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MASTER DISSERTATION

QUANTUM DISSIPATIVE HARMONIC SYSTEMS: A STUDY OF THE
SPECIFIC HEAT

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Declaration of Authorship

I, Luciano Augusto Coddato Antunes e Defaveri, declare that this thesis titled, ‘Quantum Dissipative Harmonic Systems: a Study of the Specific Heat’ and the work presented in it are my own. I confirm that:

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- Where any part of this thesis has previously been submitted for a degree or any other qualification at this Center of Research or any other institution, this has been clearly stated.
- Where I have consulted the published work of others, this is always clearly attributed.
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Abstract

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Quantum Dissipative Harmonic Systems: a Study of the Specific Heat

by Lucianno Augusto Coddato Antunes e Defaveri

We start this work by briefly introducing the reader to the theory of quantum dissipation in open quantum systems, using the Caldeira-Leggett model, with our focus being obtaining the thermodynamic properties of these systems. We show that the specific heat can become negative, which can be better understood when it is interpreted as the change of the environment specific heat when we attach an extra degree of freedom [G.-L. Ingold et al, Phys. Rev. E **79**, 061105 (2009)]. We proceed introducing the problem which was our original motivation: for a model also composed of harmonic oscillators [H. Hasegawa, J. Math. Phys. **52**, 123301 (2011)], it is possible to obtain negative specific heat in contradiction with the findings of [G.-L. Ingold et al.], where only for the free particle potential we could obtain such result. We obtain that because of the different potential re-normalizations, each system describes a different physical reality, ensuring that there is in fact no contradiction. The last chapter is dedicated to analyse the influence of the system internal interaction in its thermodynamic proprieties.

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Resumo

Departamento de Física Teórica

Dissipação Quântica em Sistemas Harmônicos: um Estudo do Calor Específico

por Lucianno Augusto Coddato Antunes e Defaveri

Começamos esse trabalho introduzindo brevemente o leitor (a leitora) sobre dissipação quântica em sistemas quânticos abertos, usando o modelo Caldeira-Leggett, com o objetivo de obter as propriedades termodinâmicas desses sistemas. Mostramos que o calor específico pode se tornar negativo, o que pode ser entendido melhor quando passamos a interpretá-lo como a mudança do calor específico do ambiente quando acrescentamos um grau de liberdade extra [G.-L. Ingold et al, Phys. Rev. E **79**, 061105 (2009)]. Prosseguimos introduzindo o problema que foi nossa motivação original: para um modelo também de osciladores harmônicos [H. Hasegawa, J. Math. Phys. **52**, 123301 (2011)] nós temos que é possível obter calores específicos negativos em contradição ao resultado de [G.-L. Ingold et al.], onde apenas para o potencial da partícula livre poderíamos obter tal resultado. Obtemos que, por causa das diferentes renormalizações do potencial, cada sistema descreve uma realidade física diferente, garantindo que de fato não há contradição. O último capítulo é dedicado a analisar diferentes a influência da interação interna do sistema em suas propriedades termodinâmicas.

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Chapter 1

Introduction

The phenomenon of dissipation has always been of great importance when dealing with real physical systems. In certain experimental situations the coupling of a system with the environment can be made so small that it can be considered negligible, but even so, no system can truly be considered *isolated*. We can illustrate how dissipation can greatly affect a system dynamics with a classical example: consider a harmonic oscillator at a nonequilibrium position with frequency Ω_0 and a velocity proportional damping γ . Assuming that the damping is very small when compared to the oscillator frequency, $\gamma \ll 2\Omega_0$, the frequency of oscillation would remain unchanged $\sqrt{\Omega_0^2 - \gamma^2/4} \approx \Omega_0$, while the system slowly approaches equilibrium. In that case, for a time scale much smaller than to $2/\gamma$, we could neglect the damping. In other hand, having a damping $\gamma > 2\Omega_0$ would cause the dynamics of the system to change dramatically, from an oscillation that slowly decreases its amplitude to an exponential decay to equilibrium position.

In order to consider dissipation in quantum mechanics it is first necessary to overcome certain obstacles since we are, in principle, restricted to the Hamiltonian formalism, where we have conservation of energy for *time independent* Hamiltonians. Classically we could simply introduce a velocity dependent damping term in the equations of motion, like in the harmonic oscillator where we would introduce a force $-\gamma\dot{q}$.

Trying to write a suitable model for dissipation, one that can be used to obtain meaningful physical results while also being analytically tractable, we can guide ourselves by classical analogy. Consider the damped harmonic oscillator; while we express the damping through a velocity dependent term, in reality, the damping arises from the interaction between the system and the environment. In the case of a pendulum - or simply a falling object - the damping arises from the interaction with the air molecules that surround the system. In the quantum regime, the damping must also arise from

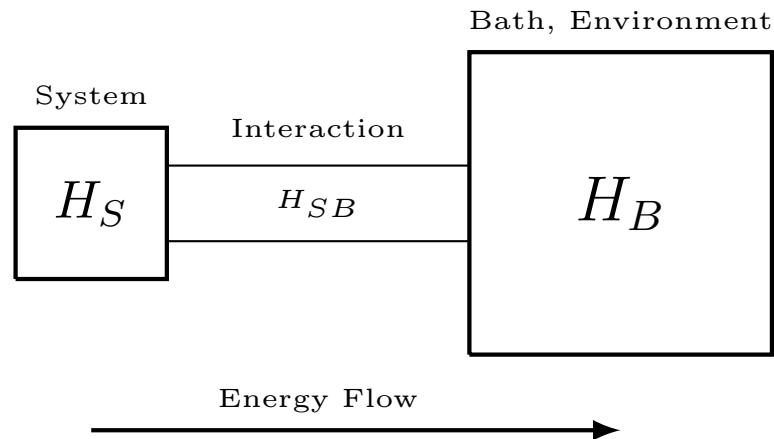


FIGURE 1.1: *This is a simple representation of the model for dissipation, the system (described by H_S) is connected to the environment (described by H_B) by a coupling (H_{SB}). Having simply a system connected to a bath is not enough to represent dissipation, since we are dealing with harmonic oscillators and it is perfectly reasonable to believe that the energy can flow from the environment *back* to the system. Because of that it is necessary to make restrictions in the coupling and bath.*

the interaction between the system degrees of freedom with the environment degrees of freedom.

The more widely used model for dissipation in condensed matter [1–19], the Caldeira-Leggett model, is composed of a system degree of freedom coupled bi-linearly to an environment represented by a collection of harmonic oscillators. It was named after Amir Caldeira and Anthony Leggett [20, 21] who successfully used the model to describe quantitatively the influence of dissipation in quantum tunnelling. Although the model is often named after them, they were not the first ones to analyse and solve for systems of harmonic oscillators with bi-linear couplings [22–25].

- In this work we are interested in analysing the thermodynamics of dissipative harmonic systems. We are particularly interested in the specific heat.

Two alternative routes have been proposed for the evaluation of the specific heat of the free particle [9]. The first, and perhaps most intuitive, is to take the derivative of the average of the kinetic energy (as obtained in [26]) by the temperature. The other method is to use the partition function ratio [1, 9, 11, 13–16] defined as

$$Z \equiv \frac{Z_{S+B}}{Z_B}, \quad (1.1)$$

to derive the thermodynamic properties of the system. Both methods can yield different results, in particular, using the partition function ratio the specific heat could assume negative values. Initially this information comes as a shock since from basic textbooks

in statistical physics we have built the idea that an increase in the temperature of a system will *necessarily* cause an increase in its internal energy. However, it is known that the specific heat in micro canonical ensembles can become negative. One example is a self-gravitating system introduced in [27] whose specific heat is negative and constant with respect to the temperature.

This is not the case for canonical ensembles, where the specific heat is always positive,

$$\frac{\partial}{\partial T} \langle E \rangle = \frac{\langle E^2 \rangle - \langle E \rangle^2}{k_B T^2}. \quad (1.2)$$

The appearance of negative specific heat using the canonical formalism raised some eyebrows regarding the system's stability and if the theory leading to such result needed revision [9].

Later work would prove that the system, even with negative specific heat, would remain stable [11]. It also provided an explanation for the appearance of anomalous values in the heat capacity. The specific heat, as calculated using (1.1), becomes the difference

$$C = k_B \beta^2 \frac{\partial^2}{\partial \beta^2} \ln \left(\frac{Z_{S+B}}{Z_B} \right) = C_{S+B} - C_B. \quad (1.3)$$

We could interpret (1.3) as the change in the environment specific heat when an extra degree of freedom is attached to it. If we are considering a free particle, the specific heat may become negative. That is not the case for the harmonic oscillator, where, as a function of the temperature, it may present a "dip" in its value; however it can never become negative, as we show in this dissertation. This difference can be explained since the uncoupled specific heat of the free particle is smaller than the harmonic oscillator by a factor of two (see also [11]). We would also like to point out that obtaining a "dip" is a result just as surprising as obtaining negative value.

We dedicate the beginning of chapter 2 to discuss the Caldeira-Leggett model to obtain the Langevin equation for the system alone and demonstrate how it can effectively describe dissipation. Still in chapter 2, we proceed to re-obtain the results in [9, 11] using a new method introduced in [14], which we believe contains a valuable new insight to the analysis.

In chapter 3 we start by introducing a new model, that we are going to label as the $N_S + N_B$ model, as defined in [13]. This model is particularly interesting since it contains a system with one or more (N_S) degrees of freedom linearly coupled to a bath with N_B degrees of freedom. We are also faced with a distinct problem: in this

model, the specific heat of the harmonic oscillator can indeed become negative. At first this would suggest that the results are contradictory, however such result is directly connected with the choice of coupling, different from the Caldeira-Leggett model, which is causing a potential renormalization on the bath oscillators. We have dedicated the second half of chapter 3 to elucidate that matter.

Our last chapter is exclusively dedicated to analysing systems with more than one degree of freedom that are also linearly coupled with each other. This will allow us to isolate the effects of the internal coupling between the system degrees of freedom from the renormalization effects. Unlike in the $N_S + N_B$ model, in chapter 4 we study ways of coupling with the environment that remain consistent with the Caldeira-Leggett model. The most intuitive way of coupling would be to simply linearly couple all the system degrees of freedom to the same bath. Another less straight forward way would be to couple each degree of freedom, or groups of degrees of freedom to individual baths. This last coupling is already being used when analysing dissipative diamagnetism [10, 12].

Let us summarize our results:

- using the method introduced by G.-L. Ingold [14], we obtained an expression for the change in the density of eigen-frequencies for the harmonic oscillator,
- we proceeded to use the change in the density to prove that for the Drude bath, the harmonic oscillator can never have negative specific heat,
- we compared the models used by G.-L. Ingold et al. [11] and H. Hasegawa [13], in order to pin-point the reason for the results being qualitative different,
- having reached the conclusion that the difference in the results arises from the different potential renormalizations, we assume a general renormalization in order to study its effects on minimal models,
- we finish our work by studying different models for systems with several degrees of freedom in accordance with the Caldeira-Leggett model¹.

¹We must credit in the last two items of this list the heavy collaboration with Professor Gert-Ludwig Ingold, from Augsburg University, Germany.

Chapter 2

Single Degree of Freedom

The model of a single degree of freedom coupled to environmental degrees of freedom, although simple, can serve as a very solid base to analyse dissipative quantum systems in general. In classical mechanics, we can express dissipation simply by introducing a velocity dependent term in our equation of motion. For a classical harmonic oscillator with one degree of freedom we would have:

$$\ddot{q} + \gamma\dot{q} + \Omega_0^2 q = 0, \quad (2.1)$$

where Ω_0 is the system frequency and γ its damping constant.

Within the quantum regime we can write the time evolution of an operator in the Heisenberg picture by using the Heisenberg equation,

$$\dot{\phi} = \frac{i}{\hbar} [H, \phi], \quad (2.2)$$

where H is the Hamiltonian of the system. The commutation relation of the position and momentum operators

$$[q, p] = i\hbar. \quad (2.3)$$

For simplicity, from now on we shall refer to the operators of position and momentum as coordinates.

We start this chapter by obtaining the Langevin equation for our quantum system through the removal of the bath coordinates in the system equation of motion. After

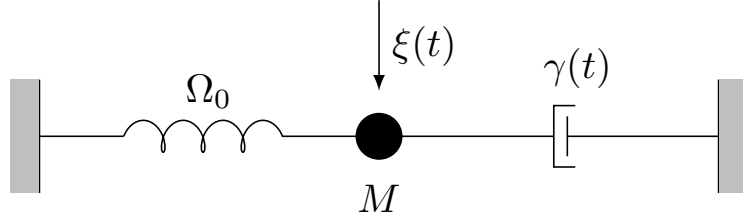


FIGURE 2.1: *A representation of a general damped harmonic oscillator system. We have the damping represented by $\gamma(t)$ and the fluctuating force $\xi(t)$.*

we remove the bath, the final equation contains a damping that isn't memory-free,

$$\ddot{q} + \int_0^t \gamma(t-s)\dot{q}(s)ds + \Omega_0^2 q = \xi(t). \quad (2.4)$$

We also obtain the fluctuation force term $\xi(t)$, which will provide the fluctuation around the equilibrium position. Note that one would simply need to define the damping as $\gamma(t) = 2\gamma\delta(t)$, referred to as ohmic damping, to re-obtain equation (2.1). This more general equation is often referred as Langevin equation [1–3].

Latter in this chapter we use the exact value of (1.1), obtained using path integrals, to calculate the specific heat. After that we introduce an alternative method for the calculations, as shown in [14] for the case of the free particle (here we will also use it to solve the Harmonic Oscillator), and show that both methods yields the same result. This new method consists on taking the bath perspective, and express the change in the specific heat (and other thermodynamic functions) by using a new function that represents the change in the density of eigen-states.

2.1 The System Perspective

First and foremost we need to define the Hamiltonians for our system and bath. The system Hamiltonian is going to be defined as a particle of mass M and potential V

$$H_S = \frac{P^2}{2M} + V(q), \quad (2.5)$$

where the system coordinates are (q, p) for position and momentum respectively. Throughout this chapter we are going to consider only two possibilities for the potential:

1. the free particle $V = 0$,
2. the harmonic oscillator $V(q) = M\Omega_0^2 q^2/2$.

Despite the fact we freely use the terms "free particle" and "harmonic oscillator", our system Hamiltonian can be abstracted to represent any sort of degree of freedom under a potential.

The bath Hamiltonian is defined as:

$$H_B = \sum_{n=1}^{\infty} \left(\frac{p_n^2}{2m_n} + \frac{m_n \omega_n^2}{2} x_n^2 \right). \quad (2.6)$$

The interaction Hamiltonian needs to be defined with some care:

$$H_{SB} = \sum_{n=0}^{\infty} \left\{ -c_n x_n q + \frac{c_n^2}{2m_n \omega_n^2} q^2 \right\}. \quad (2.7)$$

Here we have the bilinear coupling term proportional to c_n and an extra term that exclusively affects the system coordinates. Latter on in this section we will see that, even though it is not required to express dissipation, without this term we would obtain an unwanted potential re-normalization. Using this interaction Hamiltonian we can write the complete Hamiltonian as

$$H = \frac{P^2}{2M} + \frac{M\Omega_0^2}{2} q^2 + \sum_{n=1}^{\infty} \left\{ \frac{p_n^2}{2m_n} + \frac{m_n \omega_n^2}{2} \left(\frac{c_n}{m_n \omega_n^2} q - x_n \right)^2 \right\}. \quad (2.8)$$

Using the Heisenberg equations, we can obtain the equations of motion (time evolution) of the position and momentum operators for the system and the bath:

$$\ddot{x}_n + \omega_n^2 x_n = \frac{c_n}{m_n} q, \quad (2.9)$$

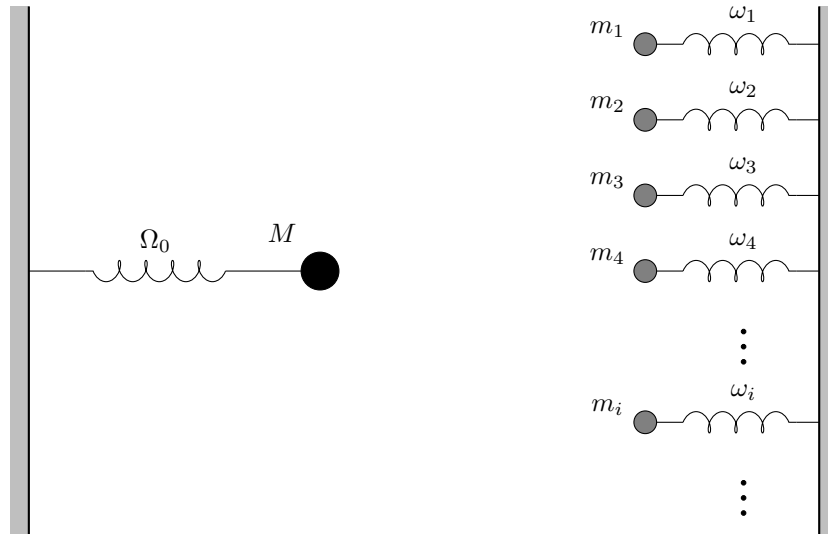
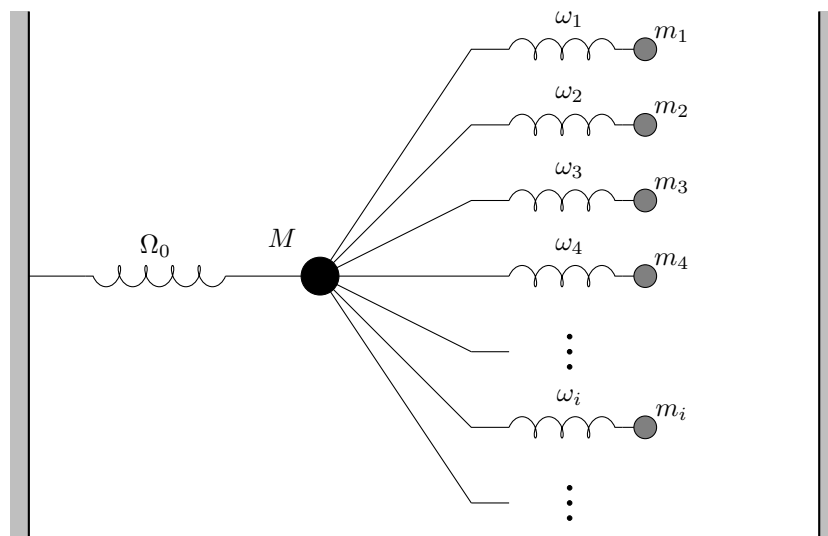
$$M\ddot{q} + M\Omega_0 q = \sum_{n=1}^{\infty} \left(c_n x_n - \frac{c_n^2}{m_n \omega_n^2} q \right), \quad (2.10)$$

where we have already considered that $p = M\dot{q}$ and $p_n = m_n \dot{x}_n$. We can remove the bath coordinates from the system equations by solving the bath equations exactly. The homogeneous solution can be obtained easily using the initial values $(x_n(0), p_n(0))$ and for the solution of the inhomogeneous equation we can use the Green function of the harmonic oscillator:

$$x_n(t) = x_n(0) \cos(\omega_n t) + \frac{p_n(0)}{m_n \omega_n} \sin(\omega_n t) + \int_0^t ds \frac{c_n}{\omega_n} q(s) \sin(\omega_n(t-s)). \quad (2.11)$$

We can work on the last expression integrating by parts to obtain

$$\int_0^t \frac{ds}{\omega_n} \sin(\omega_n(t-s)) q(s) = \frac{q(t)}{\omega_n^2} - \frac{\cos \omega_n(t)}{\omega_n^2} q(0) - \int_0^t \frac{ds}{\omega_n^2} \cos(\omega_n(t-s)) \dot{q}(s). \quad (2.12)$$

(a) *Uncoupled system.*(b) *Coupled system.*FIGURE 2.2: *This is a representation of the Caldeira-Leggett model using classical springs to represent the interactions.*

Replacing this result in (2.10) we obtain the Langevin equation for the system:

$$\ddot{q} + \int_0^t ds \gamma(t-s) \dot{q}(s) + \Omega_0^2 q = \xi(t), \quad (2.13)$$

with the fluctuating force term:

$$\xi(t) = \frac{1}{M} \sum_{n=1}^{\infty} c_n \left\{ \left(x_n(0) - \frac{c_n^2}{m_n \omega_n^2} q(0) \right) \cos(\omega_n t) + \frac{p_n(0)}{m_n \omega_n} \sin(\omega_n t) \right\}, \quad (2.14)$$

and the damping kernel:

$$\gamma(t) = \frac{1}{M} \sum_{n=1}^{\infty} \frac{c_n^2}{m_n \omega_n^2} \cos(\omega_n t). \quad (2.15)$$

If the term $\sum_{n=1}^{\infty} c_n^2 / 2m_n \omega_n^2 q^2$ wasn't included in the interaction Hamiltonian we would now have an effective potential $V'_{\text{eff}}(q) = M (\Omega_0^2 - \sum_{n=1}^{\infty} c_n^2 / M m_n \omega_n^2) q$, which would have changed our system beyond damping. In chapter 3 we shall discuss in more detail situations where the potential is renormalized, for now it is sufficient to note that if we want to compare systems subjected to the same potential for different couplings, we need to define the extra term in H_{SB} .

