC BY-NC-SA 4.0*
  - 5: Einstein and Markov Equations for Brownian Motion- Historical Foundations and Modern Perspective - *CC BY-NC-SA 4.0*
  - 6: Power Balance and the Necessity of Dissipation- Pedagogical Derivation of the Generalized Langevin Equation - *CC BY-NC-SA 4.0*
  - 7: Classical Linear Response Theory and the Kubo Formula - *CC BY-NC-SA 4.0*
  - 8: Fluctuation-Dissipation Relations and Frequency-Dependent Johnson Nyquist Noise - *CC BY-NC-SA 4.0*
    - 8.1: Introduction - *CC BY-NC-SA 4.0*
    - 8.2: Theoretical Framework - *CC BY-NC-SA 4.0*
    - 8.3: Spectral Density and Bandwidth - *CC BY-NC-SA 4.0*
    - 8.4: Application of FTD to Electrical Resistance - *CC BY-NC-SA 4.0*
    - 8.5: Derivation of the Voltage Spectral Density - *CC BY-NC-SA 4.0*
    - 8.6: Derivation of the Voltage Spectral Density - *CC BY-NC-SA 4.0*

- 8.7: Frequency-Dependent Noise Density - *CC BY-NC-SA 4.0*
- 8.8: RC Circuit- Series Configuration - *CC BY-NC-SA 4.0*
- 8.9: RC Circuit- Parallel Configuration - *CC BY-NC-SA 4.0*
- 8.10: The L-R Shunted by C Equivalent Circuit Model - *CC BY-NC-SA 4.0*
- 8.11: LCR Circuit and Charge Fluctuations - *CC BY-NC-SA 4.0*
- 8.12: Johnson Noise Thermometry (JNT) - *CC BY-NC-SA 4.0*
- 8.13: Conclusion - *CC BY-NC-SA 4.0*
- 8.14: Appendix A - *CC BY-NC-SA 4.0*
- 8.15: Appendix B - *CC BY-NC-SA 4.0*
- 8.16: Appendix C - *CC BY-NC-SA 4.0*
- 8.17: Appendix D - *CC BY-NC-SA 4.0*
- 8.18: Bibliography - *CC BY-NC-SA 4.0*

◦ 9: Onsager Relations - *CC BY-NC-SA 4.0*
- 9.1: Introduction and Roadmap - *CC BY-NC-SA 4.0*
- 9.2: Classical FDT from Liouville Dynamics - *CC BY-NC-SA 4.0*
- 9.3: Proof of the Regression Hypothesis - *CC BY-NC-SA 4.0*
- 9.4: Connection to the Power Spectral Density - *CC BY-NC-SA 4.0*
- 9.5: Onsager-Casimir Reciprocal Relations - *CC BY-NC-SA 4.0*
- 9.6: Modification by an External Magnetic Field - *CC BY-NC-SA 4.0*
- 9.7: Summary and Logical Chain - *CC BY-NC-SA 4.0*
- 9.8: Bibliography - *CC BY-NC-SA 4.0*

◦ 10: Electrokinetics in a Tube - *CC BY-NC-SA 4.0*

◦ 11: From Microscopic Reversibility to Macroscopic Irreversibility - *CC BY-NC-SA 4.0*

◦ 12: Magalinski's Derivation of the Memory Function and the Generalized Langevin Equation for a System Coupled to a Bath of Harmonic Oscillators - *CC BY-NC-SA 4.0*

◦ 13: Mori-Zwanzig Formulation - *CC BY-NC-SA 4.0*

◦ 14: The Magalinski Model- A Physical Realization of Mori-Zwanzig Dynamics - *CC BY-NC-SA 4.0*

◦ 15: Derivation of the Nakajima-Zwanzig and Mori-Zwanzig Formalisms - *CC BY-NC-SA 4.0*

◦ 16: Quantum Linear Response Theory - *CC BY-NC-SA 4.0*

◦ 17: Generalized Langevin Dynamics for an Arbitrary Potential- Thermal Renormalization and Stability - *CC BY-NC-SA 4.0*

◦ 18: Quantum Mori-Zwanzig Formulation of the Magalinski Model - *CC BY-NC-SA 4.0*

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