The proprieties of the fluctuating force are not relevant in our discussion [14, 15]. The damping kernel is the only element responsible for the damping. This allows us to define a new function J , which we will call spectral density of bath modes

$$J(\omega) = \pi \sum_{n=1}^{\infty} \frac{c_n^2}{2m_n \omega_n} \delta(\omega - \omega_n), \quad (2.16)$$

allowing us to re-write the damping kernel as

$$\gamma(t) = \frac{2}{\pi M} \int_0^{\infty} d\omega \frac{J(\omega)}{\omega} \cos(\omega t). \quad (2.17)$$

Even though equation (2.16) shows we could replace $c_n = m_n \omega_n^2$ without any loss of generality, we are going to maintain it so that we can later on keep track of terms from the coupling and from the bath.

Note also that we are not required to specify all the individual c_n , ω_n and m_n , instead we can simply define $J(\omega)$ for it contains all the proprieties regarding the bath and the coupling [1, 2, 15]. This result is of great importance, not only we can write $J(\omega)$ using the microscopic proprieties of a given environment, we can also define it phenomenologically [2].

Considering that our system of oscillators was disturbed from equilibrium position of minimal energy, we need to have the system to loose energy until returns to the equilibrium. If $\gamma(t)$ is always positive, like for the classical damping constant γ , we would have an irreversible energy flow from the system to the environment. However, even if $\gamma(t)$ becomes negative for a given interval of time, as long as we have the damping strength γ_0 to be positive [1]

$$\gamma_0 = \int_0^{\infty} dt \gamma(t) \quad (2.18)$$

we will have dissipation and converge to equilibrium.

For environments composed of a finite number of harmonic oscillators, after a certain time, the Poincaré recurrence time, the system returns arbitrarily close to its original configuration. On the other hand, if we had an infinite number of environment harmonic oscillators, Poincaré recurrence time becomes inaccessible [28, 29]. A simple way of achieving that is to define $J(\omega)$ so that we no longer have a discrete but a continuous distribution of frequencies.

We could re-obtain the classical ohmic damping by choosing

$$J(\omega) = M\gamma\omega, \quad (2.19)$$

which would render a memory free damping. This choice for $J(\omega)$ is not very realistic since it diverges for high frequencies. One way to work around this is to introduce cutoff frequency ω_c . We could use the step function Θ ,

$$J(\omega) = M\gamma\omega \Theta(\omega_c - \omega), \quad (2.20)$$

to describe the cutoff. Since the step function can be difficult to work with, we are going to use a more convenient algebraic cutoff as in [16]:

$$J(\omega) = M\gamma\omega^s \frac{\omega_c^{2p-s+1}}{(\omega_c^2 + \omega^2)^p} \quad (2.21)$$

that leads to a converging $\gamma(t)$ for $0 < s < 2p + 2$. For small frequencies, $J(\omega) \propto \omega^s$. When $s = 1$, we refer to the damping as being *Ohmic*, even though it has a cutoff, $s < 1$ is referred as sub-Ohmic damping and $s > 1$ as super-Ohmic damping. A particular case of Ohmic damping for $s = p = 1$ is often referred to as the Drude bath

$$J_D(\omega) = M\gamma\omega \frac{\omega_D^2}{\omega_D^2 + \omega^2}. \quad (2.22)$$

This type of bath has been extensively used [1, 9, 11, 15, 16]. In this work we will often use it to obtain analytical exact solutions. All the calculations made in this chapter will assume our bath to be Ohmic.

2.2 Short Digression on Thermodynamics

In order to discuss the thermodynamics of our system we need first to remind ourselves of some definitions from statistical physics. We start from the quantum canonical partition function:

$$Z = \text{tr} \exp(-\beta \hat{H}) = \sum_{n=1}^{\infty} \langle n | \exp(-\beta \hat{H}) | n \rangle = \sum_{n=1}^{\infty} \exp(-\beta E_n), \quad (2.23)$$

where we are taking $|n\rangle$ to be a complete set of the Hamiltonian eigenstates.

In our problem we only employ harmonic potentials so that it is possible in both cases to transform the coordinates in such way that the complete Hamiltonian can be re-written in an uncoupled form:

$$H = \sum_{i=1}^N \hbar \lambda_i \left(\hat{n}_i + \frac{1}{2} \right), \quad (2.24)$$

where λ_i represents the eigen-frequencies of the complete Hamiltonian and \hat{n}_i the number operator of the i -th eigen-frequency. Since it is a system with several degrees of freedom, the basis of energy becomes: $|n_1 n_2 \dots n_N\rangle$ and the partition function is written as:

$$Z = \sum_{\{n_i\}} \langle n_1 n_2 \dots n_N | \exp(-\beta \hat{H}) | n_1 n_2 \dots n_N \rangle, \quad (2.25)$$

where we are taking $\{n_i\}$ to mean all possible values of $n_1 n_2 \dots n_N$. Thus

$$Z = \sum_{\{n_i\}} \exp \left(-\beta \sum_{i=1}^N \hbar \lambda_i \left(n_i + \frac{1}{2} \right) \right) = \sum_{\{n_i\}} \prod_{i=1}^N \exp \left(-\beta \hbar \lambda_i \left(n_i + \frac{1}{2} \right) \right), \quad (2.26)$$

and by changing the order in which we evaluate the product and the summation we drop $\{n_i\}$ and use just n_i from 0 to ∞ since the new coordinates are uncoupled. Contemplating all possible combinations we get

$$Z = \prod_{i=1}^N \sum_{n_i=1}^{\infty} \exp \left(-\beta \sum_{i=1}^N \hbar \lambda_i \left(n_i + \frac{1}{2} \right) \right) = \prod_{i=1}^N \frac{\text{csch} \left(\frac{\beta \hbar \lambda_i}{2} \right)}{2}. \quad (2.27)$$

Of course, the partition function of a system of uncoupled harmonic oscillators is equal to the product of the partition function of each oscillator.

$$Z = \prod_{i=1}^N Z_i \quad ; \quad Z_i = \frac{1}{2 \sinh \left(\frac{\beta \hbar \lambda_i}{2} \right)}. \quad (2.28)$$

From the last equation we can obtain expressions for the energy and the specific heat as:

$$E(T) = -\frac{\partial}{\partial\beta} \ln Z = -\sum_{i=1}^N \frac{\partial}{\partial\beta} \ln Z_i = \sum_{i=1}^N \left(\frac{\hbar\lambda_i}{2}\right) \frac{1}{\tanh\left(\frac{\beta\hbar\lambda_i}{2}\right)}, \quad (2.29)$$

$$C(T) = -\beta^2 \frac{\partial^2}{\partial\beta^2} \ln Z = \sum_{i=1}^N \left(\frac{\hbar\lambda_i\beta}{2}\right)^2 \frac{1}{\sinh^2\left(\frac{\hbar\lambda_i\beta}{2}\right)}. \quad (2.30)$$

Note that the only information required from the system to obtain both quantities are the eigen-frequencies. We can define the density of eigen-frequencies:

$$\rho(\omega) = \sum_{i=1}^N \delta(\omega - \lambda_i), \quad (2.31)$$

with two auxiliary functions:

$$E_{\text{ho}}(\omega) = \left(\frac{\hbar\omega}{2}\right) \frac{1}{\tanh\left(\frac{\beta\hbar\omega}{2}\right)} \quad ; \quad C_{\text{ho}}(\omega) = \left(\frac{\hbar\omega\beta}{2}\right)^2 \frac{1}{\sinh^2\left(\frac{\hbar\omega\beta}{2}\right)}, \quad (2.32)$$

with the subscript standing for Harmonic Oscillator. Now we can rewrite (2.29) and (2.30) as:

$$E(T) = \int_0^\infty \rho(\omega) E_{\text{ho}}(\omega) d\omega \quad (2.33)$$

$$C(T) = \int_0^\infty \rho(\omega) C_{\text{ho}}(\omega) d\omega \quad (2.34)$$

In the case of an open quantum system, using the partition function ratio (1.1) we obtain that:

$$\begin{aligned} E(T) &= E_{S+B}(T) - E_B(T) = \\ &= \int_0^\infty (\rho_{S+B}(\omega) - \rho_B(\omega)) E_{\text{ho}}(\omega) d\omega, \end{aligned} \quad (2.35)$$

$$\begin{aligned} C(T) &= C_{S+B}(T) - C_B(T) = \\ &= \int_0^\infty (\rho_{S+B}(\omega) - \rho_B(\omega)) C_{\text{ho}}(\omega) d\omega. \end{aligned} \quad (2.36)$$

We introduce now a new function that we call shift in the density of eigen-frequencies [14]:

$$\Delta\rho(\omega) = \rho_{S+B}(\omega) - \rho_B(\omega) \quad (2.37)$$

which can be used to obtain the energy, the specific heat and other thermodynamic properties described by the logarithm of (1.1). Taking $N \rightarrow \infty$ and using a continuous distribution of frequencies, we can replace (2.31), as we did for $J(\omega)$, by a smooth continuous function.

2.3 Using the Exact Partition Function Ratio

It is possible to calculate (1.1) using path integrals for the harmonic oscillator and free particle potentials [15]. Since the thermodynamic properties described by (1.1) are going to be derived using the logarithm of this expression

$$\ln \frac{Z_{S+B}}{Z_B} = \ln Z_{S+B} - \ln Z_B, \quad (2.38)$$

we can interpret the result as the difference caused in the environment properties once we couple the additional degree of freedom from the system. This can be clearly visualized in a experimental situation where, once the coupling is introduced, we can only perform measurements in the complete environment.

In this section our aim is to mathematically calculate the specific heat using the partition function ratio for the free particle

$$Z_1 = \frac{L}{\hbar} \sqrt{\left(\frac{2\pi M}{\beta}\right)} \prod_{n=1}^{\infty} \frac{\nu_n}{\nu_n + \hat{\gamma}(\nu_n)}, \quad (2.39)$$

where L represents the volume where the system is restricted to and will not interfere with the specific heat. Also for the harmonic oscillator:

$$Z_2 = \frac{1}{\hbar\beta\Omega_0} \prod_{n=1}^{\infty} \frac{\nu_n^2}{\nu_n^2 + \nu_n \hat{\gamma}(\nu_n) + \Omega_0^2} \quad (2.40)$$

where $\nu_n = 2\pi n/\hbar\beta$ are the Matsubara frequencies and the hat operator represents the Laplace transform [2, 9, 11].

Since in a later section we will obtain these same results, we have decided to postpone an analysis until the end of the chapter. Because of that, this section will be focused only in the mathematical evaluation of the specific heat.

2.3.1 Series Expansion for the General Bath

We first calculate the energy for the free particle using an Ohmic damping without further specifying $J(\omega)$:

$$\begin{aligned} U_1 &= -\frac{\partial}{\partial\beta} \ln Z_1 = -\frac{\partial}{\partial\beta} \left\{ -\frac{\ln\beta}{2} + \sum_{n=1}^{\infty} (\ln\nu_n - \ln(\nu_n + \hat{\gamma}(\nu_n))) \right\} = \\ &= \frac{1}{2\beta} \left\{ 1 + 2 \sum_{n=1}^{\infty} \left(\frac{\hat{\gamma}(\nu_n) - \nu_n \hat{\gamma}'(\nu_n)}{\nu_n + \hat{\gamma}(\nu_n)} \right) \right\}, \end{aligned} \quad (2.41)$$

and for the harmonic oscillator:

$$\begin{aligned} U_2 &= -\frac{\partial}{\partial\beta} \left\{ -\ln\beta + \sum_{n=1}^{\infty} (\ln\nu_n^2 - \ln(\nu_n^2 + \nu_n \hat{\gamma}(\nu_n)) + \Omega_0^2) \right\} = \\ &= \frac{1}{\beta} \left\{ 1 + \sum_{n=1}^{\infty} \left(\frac{\nu_n \hat{\gamma}(\nu_n) - \nu_n^2 \hat{\gamma}'(\nu_n) + 2\Omega_0^2}{\nu_n^2 + \nu_n \hat{\gamma}(\nu) + \Omega_0^2} \right) \right\}. \end{aligned} \quad (2.42)$$

We calculate the energy so that latter we can derive the specific heat.

Defining the functions:

$$f_1(x) = \frac{\hat{\gamma}(x) - x\hat{\gamma}'(x)}{x + \hat{\gamma}(x)}, \quad (2.43)$$

$$f_2(x) = \frac{x\hat{\gamma}(x) - x^2\hat{\gamma}'(x) + 2\Omega_0^2}{x^2 + x\hat{\gamma}(x) + \Omega_0^2}, \quad (2.44)$$

it is easy to see that we can rewrite the expressions for the energy as:

$$U_1 = \frac{1}{\beta} \left\{ \frac{1}{2} + \sum_{n=1}^{\infty} f_1(\nu_n) \right\}, \quad (2.45)$$

$$U_2 = \frac{1}{\beta} \left\{ 1 + \sum_{n=1}^{\infty} f_2(\nu_n) \right\}. \quad (2.46)$$

We can then use the Euler-Maclaurin formula,

$$\begin{aligned} \sum_{n=0}^{\infty} g(i) &= \int_0^{\infty} g(x)dx + \frac{1}{2}(g(\infty) + g(0)) + \\ &+ \sum_{k=1}^{\infty} \frac{B_{2k}}{(2k)!} \left(g^{2k-1}(\infty) - g^{2k-1}(0) \right), \end{aligned} \quad (2.47)$$

where g is a continuous function and B_k are the Bernoulli numbers, to obtain final expression for the energy as a low temperature series:

$$U_1 = \frac{\hbar}{2\pi} \left\{ \int_0^\infty f_1(x) dx + \sum_{k=1}^{\infty} \frac{B_{2k}}{(2k)!} \left(\frac{2\pi}{\hbar} k_B T \right)^{2k} \left(f_1^{2k-1}(\infty) - f_1^{2k-1}(0) \right) \right\}, \quad (2.48)$$

$$U_2 = \frac{\hbar}{2\pi} \left\{ \int_0^\infty f_2(x) dx + \sum_{k=1}^{\infty} \frac{B_{2k}}{(2k)!} \left(\frac{2\pi}{\hbar} k_B T \right)^{2k} \left(f_2^{2k-1}(\infty) - f_2^{2k-1}(0) \right) \right\}. \quad (2.49)$$

The specific heat can be directly evaluated as:

$$C_1 = \sum_{k=1}^{\infty} \frac{B_{2k}}{(2k-1)!} \left(\frac{2\pi}{\hbar} k_B T \right)^{2k-1} \left(f_1^{2k-1}(\infty) - f_1^{2k-1}(0) \right), \quad (2.50)$$

$$C_2 = \sum_{k=1}^{\infty} \frac{B_{2k}}{(2k-1)!} \left(\frac{2\pi}{\hbar} k_B T \right)^{2k-1} \left(f_2^{2k-1}(\infty) - f_2^{2k-1}(0) \right), \quad (2.51)$$

with the leading terms being:

$$C_1 = \frac{\pi}{3} \frac{1 + \hat{\gamma}'(0)}{\hat{\gamma}(0)} \frac{k_B T}{\hbar} + O(T^3), \quad (2.52)$$

$$C_2 = \frac{\pi}{3} \frac{\hat{\gamma}(0)}{\Omega_0^2} \frac{k_B T}{\hbar} + O(T^3). \quad (2.53)$$

2.3.2 Solution for the Drude Bath

We can now obtain an analytical result using the Drude bath (2.22),

$$\hat{\gamma}(z) = \gamma \frac{\omega_D}{z + \omega_D}, \quad (2.54)$$

for the free particle:

$$\begin{aligned} Z_1 &= \frac{L}{\hbar} \sqrt{\left(\frac{2\pi M}{\beta} \right)} \prod_{n=1}^{\infty} \frac{\nu_n(\nu_n + \omega_D)}{\nu_n^2 + \omega_D \nu_n + \gamma \omega_D} \\ &= \frac{L}{\hbar} \sqrt{\left(\frac{2\pi M}{\beta} \right)} \prod_{n=1}^{\infty} \frac{\left(1 + \frac{\omega_D}{\nu_n} \right)}{\left(1 + \frac{\omega_1}{\nu_n} \right) \left(1 + \frac{\omega_2}{\nu_n} \right)}; \end{aligned} \quad (2.55)$$

$$\ln Z_1 = D_1 + \sum_{n=1}^{\infty} \left\{ \ln \left(1 + \frac{\omega_D}{\nu_n} \right) - \ln \left(1 + \frac{\omega_1}{\nu_n} \right) - \ln \left(1 + \frac{\omega_2}{\nu_n} \right) - \frac{\ln \beta}{2} \right\}, \quad (2.56)$$

where D_1 stands for terms that are constant in β and the frequencies ω_1 and ω_2 are the roots of the polynomial in the denominator of (2.55)

$$x^2 + \omega_D x + \gamma \omega_D = (x + \omega_1)(x + \omega_2), \quad (2.57)$$

$$\omega_{1,2} = \frac{1}{2} \left(\omega_D \pm \sqrt{1 - \frac{4\gamma}{\omega_D}} \right). \quad (2.58)$$

Note that we could have $1 - 4\gamma/\omega_D < 0$, which would make ω_1 and ω_2 be complex valued numbers (complex conjugate of each other). It is important to note that these frequencies do not represent observable quantities, the partition function is always real making the energy or the specific heat also real.

The specific heat becomes:

$$\begin{aligned} \frac{C_1}{k_B} = \beta^2 \frac{\partial^2}{\partial \beta^2} \ln Z_1 = \sum_{n=1}^{\infty} \left\{ \left(\frac{\hbar\beta\omega_1}{2\pi} \right)^2 \frac{1}{\left(n + \frac{\hbar\beta\omega_1}{2\pi} \right)^2} + \left(\frac{\hbar\beta\omega_2}{2\pi} \right)^2 \frac{1}{\left(n + \frac{\hbar\beta\omega_2}{2\pi} \right)^2} - \right. \\ \left. - \left(\frac{\hbar\beta\omega_D}{2\pi} \right)^2 \frac{1}{\left(n + \frac{\hbar\beta\omega_D}{2\pi} \right)^2} \right\} + \frac{1}{2}, \end{aligned} \quad (2.59)$$

that we can simplify using the definition of the Trigamma function:

$$\psi'(z) = \sum_{n=0}^{\infty} \frac{1}{(n+z)^2} ; \quad \psi'(1+z) = \sum_{n=1}^{\infty} \frac{1}{(n+z)^2}, \quad (2.60)$$

and with the recurrence relation:

$$\psi'(1+z) = \psi'(z) - \frac{1}{z^2}. \quad (2.61)$$

We thus obtain:

$$\begin{aligned} \frac{C_1}{k_B} = \left(\frac{\hbar\beta\omega_1}{2\pi} \right)^2 \psi' \left(\frac{\hbar\beta\omega_1}{2\pi} \right) + \left(\frac{\hbar\beta\omega_2}{2\pi} \right)^2 \psi' \left(\frac{\hbar\beta\omega_2}{2\pi} \right) - \\ - \left(\frac{\hbar\beta\omega_D}{2\pi} \right)^2 \psi' \left(\frac{\hbar\beta\omega_D}{2\pi} \right) - \frac{1}{2}. \end{aligned} \quad (2.62)$$

For the harmonic oscillator, one has alternatively:

$$\begin{aligned} Z_2 &= \frac{1}{\hbar\beta\Omega_0} \prod_{n=1}^{\infty} \frac{\nu_n^2(\nu_n + \omega_D)}{\nu_n^3 + \omega_D\nu_n^2 + (\Omega_0^2 + \gamma\omega_D)\nu_n + \omega_D\Omega_0^2} \\ &= \frac{1}{\hbar\beta\Omega_0} \prod_{n=1}^{\infty} \frac{\left(1 + \frac{\omega_D}{\nu_n}\right)}{\left(1 + \frac{\omega_1}{\nu_n}\right)\left(1 + \frac{\omega_2}{\nu_n}\right)\left(1 + \frac{\omega_3}{\nu_n}\right)}, \end{aligned} \quad (2.63)$$

$$\ln Z_2 = D_2 - \ln \beta + \sum_{n=1}^{\infty} \left\{ \ln \left(1 + \frac{\omega_D}{\nu_n}\right) - \ln \left(1 + \frac{\omega_1}{\nu_n}\right) - \right. \quad (2.64)$$

$$\left. - \ln \left(1 + \frac{\omega_2}{\nu_n}\right) - \ln \left(1 + \frac{\omega_3}{\nu_n}\right) \right\} \quad (2.65)$$

Similarly to before, D_2 stands for terms that are constant in β and the frequencies ω_1 , ω_2 and ω_3 are the roots of the polynomial in the denominator of (2.63)

$$x^3 + \omega_D x^2 + (\Omega_0^2 + \gamma\omega_D)x + \omega_D\Omega_0^2 = (x + \omega_1)(x + \omega_2)(x + \omega_3), \quad (2.66)$$

the actual expression of the individual frequencies is omitted because they would be very extensive without further physical insight. We would like to point out that, since this is a third degree polynomial, it is possible that two of these frequencies become imaginary (ω_1 and ω_2) and complex conjugate of each other. Once again we would nonetheless obtain only real observables.

Then one arrives at the final expression

$$\begin{aligned} \frac{C_2}{k_B} &= \sum_{n=1}^{\infty} \left\{ \left(\frac{\hbar\beta\omega_1}{2\pi}\right)^2 \frac{1}{\left(n + \frac{\hbar\beta\omega_1}{2\pi}\right)^2} + \left(\frac{\hbar\beta\omega_2}{2\pi}\right)^2 \frac{1}{\left(n + \frac{\hbar\beta\omega_2}{2\pi}\right)^2} + \right. \\ &\quad \left. + \left(\frac{\hbar\beta\omega_3}{2\pi}\right)^2 \frac{1}{\left(n + \frac{\hbar\beta\omega_3}{2\pi}\right)^2} - \left(\frac{\hbar\beta\omega_D}{2\pi}\right)^2 \frac{1}{\left(n + \frac{\hbar\beta\omega_D}{2\pi}\right)^2} \right\}, \end{aligned} \quad (2.67)$$

$$\begin{aligned} \frac{C_2}{k_B} &= \left(\frac{\hbar\beta\omega_1}{2\pi}\right)^2 \psi' \left(\frac{\hbar\beta\omega_1}{2\pi}\right) + \left(\frac{\hbar\beta\omega_2}{2\pi}\right)^2 \psi' \left(\frac{\hbar\beta\omega_2}{2\pi}\right) + \\ &\quad + \left(\frac{\hbar\beta\omega_3}{2\pi}\right)^2 \psi' \left(\frac{\hbar\beta\omega_3}{2\pi}\right) - \left(\frac{\hbar\beta\omega_D}{2\pi}\right)^2 \psi' \left(\frac{\hbar\beta\omega_D}{2\pi}\right) - 1. \end{aligned} \quad (2.68)$$

2.4 The Bath Perspective

The specific heat obtained using (1.1) can be understood as the change in the environment specific heat caused by the coupling with an extra degree of freedom [11]. So,

obtaining the shift in the eigen-frequency density (2.31) can be seen not only as an alternative method for obtaining the thermodynamic properties associated with (1.1) but also could provide an additional physical insight in the effects of the coupling.

Like in last section, we start with the series expansion of a general bath and proceed to obtain the exact solution for the Drude bath. Let us define the scaled variables:

$$\begin{aligned}\tilde{q} &= \sqrt{M}q, & \tilde{x}_n &= \sqrt{m_n}x_n, \\ \tilde{p} &= \frac{p}{\sqrt{M}}, & \tilde{p}_n &= \frac{p_n}{\sqrt{m_n}}.\end{aligned}\quad (2.69)$$

With this choice, the Hamiltonian (2.8) takes the form of:

$$\begin{aligned}H &= \frac{1}{2} \left(\tilde{p}^2 + \left(\Omega_0^2 + \sum_{n=1}^{N_S} \frac{c_n^2}{Mm_n\omega_n^2} \right) \tilde{q}^2 \right) + \frac{1}{2} \sum_{n=1}^{N_S} (\tilde{p}_n^2 + \omega_n^2 \tilde{x}_n^2) - \\ &- \sum_{n=1}^{N_S} \frac{c_n}{\sqrt{m_n M}} \tilde{x}_n \tilde{q}.\end{aligned}\quad (2.70)$$

In matrix form it is possible to write:

$$2H = \begin{pmatrix} \tilde{p} & \tilde{p}_1 & \dots & \tilde{p}_N \end{pmatrix} \hat{I} \begin{pmatrix} \tilde{p} \\ \tilde{p}_1 \\ \vdots \\ \tilde{p}_{N_S} \end{pmatrix} + \begin{pmatrix} \tilde{q} & \tilde{x}_1 & \dots & \tilde{x}_N \end{pmatrix} \hat{A} \begin{pmatrix} \tilde{q} \\ \tilde{x}_1 \\ \vdots \\ \tilde{x}_{N_S} \end{pmatrix}, \quad (2.71)$$

where we define the matrix \hat{A} as:

$$\mathbf{A} = \begin{pmatrix} \Omega_0^2 + \frac{c_n^2}{Mm_n\omega_n^2} & -\frac{c_1}{\sqrt{m_1 M}} & -\frac{c_2}{\sqrt{m_2 M}} & \dots & -\frac{c_N}{\sqrt{m_N M}} \\ -\frac{c_1}{\sqrt{m_1 M}} & \omega_1^2 & 0 & \dots & 0 \\ -\frac{c_2}{\sqrt{m_2 M}} & 0 & \omega_1^2 & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & 0 \\ -\frac{c_N}{\sqrt{m_N M}} & 0 & 0 & 0 & \omega_N^2 \end{pmatrix}. \quad (2.72)$$

The eigenvalues of \hat{A} are the squared eigen-frequencies of the coupled system. Let's write the eigenvalue equations:

$$\begin{aligned}\hat{A}\vec{v} &= \Omega^2\vec{v}, \\ \left(\Omega_0^2 + \frac{c_n^2}{Mm_n\omega_n^2} \right) v_0 - \sum_{n=1}^{\infty} \frac{c_n}{\sqrt{m_n M}} v_n &= \Omega^2 v_0, \\ -\frac{c_n}{\sqrt{m_n M}} v_0 + \omega_n^2 v_n &= \Omega^2 v_n.\end{aligned}\quad (2.73)$$

We can solve for v_n from the third equation and replace it on the second equation. It is possible then to cancel out v_0 and obtain the expression:

$$\Omega_0^2 + \frac{c_n^2}{Mm_n\omega_n^2} + \sum_{n=1}^{N_S} \frac{c_n^2}{m_n M} (\Omega^2 - \omega_n^2)^{-1} = \Omega^2, \quad (2.74)$$

which can be further simplified to:

$$\sum_{n=1}^{N_S} \frac{c_n^2}{m_n\omega_n^2 (\Omega^2 - \omega_n^2)} = M \left(\frac{\Omega^2 - \Omega_0^2}{\Omega^2} \right). \quad (2.75)$$

If we take Ω_0 to be zero and Ω to be nonzero we recover the result for the free particle [14],

$$\sum_{n=1}^{\infty} \frac{c_n^2}{m_n\omega_n^2 (\Omega^2 - \omega_n^2)} = M. \quad (2.76)$$

If we take a look at the definitions of the partition function ratio in previous section it is clear that taking the limit when $\Omega_0 \rightarrow 0$, for the harmonic potential will not yield the result for the free particle. Taking this limit represents the loss of a degree of freedom, which completely changes the system. Therefore we will now separate into free particle and harmonic oscillator to avoid running into problems.

2.4.1 The Expression for the Eigen-Frequencies

Continuing the calculations, we shall now define, without loss of generality (since we can still redefine m_n and/or c_n), the eigenfrequencies of the environmental oscillator as $\omega_n = n\Delta$, where Δ represents the spacing between two consecutive frequencies. With this definition we can recover the result for continuous frequencies by calculating the limit where Δ vanishes.

It is also convenient to find an expression for the masses m_n as a function of the bath eigen-frequencies. Using the definition of the spectral density as in (2.16), integrated with a continuous function f , gives us the relation:

$$\int_0^{\infty} d\omega J(\omega) f(\omega) = \sum_{n=1}^{\infty} \frac{c_n^2}{m_n\omega_n} f(\omega_n). \quad (2.77)$$

Replacing the original spectral density (composed of a sum of deltas) by a smooth function, it is possible to replace the integral on the left hand side of the equation above by a summation of step Δ , allowing to isolate the mass term m_n and obtain an expression as a function of the eigenfrequencies:

$$\sum_{n=1}^{\infty} \Delta J(n\Delta) f(n\Delta) = \frac{\pi}{2} \sum_{n=1}^{\infty} \frac{c_n^2}{m_n(n\Delta)} f(n\Delta), \quad (2.78)$$

and thus:

$$\frac{c_n^2}{m_n(n\Delta)^2} = \frac{2}{\pi} \frac{J(n\Delta)}{n\Delta} \Delta. \quad (2.79)$$

Since we are dealing with Ohmic baths, $J(\omega) \propto \omega$ for $\omega \approx 0$, $J(n\Delta)/(n\Delta)$ does not diverge.

The last equation allows us to rewrite (2.75) in the following form:

$$\sum_{n=1}^{\infty} \frac{c_n^2}{m_n \omega_n^2 (\Omega^2 - \omega_n^2)} = \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{J(n\Delta)}{n\Delta} \frac{\Delta}{(\Omega^2 - (n\Delta)^2)} = M \left(1 - \frac{\Omega_0^2}{\Omega^2} \right). \quad (2.80)$$

Since $J(n\Delta)/(n\Delta)$ is a well behaved even function (see (2.21)), it can be written as a series of $(n\Delta)^2$ expansion around Ω^2 ,

$$\frac{J(x)}{x} = \frac{J(\Omega)}{\Omega} + \sum_{n=1}^{\infty} a_n (x^2 - \Omega^2)^n, \quad (2.81)$$

where

$$a_n = \frac{1}{n!} \frac{d^n}{d(x^2)^n} \left. \frac{J(x)}{x} \right|_{x=\Omega} (x^2 - \Omega^2), \quad (2.82)$$

that when applied at summation (2.79)

$$\sum_{n=1}^{\infty} \frac{J(n\Delta)}{n\Delta (\Omega^2 - (n\Delta)^2)} = \sum_{n=1}^{\infty} \frac{J(\Omega)}{\Omega (\Omega^2 - (n\Delta)^2)} - \sum_{n=1}^{\infty} a_n (x^2 - \Omega^2)^{n-1}, \quad (2.83)$$

allows us to isolate the first term as the singular term. If we take the spacing to be very small, $\Delta \rightarrow 0$, the well behaved terms can be expressed in the form of an integral ($\Delta \approx d\omega$). Equivalently we have:

$$\sum_{n=1}^{\infty} \frac{J(\Omega)}{\Omega (\Omega^2 - (n\Delta)^2)} + \int_0^{\infty} d\omega \left\{ \left(\frac{J(\omega)}{\omega} - \frac{J(\Omega)}{\Omega} \right) \frac{1}{\Omega^2 - \omega^2} \right\}, \quad (2.84)$$

We can use residue techniques to calculate

$$\int_0^{\infty} \frac{d\omega}{\Omega^2 - \omega^2} \frac{J(\omega)}{\omega} = 0. \quad (2.85)$$

Using the definition of the Laplace transform of the damping kernel [14],

$$\hat{\gamma}(z) = \frac{2}{\pi M} \int_0^\infty d\omega \frac{J(\omega)}{\omega} \frac{z}{\omega^2 + z^2}, \quad (2.86)$$

we can obtain the second term:

$$-\hat{\gamma}(i\Omega) = \frac{2}{\pi M} \int_0^\infty d\omega \frac{J(\omega)}{\omega} \frac{i\Omega}{\Omega^2 - \omega^2}, \quad (2.87)$$

$$-\frac{\pi M \operatorname{Im} \hat{\gamma}(i\Omega)}{2 \Omega} = \int_0^\infty \frac{J(\omega)}{\omega} \frac{d\omega}{\Omega^2 - \omega^2}. \quad (2.88)$$

We solve the summation using:

$$\cot x = \frac{1}{x} + 2x \sum_{n=0}^{\infty} \frac{1}{x^2 - \pi^2 n^2}, \quad (2.89)$$

$$\sum_{n=1}^{\infty} \frac{1}{\Omega^2 - n^2 \Delta^2} = \frac{1}{2} \left(\pi \frac{\cot\left(\frac{\pi\Omega}{\Delta}\right)}{\Omega} - \frac{\Delta}{\Omega^2} \right). \quad (2.90)$$

Using all these results, we can rewrite equation (2.75) as:

$$\cot\left(\frac{\pi\Omega}{\Delta}\right) - \frac{\Delta}{\pi\Omega} = G(\Omega), \quad (2.91)$$

where we have defined the function $G(\Omega)$ to make (2.75) more compact:

$$G(\Omega) = \frac{M}{J(\Omega)} (\Omega^2 - \Omega_0^2 + \Omega \operatorname{Im} \hat{\gamma}(i\Omega)). \quad (2.92)$$

In the case of the free particle the calculations would be the same, but we use instead lower case letter g :

$$g(\Omega) = \frac{M}{J(\Omega)} (\Omega^2 + \Omega \operatorname{Im} \hat{\gamma}(i\Omega)), \quad (2.93)$$

as obtained in [14].

2.4.2 Series Expansion for the General Bath

The shift in the eigen-frequency density appears in equations (2.35) and (2.36). It is possible to write the bath density using the spacing between consecutive frequencies Δ :

$$\rho_B(\omega) = \frac{1}{\Delta}. \quad (2.94)$$

The continuous version of (2.37) can be written as:

$$\rho_{S+B}(\omega) - \rho_B(\omega) = \frac{1}{\Delta + \epsilon(\omega)} - \frac{1}{\Delta}, \quad (2.95)$$

where $\epsilon(\omega)$ represents the actual the shift of the eigen-frequencies caused by the coupling. The term $\Delta + \epsilon(\omega)$ becomes the new spacing between to consecutive frequencies.

Given that Ω is a solution for (2.91), the next frequency, $\Omega + \Delta + \epsilon(\Omega)$ is also a solution. Since $G(\omega)$ is a well-behaved continuous function, we can expand it as series around Ω :

$$G(\Omega + \Delta + \epsilon(\Omega)) \approx G(\Omega) + G'(\Omega)(\Delta + \epsilon(\Omega)) + O(\Delta + \epsilon(\Omega)), \quad (2.96)$$

the left hand side can be expanded in the same way. Taking the difference from two consecutive frequencies and then solving for $\epsilon(\omega)$ we obtain:

$$\epsilon(\Omega) = -\frac{1}{\pi} \frac{G'(\Omega)}{1 + G^2(\Omega)} \Delta^2 + O(\Delta^3). \quad (2.97)$$

That information allows us to rewrite the expression for the change in spectral density as:

$$\rho_{S+B} - \rho_B = \frac{1}{\Delta + \epsilon(\Omega)} - \frac{1}{\Delta} = \frac{1}{\pi} \frac{G'(\Omega)}{1 + G^2(\Omega)}, \quad (2.98)$$

as $\Delta \rightarrow 0$. Using the same calculations we can obtain this result for $g(\omega)$.

Using our last result in equation (2.36) we obtain

$$\frac{C_2}{k_B} = \int_0^\infty \frac{1}{\pi} \frac{G'(\omega)}{1 + G^2(\omega)} \left(\frac{\hbar\beta\omega}{2 \sinh \frac{\hbar\beta\omega}{2}} \right)^2 d\omega, \quad (2.99)$$

where we use C_2 since the capital $G(\omega)$ means we are dealing with the harmonic oscillator. We wish to expand last expression as a series of T for low temperatures, however the only function of T is the hyperbolic sine term, which has all its derivatives equal to zero for $T = 0$. First, we need need to change the variables to

$$x = \frac{\hbar k_B \omega}{2T}, \quad (2.100)$$

so that we may have

$$\frac{C_2}{k_B} = \frac{2}{\pi} \int_0^\infty \frac{G'(\frac{2k_B T x}{\hbar})}{1 + G^2(\frac{2k_B T x}{\hbar})} \left(\frac{x}{\sinh x} \right)^2 \left(\frac{k_B T}{\hbar} \right) dx. \quad (2.101)$$

where we now can expand the first term as a series

$$\frac{G'(y)}{1 + G^2(y)} = \frac{G'(0)}{1 + G^2(0)} + O(y^2), \quad (2.102)$$

for low temperatures. We know that $G'(\omega)$ is an even function from its definition (2.92) (it easier to see if we take $\text{Im}\hat{\gamma}(iy) = \{\hat{\gamma}(iy) - \hat{\gamma}(-iy)\} / 2i$, where $y = 2k_B T x / \hbar$).

The specific heat expansion for the harmonic oscillator reads:

$$\frac{C_2}{k_B} = \frac{\pi}{3} \frac{G'(0)}{1 + G^2(0)} \left(\frac{k_B T}{\hbar} \right) + O(T^3). \quad (2.103)$$

All previous calculations are true for $g(\omega)$, allowing us to obtain the expansion for the free particle

$$\frac{C_1}{k_B} = \frac{\pi}{3} \frac{g'(0)}{1 + g^2(0)} \left(\frac{k_B T}{\hbar} \right) + O(T^3). \quad (2.104)$$

Calculating the leading terms in T :

$$\frac{G'(0)}{1 + G^2(0)} = \lim_{y \rightarrow 0} \frac{M \Omega_0^2 \frac{J'(y)}{J^2(y)}}{\frac{M^2 \Omega_0^4}{J^2(y)}} = \frac{1}{\Omega_0^2} \frac{J'(0)}{M} = \frac{\gamma(0)}{\Omega_0^2}, \quad (2.105)$$

and

$$\frac{g'(0)}{1 + g^2(0)} = \frac{1 + \gamma'(0)}{\gamma(0)}, \quad (2.106)$$

leading to the final results:

$$\frac{C_1}{k_B} = \frac{\pi}{3} \frac{1 + \hat{\gamma}'(0)}{\hat{\gamma}(0)} \left(\frac{k_B T}{\hbar} \right) + O(T^3), \quad (2.107)$$

$$\frac{C_2}{k_B} = \frac{\pi}{3} \frac{\hat{\gamma}(0)}{\Omega_0^2} \left(\frac{k_B T}{\hbar} \right) + O(T^3), \quad (2.108)$$

as obtained in previous the previous section and [9].

2.4.3 Exact Solution for the Drude Bath

Considering the Drude bath and the free particle potential, we can evaluate:

$$\begin{aligned} \frac{g'(\omega)}{1 + g^2(\omega)} &= \frac{\gamma \omega_D^2 (3\omega^2 - \omega_D(\gamma - \omega_D))}{(\omega^2 + \omega_D^2)(\omega^4 + \omega^2 \omega_D(\omega_D - \gamma) + \gamma^2 \omega_D^2)} = \\ &= \frac{\omega_D(x^2 + \gamma \omega_D)}{\omega^4 + \omega^2 \omega_D(\omega_D - \gamma) + \gamma^2 \omega_D^2} - \frac{\omega_D}{\omega^2 + \omega_D^2}. \end{aligned} \quad (2.109)$$

To further simplify the expression we are going to solve the biquadratic equation on the denominator:

$$x^2 + x\omega_D(\omega_D - \gamma) + \gamma^2\omega_D^2 = (x - x_1)(x - x_2), \quad (2.110)$$

$$\frac{1}{2} \left(2\gamma\omega_D - \omega_D^2 \pm \omega_D^2 \sqrt{1 - \frac{4\gamma}{\omega_D}} \right) = x_{1,2}. \quad (2.111)$$

Using the definitions of ω_1 and ω_2 in (2.55) we obtain that:

$$x_1 = -\omega_1^2 \quad ; \quad x_2 = -\omega_2^2. \quad (2.112)$$

Also note that the numerator can be written as:

$$\omega_D x^2 + \gamma\omega_D^2 = (\omega_1 + \omega_2)x^2 + \omega_1\omega_2(\omega_1 + \omega_2), \quad (2.113)$$

therefore we can write $\Delta\rho$ as a sum of Lorentzians:

$$\rho_{S+B} - \rho_B = \frac{1}{\pi} \left\{ \frac{\omega_1}{x^2 + \omega_1^2} + \frac{\omega_2}{x^2 + \omega_2^2} - \frac{\omega_D}{x^2 + \omega_D^2} \right\} \quad (2.114)$$

For the range of values $\omega_D < 4\gamma$, the frequencies ω_1 and ω_2 become complex. We have mentioned in section 2.3.2. Since they are also necessarily complex conjugate, $\omega_{1,2} = \text{Re}(\omega) \pm i\text{Im}(\omega)$, expression (2.114) will remain real, the only difference being that the Lorentzians will no longer be centred at the origin,

$$\frac{\omega_1}{x^2 + \omega_1^2} + \frac{\omega_2}{x^2 + \omega_2^2} = \frac{\text{Re}(\omega)}{\text{Re}(\omega)^2 + (x + \text{Im}(\omega))^2} + \frac{\text{Re}(\omega)}{\text{Re}(\omega)^2 + (x - \text{Im}(\omega))^2}. \quad (2.115)$$

Replacing (2.114) in (2.36), we obtain the expression:

$$C_1(T) = \int_0^\infty \frac{1}{\pi} \left\{ \frac{\omega_1}{x^2 + \omega_1^2} + \frac{\omega_2}{x^2 + \omega_2^2} - \frac{\omega_D}{x^2 + \omega_D^2} \right\} \left(\frac{\hbar\omega\beta}{2 \sinh(\hbar\omega\beta/2)} \right) d\omega, \quad (2.116)$$

whose calculation is very extensive and does not provide any additional physical insight on the problem. The final result is:

$$\begin{aligned} \frac{C_1}{k_B} &= \left(\frac{\hbar\beta\omega_1}{2\pi} \right)^2 \psi' \left(\frac{\hbar\beta\omega_1}{2\pi} \right) + \left(\frac{\hbar\beta\omega_2}{2\pi} \right)^2 \psi' \left(\frac{\hbar\beta\omega_2}{2\pi} \right) - \\ &- \left(\frac{\hbar\beta\omega_D}{2\pi} \right)^2 \psi' \left(\frac{\hbar\beta\omega_D}{2\pi} \right) - \frac{1}{2}, \end{aligned} \quad (2.117)$$

which is same result obtained in section 2.3. The complete calculation can be found in Appendix A.3.

Considering now the harmonic oscillator,

$$\rho_{S+B} - \rho_B = \frac{1}{\pi} \left\{ \frac{\text{num}(\omega)}{\text{den}(\omega)} - \frac{\omega_D}{\omega^2 + \omega_D^2} \right\}, \quad (2.118)$$

where we have defined:

$$\text{num}(x) = \omega_D x^4 + (\gamma \omega_D^2 - 2\Omega_0^2 \omega_D) + \omega_D \Omega_0^4 + \gamma \Omega_0^2 \omega_D^2, \quad (2.119)$$

$$\begin{aligned} \text{den}(x) &= x^6 + (\omega_D^2 - 2\gamma \omega_D - 2\Omega_0^2) x^4 + \\ &+ (\Omega_0^4 + 2\gamma \Omega_0^2 \omega_D - 2\omega_D^2 \Omega_0^2 + \gamma^2 \omega_D^2) x^2 + \omega_D^2 \Omega_0^4, \end{aligned} \quad (2.120)$$

for simplicity. We are once again faced with a logistic problem: the expressions for the roots are too lengthy and algebraical manipulation would take an excessive amount of space to demonstrate any propriety by directly using them.

Our denominator can be written as:

$$\text{den}(x) = (x - x_1)(x - x_2)(x - x_3), \quad (2.121)$$

We now need to demonstrate that:

$$x_1 = -\omega_1^2 ; \quad x_2 = -\omega_2^2 ; \quad x_3 = -\omega_3^2, \quad (2.122)$$

and:

$$\frac{\text{num}(x)}{\text{den}(x)} = \frac{\omega_1}{x^2 + \omega_1^2} + \frac{\omega_2}{x^2 + \omega_2^2} + \frac{\omega_3}{x^2 + \omega_3^2}. \quad (2.123)$$

These results are demonstrated using alternative methods in Appendix [A.1](#) and Appendix [A.2](#) since, as we said before, the expressions are too lengthy and this calculation does not provide any additional physical insight on the problem. Using again the result in appendix [A.3](#), we can directly write the specific heat for the harmonic oscillator:

$$\begin{aligned} \frac{C_2}{k_B} &= \left(\frac{\hbar \beta \omega_1}{2\pi} \right)^2 \psi' \left(\frac{\hbar \beta \omega_1}{2\pi} \right) + \left(\frac{\hbar \beta \omega_2}{2\pi} \right)^2 \psi' \left(\frac{\hbar \beta \omega_2}{2\pi} \right) + \\ &+ \left(\frac{\hbar \beta \omega_3}{2\pi} \right)^2 \psi' \left(\frac{\hbar \beta \omega_3}{2\pi} \right) - \left(\frac{\hbar \beta \omega_D}{2\pi} \right)^2 \psi' \left(\frac{\hbar \beta \omega_D}{2\pi} \right) - 1. \end{aligned} \quad (2.124)$$

which is the same result obtained in section [2.3.2](#).

2.5 Thermodynamic Proprieties of the Drude Bath

The shift in the density of eigenfrequencies represents a powerful tool for analyse the system thermodynamic proprieties. Having defined a specific bath, we can have a clear picture on how the coupling affects the distribution of frequencies. Note that the shift in the density is not a density itself, therefore it can assume negative values.

From equation (2.36), we can interpret C_{ho} as a function that, for a given value of temperature, weights the contributions of the shift in the density. Figure 2.3 illustrates the behaviour of C_{ho} for different values of T . For low values of T , C_{ho} takes contribution only for a small range of frequencies around the origin, becoming suppressed quickly. As we increase the temperature, the range of frequencies increases as well to a point that, when $T \rightarrow \infty$, all frequencies of $\Delta\rho$ give an equal contribution to the final result.

Within the Drude bath, $\Delta\rho$ can be written as a sum of Lorentzians in the form $a/\pi(a^2 + x^2)$ (as in (2.114) and (2.118) with (2.123)), such that when we integrate for all positive x we obtain $1/2$ - the area does not depend on a . This means that the maximum contribution that each Lorentzian can give is equal $1/2$. In the case of the free particle, where we have two positive and one negative Lorentzians, we know that for very high values of T , the specific heat becomes $k_B/2$ and for the harmonic oscillator that has three positive frequencies it becomes k_B , as in [9, 11].

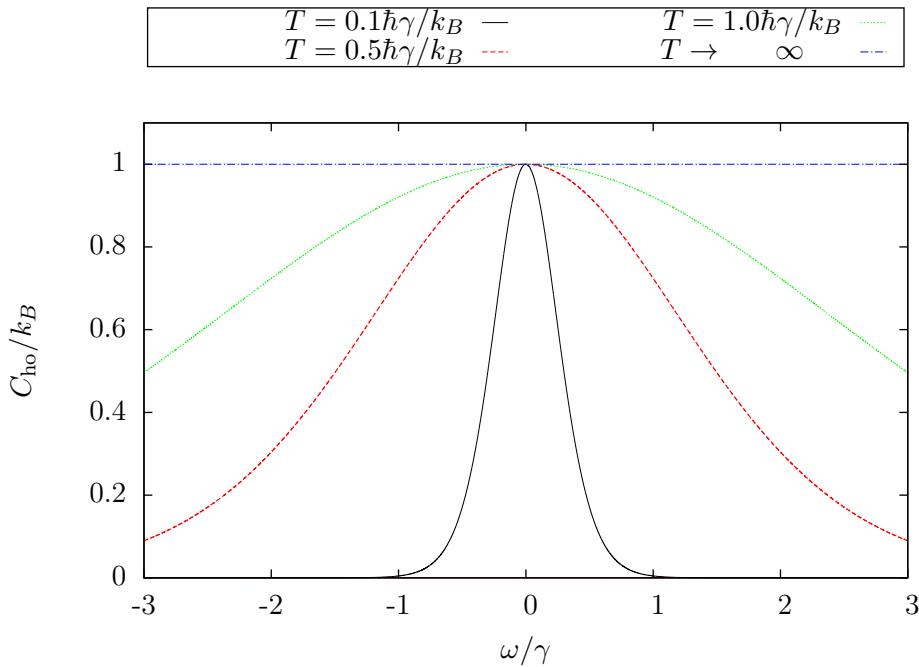


FIGURE 2.3: Behaviour of C_{HO} as a function of $\hat{\omega} = \omega/\gamma$ and $\hat{T} = k_B T/\hbar\gamma$.

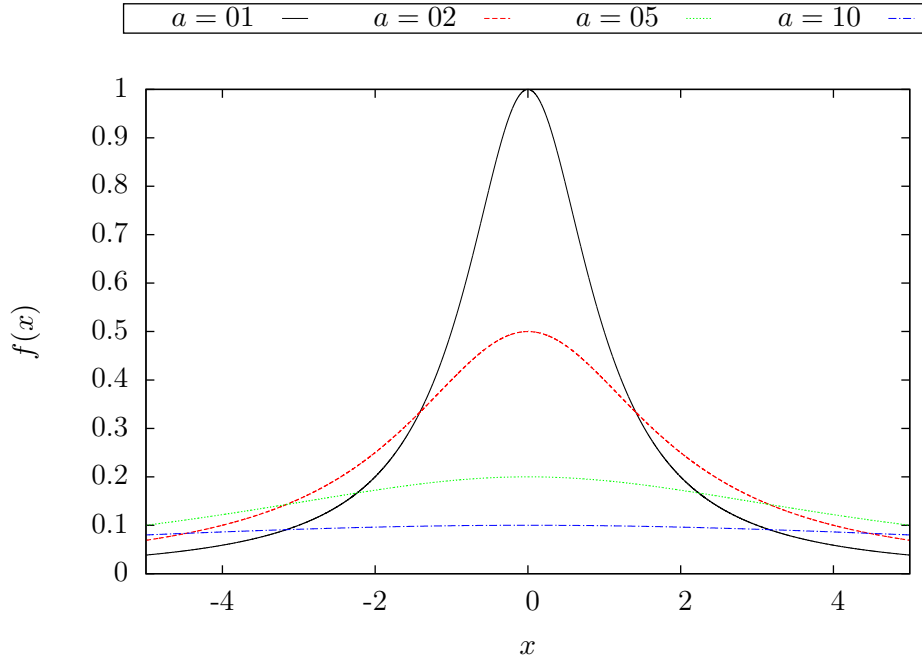


FIGURE 2.4: *Lorentzians in the form $f(x) = a/(a^2 + x^2)$, for different values of a . The area of the functions is always the same.*

2.5.1 Negative Specific Heat for the Free Particle

If we take the series expansion for the general specific heat that we obtained before ((2.52),(2.107)), its very clear that if:

$$\hat{\gamma}'(0) < -1 \quad (2.125)$$

the specific heat becomes negative for low temperatures. For the Drude bath the restriction reads:

$$\omega_D < \gamma. \quad (2.126)$$

If the damping kernel is greater than ω_D , which is our cut-off frequency, the specific heat may become negative. Since we know that without the damping we would only observe positive specific heat, it is coherent to expect that high values of the damping strength make it more likely to become negative.

In the specific case of the Drude bath we can go further and add that it is only possible to have a negative specific heat in that region ($\omega_D < \gamma$). We prove this using (2.6), the only term that may assume negative values is the shift in the eigen-frequencies since $C_{ho} > 0$. Having $\rho_{S+B} - \rho_B$ negative is necessary, but not sufficient. This holds

for any Ohmic bath:

$$\frac{1}{\pi} \frac{g'(\omega)}{1 + g^2(\omega)} < 0 \rightarrow g'(\omega) < 0. \quad (2.127)$$

in the case of the Drude bath we obtain the expression:

$$3\omega^2 - (\gamma - \omega_D)\omega_D < 0 \quad (2.128)$$

which clearly can only yield negative values if $\gamma > \omega_D$.

We can have an additional insight on how the coupling affects the frequency distribution using $\Delta\rho$. While the negative Lorentzian is always centred at the origin, the two positive ones can be shifted if the frequencies ω_1 and ω_2 become imaginary, following expression (2.115). Recalling the definition of (2.55), we see that the discriminant in the square root can become negative for $\omega_D < 4\gamma$, dislocating the Lorentzians by the imaginary values

$$\text{Im}(\omega_{1,2}) = \pm \sqrt{\frac{4\gamma}{\omega_D} - 1}. \quad (2.129)$$

And for very high values of γ :

$$\sqrt{\frac{4\gamma}{\omega_D} - 1} = \sqrt{\frac{\gamma}{4\omega_D}} \sqrt{1 - \frac{4\omega_D}{\gamma}} \approx \sqrt{\frac{\gamma}{4\omega_D}} \left(1 + \frac{2\omega_D}{\gamma}\right) + \approx \frac{1}{2} \sqrt{\frac{\gamma}{\omega_D}}. \quad (2.130)$$

As we increase the damping, the Lorentzians get shifted further and further ahead while the negative Lorentzian remains centred at the origin. This creates a window where the negative Lorentzian contribution, or the contribution of the isolated bath, becomes dominant for low values of frequencies since the damping is shifting the coupled system frequencies further ahead. When we integrate for low temperatures, C_{ho} will take the heavy contributions from the negative Lorentzian, and only for higher values of T the overall contribution becomes dominantly positive. We have illustrated this behaviour in figure 2.5, with its relative specific heat in figure 2.6.

2.5.2 Negative Specific Heat for the Harmonic Oscillator

Using the same reasoning with the Harmonic Oscillator, equations (2.53) and (2.108) indicate that for low temperatures it is impossible to have negative values for the specific heat since:

$$\frac{\gamma(0)}{\Omega_0^2} > 0 \quad \text{always,} \quad (2.131)$$

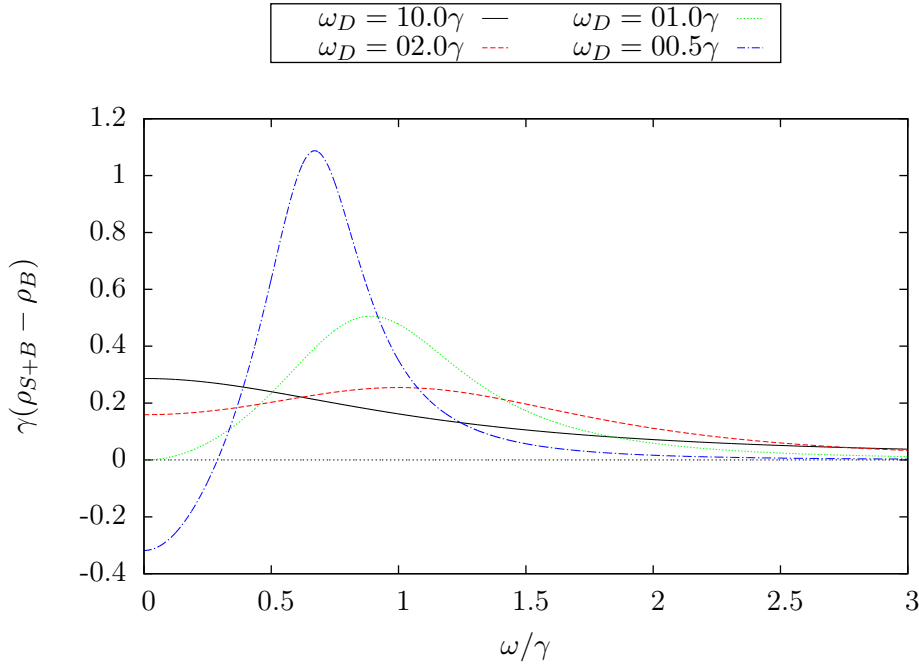


FIGURE 2.5: *Change in Spectral Density for the free particle for different values of ω_D in relation to γ .* We can see very clearly the lorentzians associated with ω_1 and ω_2 , now complex valued, begin to displace from the origin as we decrease the value of ω_D in relation to γ .

however, continuing with the chain of thought, if there is a combination of ω_D and Ω_0 that allows: $G'(\omega) < 0$, for a given ω , we cannot immediately discard the possible existence of negative specific heat. Within the Drude bath, the restriction for obtaining $G'(\omega) < 0$ can be found at appendix A.5, figure 2.7 illustrates possible combinations that allow for negative $G'(\omega)$.

Unlike the free particle, the Harmonic Oscillator always has the positive contribution of a real frequency, ω_3 ; therefore, even in the case where ω_1 and ω_2 become imaginary and are shifted from the origin, we still have a positive factor centred around the origin. We can also evaluate the value of $\Delta\rho$ at the origin

$$\rho_{S+B} - \rho_B = \frac{1}{\pi} \frac{G'(0)}{1 + G^2(0)} = \frac{\gamma}{\pi\Omega_0^2}, \quad (2.132)$$

and conclude that it is always positive. This leaves a very narrow window of frequencies in which $\Delta\rho$ can become negative. We must have that ω_1 and ω_2 are imaginary and where shifted from the origin and have the parameters ω_D , γ and Ω_0 defined in such way that between the contribution of the ω_3 Lorentzian and the next shifted one, the negative Lorentzian becomes dominant.

Since the window is so narrow, see figure 2.7, it seems that we could never obtain negative specific heat, in fact it is simple to demonstrate that, for the case of the Drude

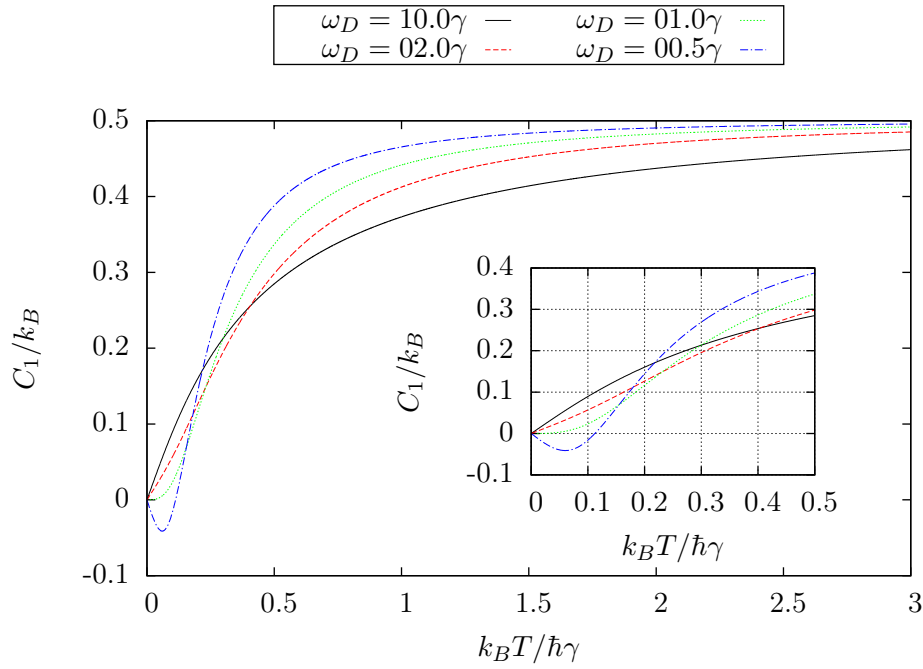


FIGURE 2.6: *Specific heat of the free particle for different values of ω_D in relation to γ .*

bath, the Harmonic Oscillator has always positive specific heat (Appendix A.4). The negative values of $G'(\omega)$ cause the specific heat to present a *dip*, in which the value of the specific shows a small decrease but never to a point where it becomes negative. Figure 2.8 illustrates that behaviour.

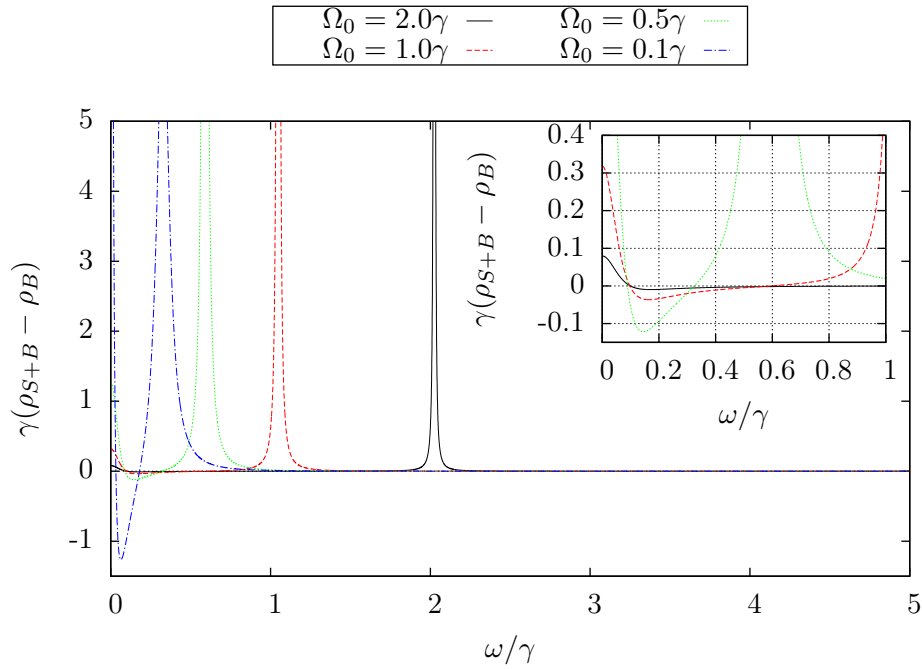


FIGURE 2.7: Change in Spectral Density for the harmonic oscillator for different values of Ω_0 in relation to γ , having fixed the value of ω_D at 0.1γ .

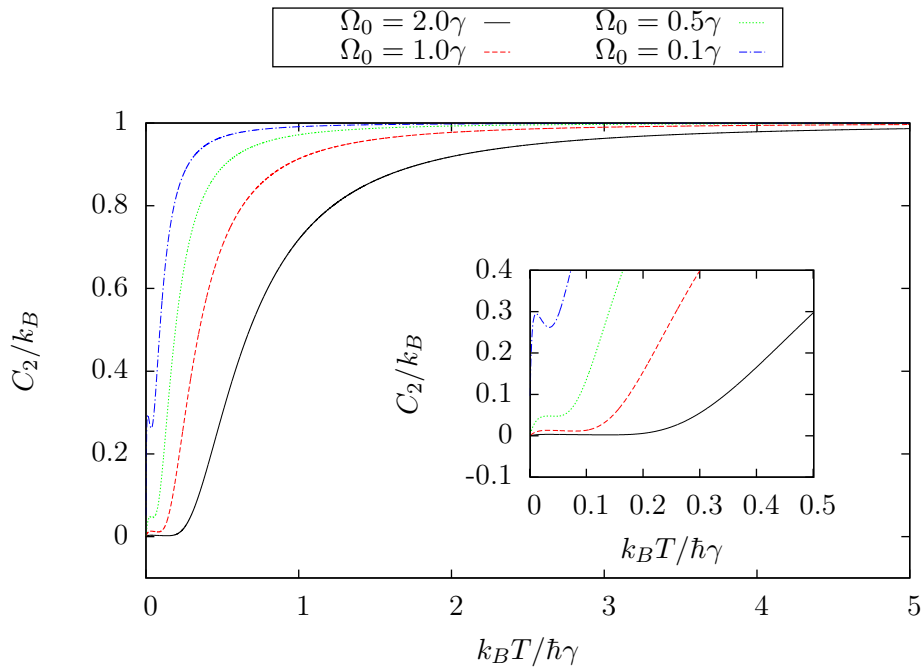


FIGURE 2.8: Specific heat of the harmonic oscillator for different values of Ω_0 in relation to γ , having fixed the value of ω_D at 0.1γ .

Chapter 3

Several Degrees of Freedom for a Finite Bath - The Effects of Potential Renormalization

In this chapter we start considering systems consisting of several interacting degrees of freedom, which will lead us to a system of Langevin equations. One of the simplest possible situation will be when we are capable of uncoupling the Langevin equations. In that case, our partition function will be written as a product of the uncoupled partition functions

$$Z = \prod_{i=1}^{N_S} Z_i, \quad (3.1)$$

where N_S stands for the number of system degrees of freedom and Z_i the partition function of the i -th degree of freedom.

The first half of this chapter will be dedicated to analysing the model introduced by H. Hasegawa [13], which we are going to label $N_S + N_B$ model, where we take the bath to be finite with N_B degrees of freedom. Our interest to analyse such model comes from the fact that, unlike what we have obtained in chapter 2, even for systems of harmonic oscillators it is still possible to have negative specific heat.

This model has a finite number of bath frequencies, because of that we have to be concerned with Poincaré recurrence time. Since we wish our system to describe dissipation, we must have that the number of bath frequencies (N_B) is much greater

than the number of system frequencies (N_S), this will make the Poincaré recurrence time to be sufficiently large [2].

It is important to note that there are differences between the model we are going to analyse here and the model analysed in chapter 2 (Caldeira-Leggett),

- the Caldeira-Leggett model has only one system degree of freedom while the $N_S + N_B$ has several interacting degrees of freedom,
- the interaction Hamiltonian is different for both models.

Our main objective in this chapter is to identify the essential source of the different results in these models. After rederiving the results found at [13], we are able to obtain, through the analysis of a minimal model with only one system degree of freedom, that the specific heat of the harmonic oscillator can become negative. We thus conclude that the interaction Hamiltonian is the main responsible for the thermodynamic differences. That is not the same to say that the extra degrees of freedom do not contribute to the negative values, chapter 4 will be dedicated to investigate their influence.

3.1 The $N_S + N_B$ Model

Our system can be understood as a ring of N_S particles where the k -th particle is connected to its neighbours, $(k + 1)$ and $(k - 1)$, by a harmonic potential. The most general Hamiltonian that can describe such system is

$$H_S = \sum_{k=1}^{N_S} \left\{ \frac{P_k^2}{2M_k} + \frac{M_k \Omega_k^2}{2} q_k^2 + \frac{K_k}{2} (q_{k+1} - q_k)^2 \right\}, \quad (3.2)$$

being represented by figure 3.1, where K_i stands for the interaction between the i -th and the $(i + 1)$ -th particle. The bath remains mostly the same of previous chapter

$$H_B = \sum_{i=1}^{N_B} \left\{ \frac{p_i^2}{2m_i} + \frac{m_i \omega_i^2}{2} x_i^2 \right\}, \quad (3.3)$$

with the only difference being that, in this chapter, we are going to analyse finite baths (N_B will always be a finite number).

Each system particle is connected to *all* N_B bath oscillators by the Hamiltonian

$$H_{SB} = \sum_{k=1}^{N_S} \sum_{i=1}^{N_B} \left\{ \frac{c_{ki}}{2} (x_i - q_k)^2 \right\}, \quad (3.4)$$

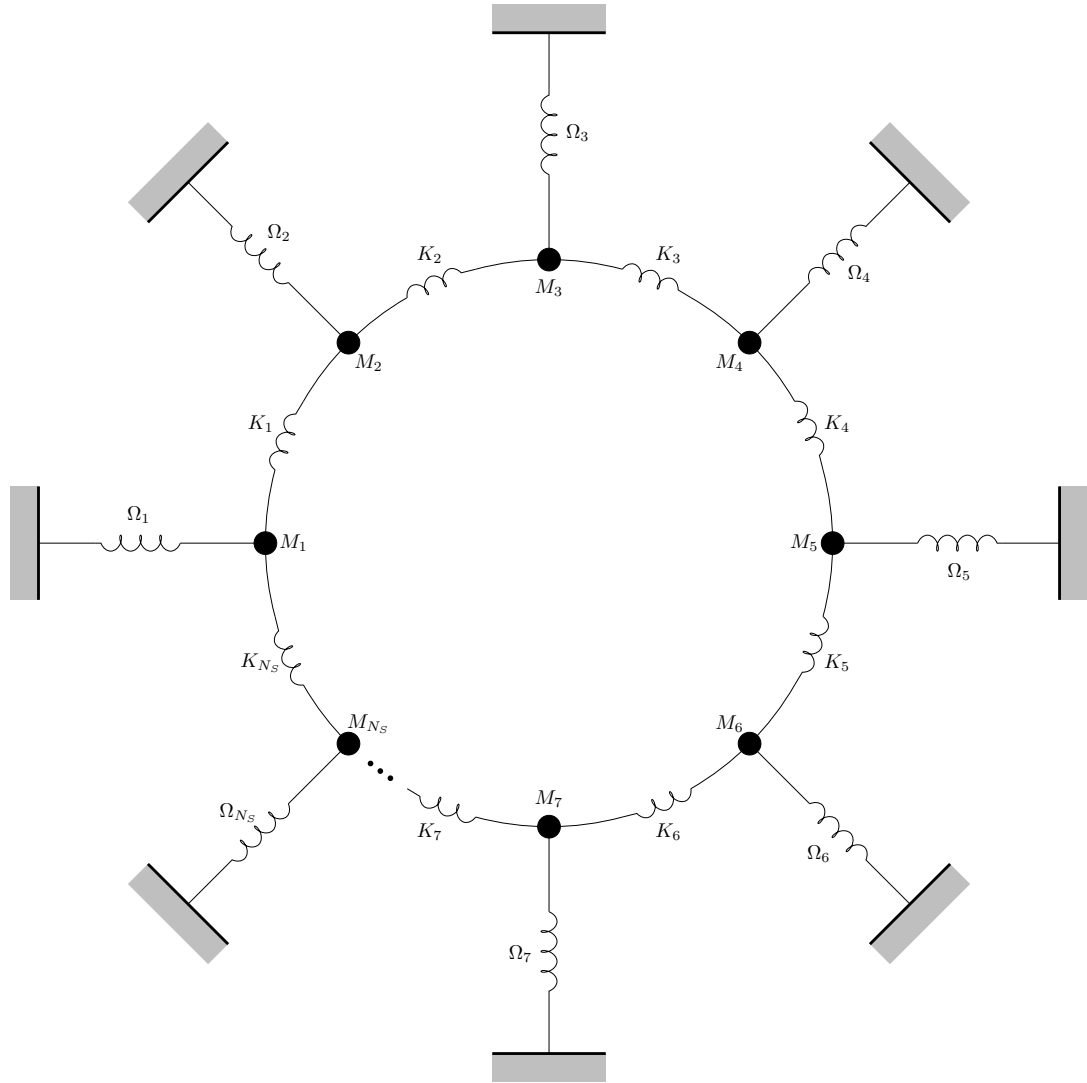


FIGURE 3.1: *The harmonic oscillator ring describing the Hamiltonian of the system (3.2). Classical springs represent both the internal interactions and the interaction with an external potential.*

represented in figure 3.2 together with H_S and H_B .

This formulation is very intuitive, the coupling can be seen as simply adding another "spring" to connect the system and the bath, as opposed to figure 2.2 where the coupling causes a change in the dependency of the bath potential from the absolute coordinates to the relative position between system and bath. Note that we are missing an equivalent quantity for the renormalizing term $\sum_{n=1}^{\infty} c_n^2 / 2m_n \omega_n^2$. This will be discussed on section 3.2, when we start to analyse the effects of the potential renormalization. We are also imposing periodic boundary conditions on all the coordinates:

$$q_k = q_{k+N_S} \quad ; \quad x_i = x_{i+N_B} \quad (3.5)$$

$$P_k = P_{k+N_S} \quad ; \quad p_i = p_{i+N_B} \quad (3.6)$$

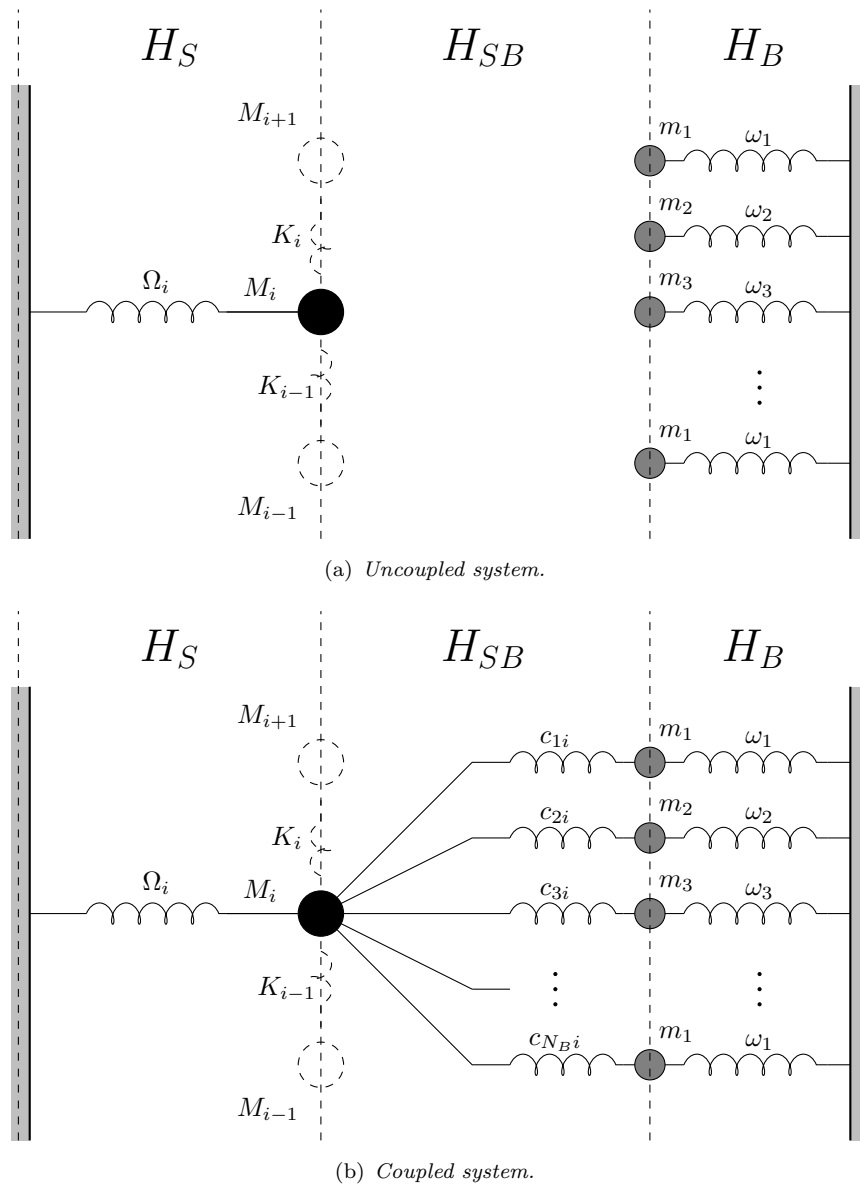


FIGURE 3.2: A simple representation of the $N_S + N_B$ model using a classical springs to represent the effects the interactions between particles and bath. The difference from the Caldeira-Leggett is very clear; unlike what we had in figure 2.2(b), where the coupling would make $H_{SB} + H_B$ change dependency from the absolute bath coordinates to the relative position between system and bath (translational invariant) here we simply introduce a "new spring" connecting system and bath.

3.1.1 Solving for the Eigenfrequencies

Since we are dealing with finite degrees of freedom, we can use expression (2.30) to directly obtain the specific heat. For that we need to obtain the eigenfrequencies for the coupled system. Let us simplify our problem by assuming that we have the same masses ($M_k = M$, $m_i = m$), system frequencies ($\Omega_k = \Omega_0$) and internal couplings ($K_k = K_0$) [13]

$$H_S = \sum_{k=1}^{N_S} \left\{ \frac{P_k^2}{2M} + \frac{M\Omega_0^2}{2} q_k^2 + \frac{K}{2} (q_{k+1} - q_k)^2 \right\}, \quad (3.7)$$

we also assume that the coupling with the bath is the same for every system degree of freedom ($c_{ik} = c_i$)

$$H_{SB} = \sum_{i=1}^{N_B} \sum_{k=1}^{N_S} \frac{c_i}{2} (x_n - q_k)^2. \quad (3.8)$$

Using the discrete Fourier transform it is possible to diagonalize the system:

$$q_k = \frac{1}{\sqrt{N_S}} \sum_{s=1}^{N_S} Q_s e^{-2\pi i \frac{ks}{N_S}} \quad ; \quad P_k = \frac{1}{\sqrt{N_S}} \sum_{s=0}^{N_S-1} \bar{P}_s e^{-2\pi i \frac{ks}{N_S}} \quad (3.9)$$

$$Q_s = \frac{1}{\sqrt{N_S}} \sum_{k=1}^{N_S} q_k e^{2\pi i \frac{ks}{N_S}} \quad ; \quad \bar{P}_s = \frac{1}{\sqrt{N_S}} \sum_{k=1}^{N_S} P_k e^{2\pi i \frac{ks}{N_S}}. \quad (3.10)$$

The spatial part of the system Hamiltonian is proportional to

$$\sum_{k=1}^{N_S} (q_{k+1} - q_k)^2 = \sum_{k=1}^{N_S} (q_{k+1}^2 + q_k^2 - 2q_{k+1}q_k), \quad (3.11)$$

and since

$$\sum_{k=1}^{N_S} q_k^2 = \sum_{k=1}^{N_S} q_{k+1}^2, \quad (3.12)$$

we can rewrite

$$\sum_{k=1}^{N_S} (q_{k+1} - q_k)^2 = \sum_{k=1}^{N_S} 2 (q_k^2 - q_{k+1}q_k). \quad (3.13)$$

Introducing the discrete Fourier transform:

$$\begin{aligned} \sum_{k=1}^{N_S} q_k^2 &= \frac{1}{N_S} \sum_{k=1}^{N_S} \left(\sum_{s=1}^{N_S} Q_s e^{\frac{-2\pi i k s}{N_S}} \right) \left(\sum_{s'=1}^{N_S} Q_{s'} e^{\frac{-2\pi i k s'}{N_S}} \right) = \\ &= \sum_{s=1}^{N_S} \sum_{s'=1}^{N_S} Q_s Q_{s'} \left(\frac{1}{N_S} \sum_{k=1}^{N_S} e^{\frac{-2\pi i k (s+s')}{N_S}} \right), \end{aligned} \quad (3.14)$$

and using the identity:

$$\delta_{l,l'} = \frac{1}{N} \sum_{n=1}^N e^{\frac{2\pi i n (l-l')}{N}}, \quad (3.15)$$

we can obtain that

$$\sum_{k=1}^{N_S} q_k^2 = \sum_{s=1}^{N_S} \sum_{s'=1}^{N_S} Q_s Q_{s'} \left(\frac{1}{N_S} \sum_{k=1}^{N_S} e^{\frac{-2\pi i k (s+s')}{N_S}} \right) = \sum_{s=1}^{N_S} Q_s Q_s^*, \quad (3.16)$$

where we have used that $Q_{-s} = Q_{N_S-s} = Q_s^*$, since q_k are hermitian.

We can also use (3.15) to rewrite:

$$\sum_{k=1}^{N_S} q_k q_{k+1} = \sum_{s=1}^{N_S} Q_s Q_s^* e^{-2\pi i \left(\frac{-s}{N_S}\right)} = \sum_{s=1}^{N_S} Q_s Q_{-s} \cos\left(\frac{2\pi s}{N_S}\right). \quad (3.17)$$

This allows us to express the system Hamiltonian in the basis of the transformed coordinates

$$H_S = \sum_{s=1}^{N_S} \left\{ \frac{\bar{P}_s \bar{P}_s^*}{2M} + \frac{1}{2} \left(M\Omega_0^2 + 4K \sin^2\left(\frac{\pi s}{N_S}\right) \right) Q_s Q_s^* \right\}, \quad (3.18)$$

where we have used the trigonometric identity $1 - \cos x = 2 \sin^2 x$.

With our transformation, the system Hamiltonian became a simple collection of non-interacting harmonic oscillator, which eigenfrequencies we are going to represent using $\bar{\Omega}_s$ defined as:

$$M\bar{\Omega}_s^2 = M\Omega_0^2 + 4K \sin^2\left(\frac{\pi s}{N_S}\right). \quad (3.19)$$

Before proceeding to the interaction Hamiltonian, we would like to point out that Q_{N_S} is proportional to the center of mass,

$$Q_{N_S} = \frac{1}{\sqrt{N_S}} \sum_{k=1}^{N_S} q_k = \sqrt{N_S} q_{CM}. \quad (3.20)$$

Applying the transformation to the interaction Hamiltonian we obtain

$$\begin{aligned}
 H_{SB} &= \sum_{i=1}^{N_B} \left\{ N_S \frac{c_i}{2} x_i^2 + \sum_{k=1}^{N_S} \left(\frac{c_i}{2} q_k^2 - c_i x_i q_k \right) \right\} \\
 &= \sum_{i=1}^{N_B} \frac{c_i}{2} \sum_{s=1}^{N_S} Q_s Q_s^* - \sqrt{N_S} Q_{N_S} \sum_{i=1}^{N_B} c_i x_i + \frac{N_S}{2} \sum_{i=1}^{N_B} c_i q_i^2. \quad (3.21)
 \end{aligned}$$

As it was obvious by looking at (3.3), we are only coupling the center of mass coordinate with the bath coordinates. Once we introduce the coupling, the system frequencies are shifted to the new frequencies $\tilde{\Omega}_s$:

$$M\tilde{\Omega}_s^2 = M\bar{\Omega}_s^2 + \sum_{i=1}^{N_B} c_i, \quad (3.22)$$

this means that there is still a *potential renormalization*, represented by the shift in the frequencies, caused by the coupling in the *uncoupled coordinates*.

It is possible to write the coupled Hamiltonian in a matrix form using the vectors:

$$\mathbf{P} = \begin{pmatrix} \bar{P}_0 \\ \vdots \\ \bar{P}_{N_S-1} \\ p_1 \\ \vdots \\ p_{N_B} \end{pmatrix}; \quad \mathbf{Q} = \begin{pmatrix} Q_1 \\ \vdots \\ Q_{N_S} \\ q_1 \\ \vdots \\ q_{N_B} \end{pmatrix}. \quad (3.23)$$

We have:

$$\begin{aligned}
 H &= \frac{1}{2} \mathbf{P}^\dagger \begin{pmatrix} \frac{1}{M} \mathbf{I}_{N_S} & \mathbf{0} \\ \mathbf{0} & \frac{1}{m} \mathbf{I}_{N_B} \end{pmatrix} \mathbf{P} + \\
 &+ \frac{1}{2} \mathbf{Q}^\dagger \begin{pmatrix} M\tilde{\Omega}_1^2 & 0 & \dots & 0 & -c_1\sqrt{N_S} & \dots & -c_{N_B}\sqrt{N_S} \\ 0 & M\tilde{\Omega}_2^2 & \dots & 0 & 0 & 0 & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & \dots & M\tilde{\Omega}_{N_S}^2 & 0 & 0 & 0 \\ 0 & 0 & \dots & -c_1\sqrt{N_S} & m\tilde{\omega}_1^2 & \dots & 0 \\ \vdots & 0 & \dots & 0 & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & -c_{N_B}\sqrt{N_S} & 0 & \dots & m\tilde{\omega}_{N_B}^2 \end{pmatrix} \mathbf{Q}, \quad (3.24)
 \end{aligned}$$

were the new frequencies are:

$$m\tilde{\omega}_n^2 = m\omega_n^2 + N_S c_n. \quad (3.25)$$

Using the cofactor expansion on:

$$\begin{vmatrix} M(\tilde{\Omega}_1^2 - \lambda^2) & 0 & \dots & 0 & -c_1\sqrt{N_S} & \dots & -c_{N_B}\sqrt{N_S} \\ 0 & M(\tilde{\Omega}_2^2 - \lambda^2) & \dots & 0 & 0 & 0 & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & \dots & M(\tilde{\Omega}_{N_S}^2 - \lambda^2) & 0 & \dots & 0 \\ 0 & 0 & \dots & -c_1\sqrt{N_S} & m(\tilde{\omega}_1^2 - \lambda^2) & \dots & 0 \\ \vdots & \vdots & \dots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & -c_{N_B}\sqrt{N_S} & 0 & \dots & m(\tilde{\omega}_{N_B}^2 - \lambda^2) \end{vmatrix} = 0, \quad (3.26)$$

we obtain the expression for the eigen-frequencies λ :

$$\prod_{s=1}^{N_S-1} (\tilde{\Omega}_s^2 - \lambda^2) \prod_{n=1}^{N_B} (\tilde{\omega}_n^2 - \lambda^2) \left\{ M(\tilde{\Omega}_{N_S}^2 - \lambda^2) - \sum_{n=1}^{N_B} \frac{c_n^2 N_S}{m(\tilde{\omega}_n^2 - \lambda^2)} \right\} = 0. \quad (3.27)$$

3.1.2 Solving for an Identical-Frequency Bath

From the first product in (3.27), i. e. $\prod_{s=1}^{N_S-1} (\tilde{\Omega}_s^2 - \lambda^2) = 0$, we can easily obtain $N_S - 1$ frequencies, all equal to $\tilde{\Omega}_s$ from $s = 1$ to $s = N_S - 1$, as eigenfrequencies of the complete system. The other $N_B + 1$ frequencies, however, cannot be found that easily. Removing the first product will still give us a $(N_B + 1)$ -th order polynomial of λ^2 .

In order solve this problem analytically we will follow Hasegawa [13] and consider the identical-frequency bath

$$\omega_n = \omega_0 \quad ; \quad c_n = c_0. \quad (3.28)$$

For this bath, (3.27) is solvable

$$(\tilde{\omega}_0^2 - \lambda^2)^{N_B-1} \left\{ mM(\tilde{\Omega}_0^2 - \lambda^2) (\tilde{\omega}_0^2 - \lambda^2) - c_0^2 N_S N_B \right\} = 0. \quad (3.29)$$

We obtain directly that $N_B - 1$ solutions are in fact $\tilde{\omega}_0$, such that $(\tilde{\omega}_0^2 - \lambda^2)^{N_B-1} = 0$. The last two frequencies are obtained by solving the biquadratic equation:

$$\lambda^4 - (\tilde{\Omega}_0^2 + \tilde{\omega}_0^2) \lambda^2 + \tilde{\Omega}_0^2 \tilde{\omega}_0^2 - c_0^2 \frac{N_S N_B}{mM} = 0, \quad (3.30)$$

whose solutions are:

$$\lambda_{\pm}^2 = \frac{1}{2} \left((\tilde{\Omega}_0^2 + \tilde{\omega}_0^2) \pm \sqrt{(\tilde{\Omega}_0^2 - \tilde{\omega}_0^2)^2 + 4c_0^2 \frac{N_S N_B}{mM}} \right). \quad (3.31)$$

Now that we have all the coupled system frequencies for any choice of parameters, it is possible to obtain the thermodynamic proprieties.

3.1.3 Thermodynamic Proprieties for the Identical Frequency Bath

From our demonstration in appendix A.4 we have concluded that if we have $\omega_i \leq \tilde{\omega}_i$ the terms in equation (2.30) obey:

$$\frac{(\beta\hbar\tilde{\omega}_i/2)^2}{\sinh^2(\beta\hbar\tilde{\omega}_i/2)} - \frac{(\beta\hbar\omega_i/2)^2}{\sinh^2(\beta\hbar\omega_i/2)} \leq 0. \quad (3.32)$$

From the form of the function $x^2/\sinh^2(x)$, we can conclude that increasing the frequency also increases a suppression effect for low temperatures. Increasing the values of N_S , N_B , c_0 shifts the coupled system frequencies for even higher values, as we can clearly see from:

$$\tilde{\omega}_0 = \sqrt{\omega_0^2 + \frac{N_S c_0}{m}} \geq \omega_0, \quad (3.33)$$

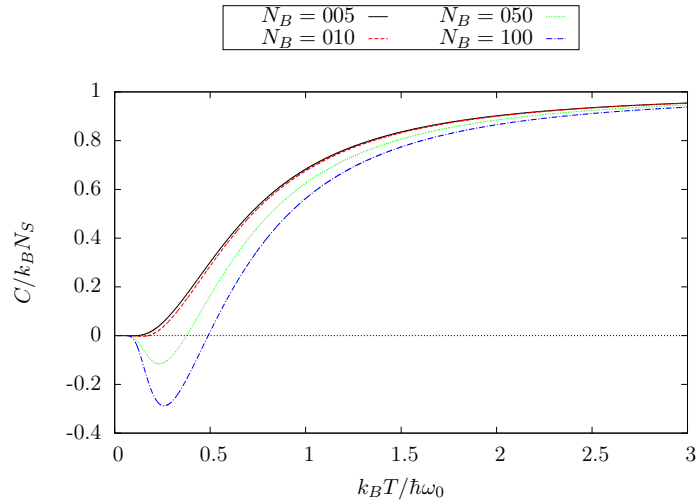
$$\tilde{\Omega}_k = \tilde{\Omega}_k + \frac{N_B c_0}{M} \quad (3.34)$$

$$\lambda_{\pm}^2 = \frac{1}{2} \left((\tilde{\Omega}_0^2 + \tilde{\omega}_0^2) \pm \sqrt{(\tilde{\Omega}_0^2 - \tilde{\omega}_0^2)^2 + 4c_0^2 \frac{N_S N_B}{mM}} \right). \quad (3.35)$$

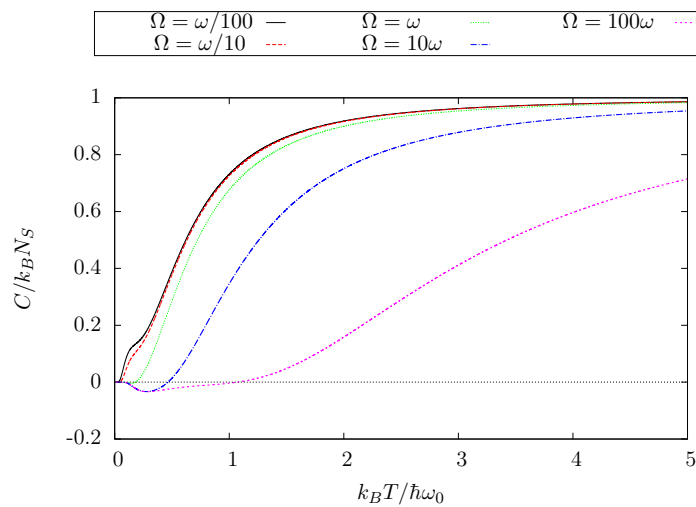
Either by increasing the values of these parameters or by increasing the value of Ω_0 , we can make C_{S+B} become heavily suppressed for low temperatures, creating a window where the negative contribution of C_B becomes dominant. The collection of figures 3.3 serves to exemplify this effect.

3.1.4 Qualitative Analysis of the General Case

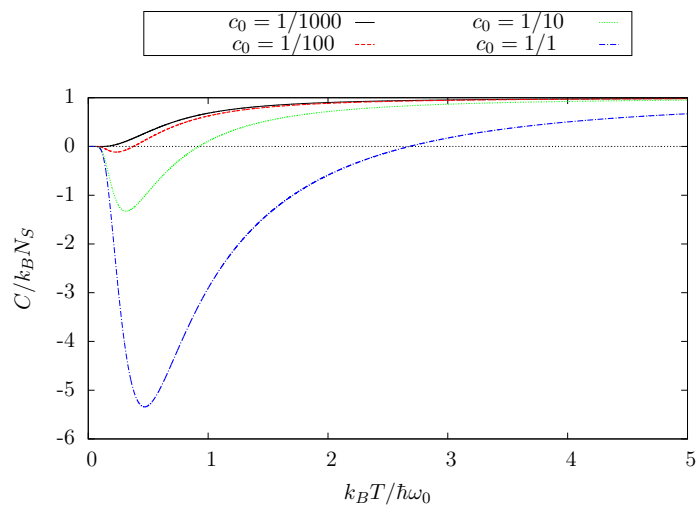
Although we cannot obtain a quantitative solution for any given (3.2) and (3.4), it is possible to provide a qualitative analysis of the results using a theorem found in the chapter about oscillations from V.I. Arnold's book [30].



(a) Increasing the values of N_B we can create an window of temperature where the specific heat becomes negative.



(b) Increasing the values of Ω_0 it is possible to have a "dip" sufficiently large to cause negative specific heat.



(c) Increasing the values of $c_0/m\omega_0^2$ we can create an window of temperature where the specific heat becomes negative. Note also that for a coupling within the range of the bath frequencies, $c_0 = m\omega_0^2$, we have a very large negative value. In Chapter 2 the lowest possible value for the specific heat was $-k_B/2$.

FIGURE 3.3: Specific Heat for the $N_S + N_B$ in the identical frequency model as we change different parameters isolated to see its influence.

Considering two systems, S and S' , with N particles, identical kinetic energy $T = T'$ and different potential energy $U(x_1, \dots, x_n)$ and $U'(x_1, \dots, x_n)$, written as:

$$U = \frac{1}{2} \vec{x} \mathbf{A} \vec{x} \quad ; \quad U' = \frac{1}{2} \vec{x} \mathbf{B} \vec{x}, \quad (3.36)$$

where: $\vec{x} = (x_1, \dots, x_N)$. We will list the eigenvalues of both matrices as $\{a_n\}$ and $\{b_n\}$ so that:

$$a_1 \leq a_2 \leq \dots \leq a_N \quad \text{and} \quad b_1 \leq b_2 \leq \dots \leq b_N. \quad (3.37)$$

The theorem states that if, for any value of \vec{x} , we have that:

$$\vec{x} \mathbf{B} \vec{x} \geq \vec{x} \mathbf{A} \vec{x}, \quad (3.38)$$

then:

$$a_1 \leq b_1, \quad a_2 \leq b_2, \quad \dots, \quad a_N \leq b_N. \quad (3.39)$$

We are going to read this statement as: when comparing two systems S and S' of harmonic oscillators with identical kinetic energy $T = T'$ and N degrees of freedom; if $U'(x_1, \dots, x_N) \geq U(x_1, \dots, x_N)$, then for every eigen-frequency ω_i of U there is an eigen-frequency ω'_i of U' so that $\omega_i \leq \omega'_i$.

Going back to the $N_S + N_B$ model, S is going to be the uncoupled system and bath and S' the coupled version. When we "turn on" the coupling, we introduce the interaction Hamiltonian where it is obvious that for any value of $\{q_k\}$ and $\{x_i\}$ we have:

$$H_{SB} = \sum_{k=1}^{N_S} \sum_{i=1}^{N_B} \frac{c_{ki}}{2} (q_k - x_i)^2 \geq 0, \quad (3.40)$$

since $c_{ik} \geq 0$ for any value of i and k . This allows us to write the relation between the eigen-frequencies:

$$\Omega_k \leq \tilde{\Omega}_k \quad \text{and} \quad \omega_i \leq \tilde{\omega}_i. \quad (3.41)$$

We can write the specific heat using (2.30):

$$\frac{C}{k_B} = \sum_{k=1}^{N_S-1} \frac{(\beta \hbar \tilde{\Omega}_k / 2)^2}{\sinh^2(\beta \hbar \tilde{\Omega}_k / 2)} + \sum_{k=1}^{N_B} \left\{ \frac{(\beta \hbar \tilde{\omega}_i / 2)^2}{\sinh^2(\beta \hbar \tilde{\omega}_i / 2)} - \frac{(\beta \hbar \omega_i / 2)^2}{\sinh^2(\beta \hbar \omega_i / 2)} \right\}. \quad (3.42)$$

We have already demonstrated in appendix A.4 that if we have $\omega_i \leq \tilde{\omega}_i$ then:

$$\frac{(\beta\hbar\tilde{\omega}_i/2)^2}{\sinh^2(\beta\hbar\tilde{\omega}_i/2)} - \frac{(\beta\hbar\omega_i/2)^2}{\sinh^2(\beta\hbar\omega_i/2)} = \delta_i \leq 0. \quad (3.43)$$

This means that for every bath oscillator we get a negative contribution on the specific heat. The specific heat becomes negative when the positive contribution of the shifted system frequencies $\tilde{\Omega}_k$ is inferior to negative one from the bath. By increasing the coupling we are also increasing the difference (3.43). Similarly, if we increase the value of bath oscillators, N_B , we are going to increase the amount of δ_i . This is in accordance with our findings for the identical frequency bath.

These results are, of course, purely qualitative and do not allow for a clear picture of how the frequencies are shifted but does allow us to conclude that the coupling mechanism pushes the frequencies to higher values.

3.2 The Effects of Potential Renormalization

Figure 3.3(c) depicts a behaviour that greatly differs from anything we expect from the Caldeira-Leggett model. In previous chapter we have obtained that for the Drude bath the specific heat could never be inferior to $-k_B/2$, while in figure 3.3(c) the difference is of the order $-7k_B$. This result served as a motivation to analyse more generally the effects of the potential renormalization.

3.2.1 Comparing Both Models

We start our analysis by comparing the simplest case of one system oscillator coupled to one bath oscillator within both the Caldeira-Leggett and the $N_S + N_B$ models:

$$H = \frac{P^2}{2M} + \frac{M\Omega_0^2}{2}q^2 + \frac{p^2}{2m} + \frac{m\omega_0^2}{2}x^2 + c_0(x - q)^2, \quad (3.44)$$

$$H' = \frac{P^2}{2M} + \frac{M\Omega_0^2}{2}q^2 + \frac{p^2}{2m} + \frac{m\omega_0^2}{2}x^2 - c_0qx + \frac{c_0^2}{2m\omega_0^2}q^2, \quad (3.45)$$

where we use ' to represent the Caldeira-Leggett model. Writing the spatial part of the Hamiltonian H as a vectorial product while also scaling out the masses ($\sqrt{M}q = \tilde{q}$, $\sqrt{m}x = \tilde{x}$) we obtain:

$$H \rightarrow \frac{1}{2} \begin{pmatrix} \tilde{q} & \tilde{x} \end{pmatrix} \begin{pmatrix} \Omega_0^2 + \frac{c_0}{M} & -\frac{c_0}{\sqrt{mM}} \\ -\frac{c_0}{\sqrt{mM}} & \omega_0^2 + \frac{c_0}{m} \end{pmatrix} \begin{pmatrix} \tilde{q} \\ \tilde{x} \end{pmatrix}, \quad (3.46)$$

which gives us the eigenvalue equation:

$$\begin{aligned} \lambda^4 - \lambda^2 \left(\Omega_0^2 + \omega_0^2 + \frac{c_0}{m} + \frac{c_0}{M} \right) + \left(\Omega_0^2 + \frac{c_0}{M} \right) \left(\omega_0^2 + \frac{c_0}{m} \right) - \frac{c_0^2}{mM} &= \\ &= (\lambda^2 - \omega_+^2) (\lambda^2 - \omega_-^2) = 0, \end{aligned} \quad (3.47)$$

where:

$$\omega_{\pm}^2 = \frac{1}{2} \left\{ \left(\Omega_0^2 + \omega_0^2 + \frac{c_0}{M} + \frac{c_0}{m} \right) \pm \sqrt{\left(\Omega_0^2 - \omega_0^2 + \frac{c_0}{M} - \frac{c_0}{m} \right)^2 + \frac{4c_0^2}{mM}} \right\}. \quad (3.48)$$

To simplify the treatment of the solution we are going to define dimension-less parameters:

$$\tilde{\Omega} = \frac{\Omega_0}{\omega_0} \quad ; \quad \tilde{c}_{(m)} = \frac{c_0}{m\omega_0^2} \quad ; \quad \tilde{c}_{(M)} = \frac{c_0}{M\omega_0^2} \quad ; \quad \lambda_{\pm} = \frac{\omega_{\pm}}{\omega_0}, \quad (3.49)$$

$$\lambda_{\pm}^2 = \frac{1}{2} \left\{ \tilde{\Omega}^2 + \tilde{c}_{(M)} + 1 + \tilde{c}_{(m)} \pm \sqrt{\left(\tilde{\Omega}^2 - 1 + \tilde{c}_{(M)} - \tilde{c}_{(m)} \right)^2 + 4\tilde{c}_{(m)}\tilde{c}_{(M)}} \right\}, \quad (3.50)$$

they are defined to use ω_0 as the primary parameter of comparison. Using (2.30) we obtain the specific heat:

$$\frac{C}{k_B} = \frac{\left(\frac{\hbar\omega_0}{2k_B T} \lambda_+ \right)^2}{\sinh^2 \left(\frac{\hbar\omega_0}{2k_B T} \lambda_+ \right)} + \frac{\left(\frac{\hbar\omega_0}{2k_B T} \lambda_- \right)^2}{\sinh^2 \left(\frac{\hbar\omega_0}{2k_B T} \lambda_- \right)} - \frac{\left(\frac{\hbar\omega_0}{2k_B T} \right)^2}{\sinh^2 \left(\frac{\hbar\omega_0}{2k_B T} \right)}. \quad (3.51)$$

Doing the same for the spatial part of H' :

$$H' \rightarrow \frac{1}{2} \begin{pmatrix} \tilde{q} & \tilde{x} \end{pmatrix} \begin{pmatrix} \Omega_0^2 + \frac{c_0^2}{Mm\omega_0^2} & -\frac{c_0}{\sqrt{mM}} \\ -\frac{c_0}{\sqrt{mM}} & \omega_0^2 \end{pmatrix} \begin{pmatrix} \tilde{q} \\ \tilde{x} \end{pmatrix}, \quad (3.52)$$

we obtain the eigenvalue equation:

$$\begin{aligned} \lambda^4 - \lambda^2 \left(\Omega_0^2 + \omega_0^2 + \frac{c_0^2}{mM\omega_0^2} \right) + \omega_0^2 \Omega_0^2 &= \\ &= (\lambda^2 - \omega_-'^2) (\lambda^2 - \omega_+'^2) = 0, \end{aligned} \quad (3.53)$$

that can be easily solved. The solutions, expressed using the same dimension-less parameters as before:

$$\lambda_{\pm}'^2 = \frac{1}{2} \left\{ \tilde{\Omega}^2 + 1 + \tilde{c}_{(m)}\tilde{c}_{(M)} \pm \sqrt{(\tilde{\Omega}^2 - 1)^2 + \tilde{c}_{(m)}\tilde{c}_{(M)} (2\tilde{\Omega}^2 + 2 + \tilde{c}_{(m)}\tilde{c}_{(M)})} \right\}. \quad (3.54)$$

Note that the terms $\tilde{c}_{(m)}$ and $\tilde{c}_{(M)}$ only appear together as $\tilde{c}_{(m)}\tilde{c}_{(M)}$. Because of that, we could avoid redundancy by easily redefining the parameters in such way that the

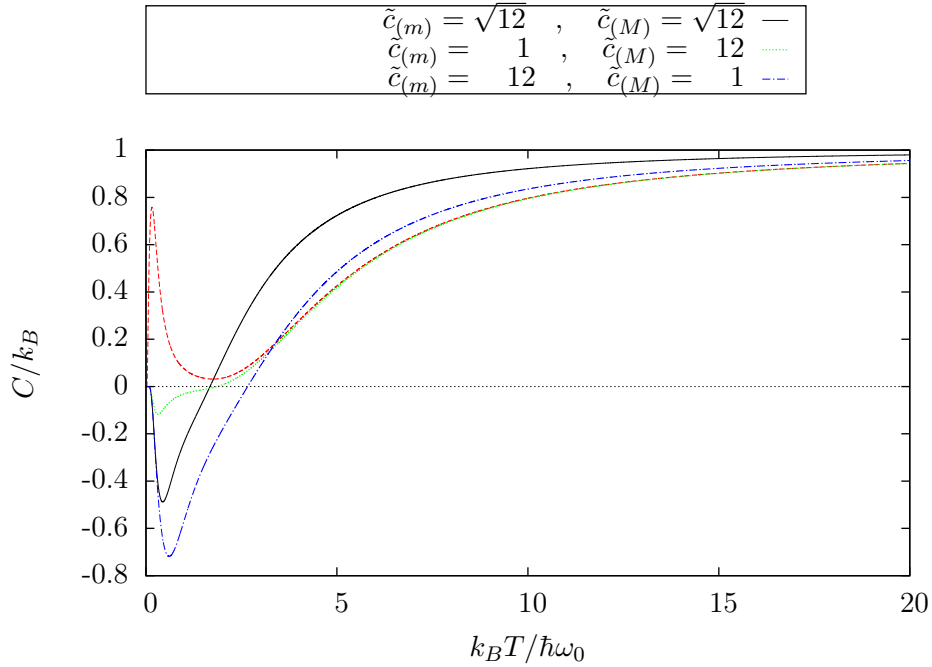


FIGURE 3.4: As we can see, for our choice of values for $\tilde{c}_{(m)}$ and $\tilde{c}_{(M)}$ we have that the product $\tilde{c}_{(m)}\tilde{c}_{(M)}$ remains the same, meaning that the standard Caldeira-Leggett version of the specific heat, in red - omitted from the top caption - stays the same. Also, $\tilde{\Omega} = 2$ for all graphs.

product becomes our new parameter. However, we will maintain the answer in these terms to allow for a direct comparison between both cases. In figure 3.4 you can see an example where we have different combinations of $\tilde{c}_{(m)}$ and $\tilde{c}_{(M)}$ and the specific heat of the standard Caldeira-Leggett model does not change. The specific heat associated with H' :

$$\frac{C'}{k_B} = \frac{\left(\frac{\hbar\omega_0}{2k_B T} \lambda'_+\right)^2}{\sinh^2\left(\frac{\hbar\omega_0}{2k_B T} \lambda'_+\right)} + \frac{\left(\frac{\hbar\omega_0}{2k_B T} \lambda'_-\right)^2}{\sinh^2\left(\frac{\hbar\omega_0}{2k_B T} \lambda'_-\right)} - \frac{\left(\frac{\hbar\omega_0}{2k_B T}\right)^2}{\sinh^2\left(\frac{\hbar\omega_0}{2k_B T}\right)}, \quad (3.55)$$

The demonstration used in Appendix A.4 to prove that the integration could never become negative applies here. All we have to do is demonstrate that at least one of the eigen-frequencies, in this case ω'_- since it is the smallest, will always be smaller than ω_0 . If we replace λ for 0 and ω_0 in expression (3.53) we get:

$$\lambda = 0 \quad \rightarrow \quad \omega_0^2 \Omega_0^2, \quad (3.56)$$

$$\lambda = \omega_0 \quad \rightarrow \quad -c_0^2/mM. \quad (3.57)$$

Therefore, one of the solutions has to be smaller than ω_0 . Because of that the specific heat calculated using the Caldeira-Leggett model is always positive for harmonic oscillators.

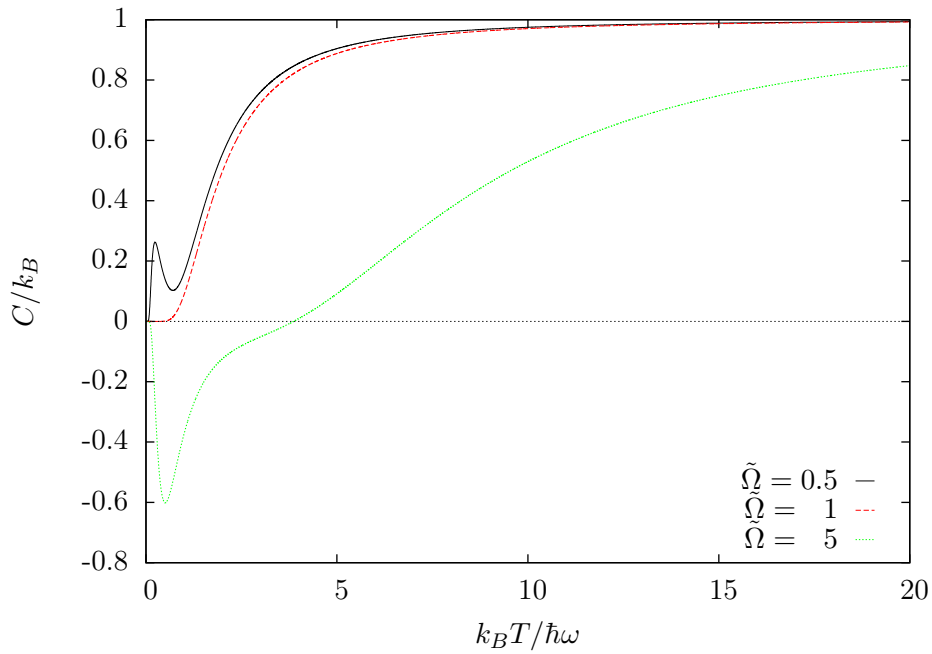


FIGURE 3.5: We illustrate here how for a fixed coupling, $\tilde{c}_{(m)} = 2$ and $\tilde{c}_{(M)} = 3$, it is possible to obtain negative values by increasing the value of $\tilde{\Omega}$.

Applying the same rationale for the specific heat within the $N_S + N_B$ model, using (3.47):

$$\lambda = 0 \rightarrow \omega_0^2 \Omega_0^2 + \frac{c_0 \Omega_0^2}{m} + \frac{c_0 \omega_0^2}{M}, \quad (3.58)$$

$$\lambda = \omega_0 \rightarrow \frac{c_0}{m} (\Omega_0^2 - \omega_0^2). \quad (3.59)$$

Therefore, by the same reasoning as before, if we have that $\Omega_0 < \omega_0$, one root must be smaller than ω_0 , making it impossible for the specific heat to become negative. On the other hand, if we have that $\Omega_0 > \omega_0$, we can no longer make such assertion. This restriction is not sufficient to ensure negative specific heat, it is however, necessary. Figure 3.5 serves as an example of how changing the frequency Ω_0 can cause negative specific heat for a fixed coupling c_0 .

It is very simple to understand such restriction. Using the theorem at section 3.1.4 we can conclude that:

$$\omega_- \geq \omega_0, \quad \omega_+ \geq \Omega_0. \quad (3.60)$$

Therefore, if we wish to have both frequencies ω_{\pm} greater than ω_0 , we need to have $\Omega_0 > \omega_0$.

3.2.2 Minimal Model for a General Potential Renormalization

The main difference between both models is how it renormalizes the potentials. To understand how the potential renormalization affects the results, let us assume a general system renormalization

$$H_{SB} = \frac{1}{2} \left(M\Delta_S + \frac{c_0^2}{m\omega_0^2} \right) q^2 - c_0 x q. \quad (3.61)$$

It becomes clear why we have decided to use this potential renormalization when we calculate the Langevin equation as we did in chapter 2 to obtain

$$\ddot{q} + \int_0^t ds \gamma(t-s) \dot{q}(s) + (\Omega_0^2 + \Delta_S) q = \xi(t), \quad (3.62)$$

where the damping kernel and the fluctuating force are defined as (2.13). We obtain from last equation that the effective potential on the Langevin equation is $M\Omega_0^2 + M\Delta_S$. Note that we *have* to impose that $\Delta_S > -\Omega_0^2$, otherwise we would switch the sign of the potential.

The spatial part of the Hamiltonian, assuming that H_S and H_B are written as (3.44), can be written as the matrix

$$\frac{1}{2} \begin{pmatrix} \tilde{q} & \tilde{x} \end{pmatrix} \begin{pmatrix} \Omega_0^2 + \Delta_S + \frac{c_0^2}{Mm\omega^2} & -\frac{c_0}{\sqrt{mM}} \\ -\frac{c_0}{\sqrt{mM}} & \omega_0^2 \end{pmatrix} \begin{pmatrix} \tilde{q} \\ \tilde{x} \end{pmatrix}, \quad (3.63)$$

with eigenvalue equation:

$$\lambda^4 - \lambda^2 \left(\Omega_0^2 + \omega_0^2 + \Delta_S + \frac{c_0^2}{mM\omega_0^2} \right) + \omega_0^2 \Omega_0^2 + \Delta_S \omega_0^2 = 0, \quad (3.64)$$

where we can employ the same technique to discover if one of the frequencies is smaller than ω_0 :

$$\lambda = 0 \quad \rightarrow \quad \omega_0^2(\Omega_0^2 + \Delta_S) \geq 0, \quad (3.65)$$

$$\lambda = \omega_0 \quad \rightarrow \quad -\frac{c_0^2}{mM} \leq 0. \quad (3.66)$$

Using our restriction that $\Delta_S \geq -\Omega_0^2$ we obtain that $\omega_0^2(\Omega_0^2 + \Delta_S)$ is either null or positive. For positive values we conclude that one of the coupled system eigenfrequencies is smaller than ω_0 , meaning that the specific heat for the harmonic oscillator is always positive [11].

If we have that $\Delta_S = -\Omega_0^2$, the Langevin equation will describe a free damped particle. The Hamiltonian will read

$$H = \frac{P^2}{2M} + \frac{p^2}{2m} + \frac{m\omega_0^2}{2}x^2 - c_0qx + \frac{c_0^2}{2m\omega_0^2}, \quad (3.67)$$

which can yield negative specific heat, as demonstrated in [11].

Despite allowing for any sort of potential renormalization for the system, imposing that the potential does not become negative, we obtained the same results as [11]. This leads us to believe that the different results of the Caldeira-Leggett and the $N_S + N_B$ model must be caused by the potential renormalization on the bath oscillators.

Motivated by this, let us define a new interaction Hamiltonian:

$$H_{SB} = \frac{m\Delta_B}{2}x^2 + \frac{1}{2} \left(M\Delta_S + \frac{c_0^2}{m(\omega_0^2 + \Delta_B)} \right) q^2 - c_0xq. \quad (3.68)$$

Note that we needed to incorporate the shifted frequency, $\omega_0^2 + \Delta_B$, in the renormalizing term in previous equation in order to ensure that the system potential in the Langevin equation be $M\Omega_0^2 + M\Delta_S$. The equations of motion of the bath coordinates are written as:

$$\ddot{x} + (\omega_0^2 + \Delta_B)x = \frac{c_0}{m}q, \quad (3.69)$$

forcing us to impose that $\Delta_B > -\omega_0^2$.

The spatial part of the coupled Hamiltonian can be written as the matrix:

$$\frac{1}{2} \begin{pmatrix} \tilde{q} & \tilde{x} \end{pmatrix} \begin{pmatrix} \Omega_0^2 + \Delta_S + \frac{c_0^2}{Mm\omega^2} & -\frac{c_0}{\sqrt{mM}} \\ -\frac{c_0}{\sqrt{mM}} & \omega_0^2 + \Delta_B \end{pmatrix} \begin{pmatrix} \tilde{q} \\ \tilde{x} \end{pmatrix}, \quad (3.70)$$

with eigenvalue equation:

$$\lambda^4 - \lambda^2 \left(\Omega_0^2 + \omega_0^2 + \Delta_B + \Delta_S + \frac{c_0^2}{mM(\omega_0^2 + \Delta_B)} \right) + (\omega_0^2 + \Delta_B)(\Omega_0^2 + \Delta_S) = 0. \quad (3.71)$$

Using the same technique as before:

$$\lambda = 0 \quad \rightarrow \quad (\omega_0^2 + \Delta_B)(\Omega_0^2 + \Delta_S) \geq 0, \quad (3.72)$$

$$\lambda = \omega_0 \quad \rightarrow \quad \Delta_B(\Omega_0^2 - \omega_0^2) - \frac{c_0^2\omega_0^2}{mM(\omega_0^2 + \Delta_B)} + \Delta_S\Delta_B. \quad (3.73)$$

We can be certain that it is possible to obtain negative specific heat for the harmonic oscillator, since the $N_S + N_B$ model is a particular case of our more general expression.

3.3 Final Remarks

In the Caldeira-Leggett model, the choice of $\Delta_B = \Delta_S = 0$ is not made for the sake of simplicity alone. We are interested in being able to compare the coupling a system under the influence of a potential V to a heat bath for different coupling strengths. Because of that our choice cannot describe every system, there are some situations, like the Lamb Shift [15], where the coupling with the environment does cause a potential renormalization.

If we take a look at the Langevin equation for the center of mass in the basis of the discrete Fourier transform [13]¹

$$M\ddot{Q}_{N_S} + M \int_0^t ds \gamma(t-s) \dot{Q}_{N_S} + M \left(\bar{\Omega}_0^2 + \sum_{i=1}^{N_B} \left\{ c_i - \frac{c_i^2}{m\tilde{\omega}_i^2} \right\} \right) Q_{N_S} = \xi(t), \quad (3.74)$$

where we have the damping kernel is defined as

$$\gamma(t) = \frac{N_S}{M} \sum_{i=1}^{N_B} \frac{c_i^2}{m\tilde{\omega}_i^2} \cos(\tilde{\omega}_i t). \quad (3.75)$$

From Langevin equation it becomes clear that the coupling causes the effective potential of the system to change. Also, the damping kernel is written with the shifted frequencies and not the uncoupled bath frequencies.

We can conclude that using this type of coupling causes us to loose comparability: for different coupling strengths we have a system with *different* effective potentials coupled to *different* heat baths. Further analysis on this type of model is required since based only in our findings with the minimal model we cannot understand exactly how the potential renormalization of the bath potential will affect our results, specially when considering more general models². We can be certain that the potential renormalization plays a central role on the specific heat anomalies. It seems to be the origin of the difference between the results of [11] and [13] and it cannot be glanced over.

¹We have adapted to our notation.

²The interpretation of these results were made with the collaboration of professor Gert-Ludwig Ingold of Augsburg University, Germany, through several email exchanges.

Chapter 4

System with Several Degrees of Freedom

At the beginning of chapter 3 we have raised two possibilities to explain the differences between the results of Ingold et al. [9, 11] and Hasegawa [13] (see the introduction of chapter 3). Having already studied the effects of the different potential renormalizations caused by the interaction Hamiltonian, we will now focus on the effects caused by the interacting system degrees of freedom. In order to isolate the effects caused by the interaction we must define new interaction Hamiltonians. They will have to preserve the bath frequency distribution and the effective potential of the Langevin equation on the system perspective.

Our calculations start by defining the system Hamiltonian as

$$H_S = \frac{P_1^2}{2M_1} + \frac{P_2^2}{2M_2} + \frac{M_1\Omega_1^2}{2}q_1^2 + \frac{M_2\Omega_2^2}{2}q_2^2 + \frac{K}{2}(q_1 - q_2)^2, \quad (4.1)$$

for a system with two oscillators. The parameter K represents the *internal coupling* between the system particles. We choose to analyse this Hamiltonian for its simplicity and will later use the results to pave the way for a system with N_S oscillators.

Our objective is to define a model that is simple enough to be analytically tractable, but not to the point where it becomes unusable to describe realistic situations.

The equations of motion for the system coordinates alone are:

$$\begin{aligned} M_1 \ddot{q}_1 &= -\{(M_1 \Omega_1 + K)q_1 - Kq_2\}, \\ M_2 \ddot{q}_2 &= -\{(M_2 \Omega_2 + K)q_2 - Kq_1\}. \end{aligned} \quad (4.2)$$

We must ensure that the potentials in the Langevin equation are the same as in equation above in order to retain comparability for different values of coupling strength.

The extra oscillator allow us to define different ways of coupling to a bath. We could have that both degrees of freedom are connected to the same bath 4.1, which is the same type of coupling that we did in chapter 3. There is also the possibility that each degree is connected to its own independent bath 4.3. We analyse both couplings ¹.

4.1 System Coupled to One Bath

Let us define the interaction Hamiltonian as

$$H_{SB} = \sum_{n=1}^{\infty} \left(\frac{c_n^2}{2m_n \omega_n^2} q_1^2 + \frac{d_n^2}{2m_n \omega_n^2} q_2^2 + \frac{c_n d_n}{m_n \omega_n^2} q_1 q_2 - c_n x_n q_1 - d_n x_n q_2 \right), \quad (4.3)$$

which makes:

$$H_{SB} + H_B = \sum_{n=1}^{\infty} \frac{p_n^2}{2m_n} + \frac{m_n \omega_n^2}{2} \left(x_n - \frac{c_n}{m_n \omega_n^2} q_1 - \frac{d_n}{m_n \omega_n^2} q_2 \right)^2. \quad (4.4)$$

It will become clear that this choice satisfies our restrictions when we obtain the Langevin equations. Figure 4.1 represents this model schematically.

4.1.1 The System perspective

Before we proceed to calculate the Langevin equations, let us first scale out the masses using the canonical transformation:

$$q_1 = \sqrt{M_1} \tilde{q}_1 \quad ; \quad q_2 = \sqrt{M_2} \tilde{q}_2, \quad (4.5)$$

$$\sqrt{M_1} P_1 = \tilde{P}_1 \quad ; \quad \sqrt{M_2} P_2 = \tilde{P}_2. \quad (4.6)$$

¹These models were proposed by during by professor Gert-Ludwig Ingold of Augsburg University, Germany, during a one month visit I made to his institution. I acknowledge the fruitful conversations we had during this period.

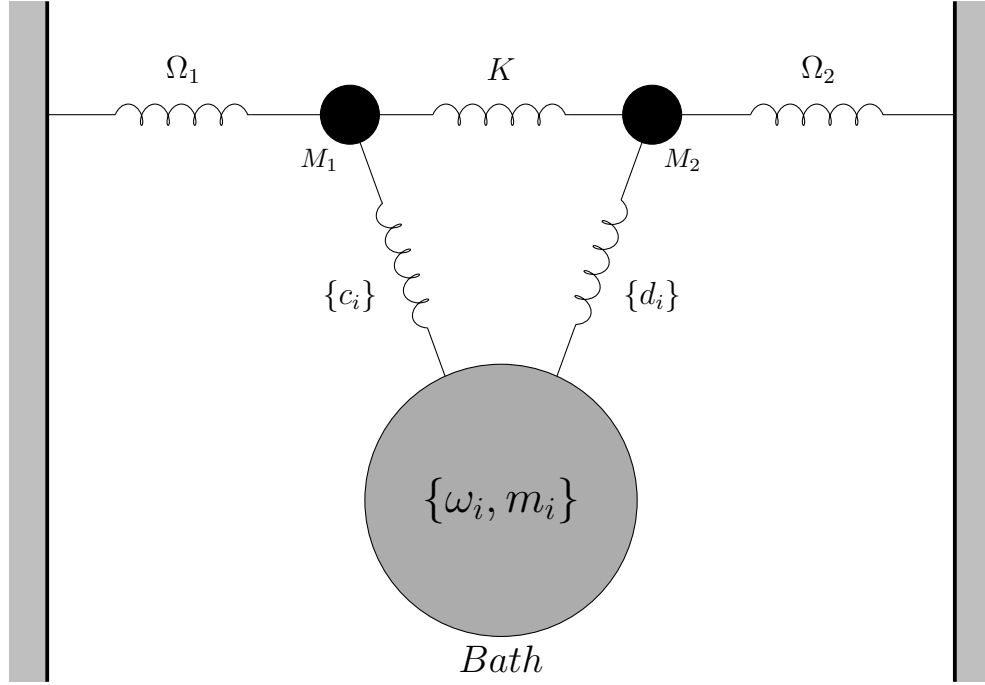


FIGURE 4.1: Representation of a model consisting of two system degrees of freedom coupled to each other, via the spring K , and coupled to a single bath. The collections of different couplings are represented by $\{c_i\}$ and $\{d_i\}$.

To further simplify the problem we shall define the new constants:

$$\tilde{K}_1 = \Omega_1^2 + \frac{K_1}{M_1} \quad ; \quad \tilde{K}_2 = \Omega_2^2 + \frac{K_2}{M_2} \quad ; \quad \tilde{K}_0 = \frac{K_0}{\sqrt{M_1 M_2}}, \quad (4.7)$$

and:

$$\sqrt{M_1} c_n = \tilde{c}_n \quad ; \quad \sqrt{M_2} d_n = \tilde{d}_n. \quad (4.8)$$

we can rewrite our Hamiltonians as:

$$H_S = \frac{1}{2} \left\{ \tilde{P}_1^2 + \tilde{P}_2^2 + \tilde{K}_1 \tilde{q}_1^2 + \tilde{K}_2 \tilde{q}_2^2 \right\} - \tilde{K}_0 \tilde{q}_1 \tilde{q}_2 \quad (4.9)$$

$$H_{SB} + H_B = \sum_{n=1}^{\infty} \frac{p_n^2}{2m_n} + \frac{m_n \omega_n^2}{2} \left(x_n - \frac{\tilde{c}_n}{m_n \omega_n^2} \tilde{q}_1 - \frac{\tilde{d}_n}{m_n \omega_n^2} \tilde{q}_2 \right)^2. \quad (4.10)$$

Now we can proceed to write the Langevin equations for the system oscillators. We start, as we did in chapter 2, using the Green's function for the harmonic oscillator to solve x_n :

$$\ddot{x}_n + \omega_n^2 x_n = \frac{\tilde{c}_n}{m_n} \tilde{q}_1 + \frac{\tilde{d}_n}{m_n} \tilde{q}_2, \quad (4.11)$$

with solutions:

$$x_n(t) = x_n(0) \cos(\omega_n t) + \frac{p_n(0)}{m_n \omega_n} \sin(\omega_n t) + \quad (4.12)$$

$$+ \int_0^t \frac{\tilde{c}_n \tilde{q}_1(s) + \tilde{d}_n \tilde{q}_2(s)}{\omega_n} \sin(\omega_n(t-s)) ds. \quad (4.13)$$

Using (2.12) in last equation we obtain that:

$$\begin{aligned} \sum_{n=1}^{\infty} \tilde{c}_n x_n &= \sum_{n=1}^{\infty} \tilde{c}_n \left\{ \left(x_n(0) - \frac{(\tilde{c}_n \tilde{q}_1(0) + \tilde{d}_n \tilde{q}_2(0))}{m_n \omega_n^2} \right) \cos(\omega_n t) + \frac{p_n(0)}{m_n \omega_n} \sin(\omega_n t) \right. \\ &\quad \left. + \frac{\tilde{c}_n \tilde{q}_1 + \tilde{d}_n \tilde{q}_2}{m_n \omega_n^2} - \int_0^t \frac{\tilde{c}_n \dot{\tilde{q}}_1(s) + \tilde{d}_n \dot{\tilde{q}}_2(s)}{m_n \omega_n^2} \cos(\omega_n(t-s)) ds \right\}, \end{aligned} \quad (4.14)$$

$$\begin{aligned} \sum_{n=1}^{\infty} \tilde{d}_n x_n &= \sum_{n=1}^{\infty} \tilde{d}_n \left\{ \left(x_n(0) - \frac{(\tilde{c}_n \tilde{q}_1(0) + \tilde{d}_n \tilde{q}_2(0))}{m_n \omega_n^2} \right) \cos(\omega_n t) + \frac{p_n(0)}{m_n \omega_n} \sin(\omega_n t) \right. \\ &\quad \left. + \frac{\tilde{c}_n \tilde{q}_1 + \tilde{d}_n \tilde{q}_2}{m_n \omega_n^2} - \int_0^t \frac{\tilde{c}_n \dot{\tilde{q}}_1(s) + \tilde{d}_n \dot{\tilde{q}}_2(s)}{m_n \omega_n^2} \cos(\omega_n(t-s)) ds \right\}. \end{aligned} \quad (4.15)$$

Defining the damping kernels:

$$\gamma_1(t) = \frac{1}{M_1} \sum_{n=1}^{\infty} \frac{c_n^2}{m_n \omega_n^2} \cos(\omega_n t) = \sum_{n=1}^{\infty} \frac{\tilde{c}_n^2}{m_n \omega_n^2} \cos(\omega_n t), \quad (4.16)$$

$$\gamma_2(t) = \frac{1}{M_2} \sum_{n=1}^{\infty} \frac{d_n^2}{m_n \omega_n^2} \cos(\omega_n t) = \sum_{n=1}^{\infty} \frac{\tilde{d}_n^2}{m_n \omega_n^2} \cos(\omega_n t), \quad (4.17)$$

$$\gamma_0(t) = \frac{1}{\sqrt{M_1 M_2}} \sum_{n=1}^{\infty} \frac{c_n d_n}{m_n \omega_n^2} \cos(\omega_n t) = \sum_{n=1}^{\infty} \frac{\tilde{c}_n \tilde{d}_n}{m_n \omega_n^2} \cos(\omega_n t), \quad (4.18)$$

where the subscript 0 stands for crossed term that couples \tilde{q}_1 and \tilde{q}_2 :

$$\begin{aligned} \tilde{\xi}_1(t) &= \sum_{n=1}^{\infty} \tilde{c}_n \left\{ \left(x_n(0) - \frac{(\tilde{c}_n \tilde{q}_1(0) + \tilde{c}_n \tilde{q}_2(0))}{m_n \omega_n^2} \right) \cos(\omega_n t) + \right. \\ &\quad \left. + \frac{p_n(0)}{m_n \omega_n} \sin(\omega_n t) \right\}, \end{aligned} \quad (4.19)$$

$$\begin{aligned} \tilde{\xi}_2(t) &= \sum_{n=1}^{\infty} \tilde{d}_n \left\{ \left(x_n(0) - \frac{(\tilde{c}_n \tilde{q}_1(0) + \tilde{d}_n \tilde{q}_2(0))}{m_n \omega_n^2} \right) \cos(\omega_n t) + \right. \\ &\quad \left. + \frac{p_n(0)}{m_n \omega_n} \sin(\omega_n t) \right\}. \end{aligned} \quad (4.20)$$

Note that we can re-write:

$$\begin{aligned} \sum_{n=1}^{\infty} \tilde{c}_n x_n &= \tilde{\xi}_1(t) - \int_0^t (\gamma_1(t-s)\dot{\tilde{q}}_1(s) + \gamma_0(t-s)\dot{\tilde{q}}_2(s)) ds + \\ &+ \sum_{n=1}^{\infty} \left(\frac{\tilde{c}_n^2}{m_n \omega_n^2} \tilde{q}_1 + \frac{\tilde{c}_n \tilde{d}_n}{m_n \omega_n^2} \tilde{q}_2 \right), \end{aligned} \quad (4.21)$$

$$\begin{aligned} \sum_{n=1}^{\infty} \tilde{d}_n x_n &= \tilde{\xi}_1(t) - \int_0^t (\gamma_2(t-s)\dot{\tilde{q}}_2(s) + \gamma_0(t-s)\dot{\tilde{q}}_1(s)) ds + \\ &+ \sum_{n=1}^{\infty} \left(\frac{\tilde{d}_n^2}{m_n \omega_n^2} \tilde{q}_2 + \frac{\tilde{c}_n \tilde{d}_n}{m_n \omega_n^2} \tilde{q}_1 \right). \end{aligned} \quad (4.22)$$

We can finally remove the bath from the equations of motion:

$$\ddot{\tilde{q}}_1 + \tilde{K}_1 \tilde{q}_1 - \tilde{K}_0 \tilde{q}_2 = \sum_{n=1}^{\infty} \left\{ \tilde{c}_n x_n - \frac{\tilde{c}_n \tilde{d}_n}{m_n \omega_n^2} \tilde{q}_2 - \frac{\tilde{c}_n^2}{m_n \omega_n^2} \tilde{q}_1 \right\}, \quad (4.23)$$

$$\ddot{\tilde{q}}_2 + \tilde{K}_2 \tilde{q}_2 - \tilde{K}_0 \tilde{q}_1 = \sum_{n=1}^{\infty} \left\{ \tilde{d}_n x_n - \frac{\tilde{c}_n \tilde{d}_n}{m_n \omega_n^2} \tilde{q}_1 - \frac{\tilde{d}_n^2}{m_n \omega_n^2} \tilde{q}_2 \right\}, \quad (4.24)$$

giving us the Langevin equations:

$$\ddot{\tilde{q}}_1 + \int_0^t [\gamma_1(t-s)\dot{\tilde{q}}_1(s) + \gamma_0(t-s)\dot{\tilde{q}}_2(s)] ds + \tilde{K}_1 \tilde{q}_1 - \tilde{K}_0 \tilde{q}_2 = \tilde{\xi}_1(t), \quad (4.25)$$

$$\ddot{\tilde{q}}_2 + \int_0^t [\gamma_0(t-s)\dot{\tilde{q}}_1(s) + \gamma_2(t-s)\dot{\tilde{q}}_2(s)] ds + \tilde{K}_2 \tilde{q}_2 - \tilde{K}_0 \tilde{q}_1 = \tilde{\xi}_2(t). \quad (4.26)$$

It is important to note that even if we had no internal coupling, $K = 0$, we would still have that the crossed damping kernel, $\gamma_0(t)$, couples the system oscillators, acting as a new internal coupling. This happens because the bath oscillators serve as "mediators", transmitting the perturbation from one system oscillator to the other. We will call this term the *indirect interaction term*. Within our model, we cannot remove the indirect interaction by redefining our parameters. We would need to add an extra term that is time dependent in order to compensate the effect of $\gamma_0(t)$.

4.1.2 The Vectorial Equation

At this point it is convenient to introduce a vectorial notation that will simplify the treatment of our equations. Having removed the bath variables, we will represent our system of differential equations using linear operators².

²It is common to see these type of operators referred to as *super-operators* since they act on other operators, in this case the position operator.

We start by defining the position vector:

$$\tilde{\mathbf{q}} = \begin{pmatrix} \tilde{q}_1 \\ \tilde{q}_2 \end{pmatrix}, \quad (4.27)$$

and the system interaction operator:

$$\hat{K} = \begin{pmatrix} \tilde{K}_1 & -\tilde{K}_0 \\ -\tilde{K}_0 & \tilde{K}_2 \end{pmatrix}. \quad (4.28)$$

We are going to use the *hat* ($\hat{}$) to mean linear operator throughout this chapter.³ Continuing with our definitions, the fluctuating force vector:

$$\xi = \begin{pmatrix} \xi_1 \\ \xi_2 \end{pmatrix}. \quad (4.29)$$

Lastly, we define the operator representing the damping kernel in two equivalent forms:

$$\begin{aligned} \hat{\Gamma}\mathbf{f}(t) &= \int_0^t ds \sum_{n=1}^{\infty} \frac{\cos(\omega_n(t-s))}{m_n\omega_n^2} \begin{pmatrix} \tilde{c}_n^2 & \tilde{c}_n\tilde{d}_n \\ \tilde{c}_n\tilde{d}_n & \tilde{d}_n^2 \end{pmatrix} \mathbf{f}(s) \\ &= \int_0^t ds \begin{pmatrix} \gamma_1(t-s) & \gamma_0(t-s) \\ \gamma_0(t-s) & \gamma_2(t-s) \end{pmatrix} \mathbf{f}(s). \end{aligned} \quad (4.30)$$

The Langevin equation, in a vectorial notation, becomes:

$$\left[\frac{d^2}{dt^2} + \hat{\Gamma} \frac{d}{dt} + \hat{K} \right] \tilde{\mathbf{q}}(t) = \xi(t). \quad (4.31)$$

Within the vectorial notation it becomes clear that if our system of equations can be uncoupled, then (4.31) can be diagonalized and solved analytically. That is certainly not the case for any given \hat{K} or $\hat{\Gamma}$. There is no doubt that \hat{K} can be diagonalized but we must ensure that both operators can be diagonalized simultaneously.

Note that $\hat{\Gamma}$ is composed of a sum of matrices, all of which, for any coupling, can be individually diagonalized, but to have that all matrices can be simultaneously diagonalized we must have that the commutator of any pair of matrices equals zero. In the summation form of (4.30),

$$\begin{pmatrix} \tilde{c}_n^2 & \tilde{c}_n\tilde{d}_n \\ \tilde{c}_n\tilde{d}_n & \tilde{d}_n^2 \end{pmatrix} \begin{pmatrix} \tilde{c}_m^2 & \tilde{c}_m\tilde{d}_m \\ \tilde{c}_m\tilde{d}_m & \tilde{d}_m^2 \end{pmatrix} - \begin{pmatrix} \tilde{c}_m^2 & \tilde{c}_m\tilde{d}_m \\ \tilde{c}_m\tilde{d}_m & \tilde{d}_m^2 \end{pmatrix} \begin{pmatrix} \tilde{c}_n^2 & \tilde{c}_n\tilde{d}_n \\ \tilde{c}_n\tilde{d}_n & \tilde{d}_n^2 \end{pmatrix} = 0. \quad (4.32)$$

³Not to be confused with the *hat* used to represent the Laplace transform of the damping kernel $\hat{\gamma}(z)$.

From last expression we can obtain a restriction for \tilde{c}_n and \tilde{d}_n :

$$-\tilde{c}_n \tilde{c}_m^2 \tilde{d}_n + \tilde{c}_n^2 \tilde{c}_m \tilde{d}_m - \tilde{c}_m \tilde{d}_n^2 \tilde{d}_m + \tilde{c}_n \tilde{d}_n \tilde{d}_m^2 = 0. \quad (4.33)$$

Let us further assume that $\tilde{c}_n = \tilde{c}_0$ and $\tilde{d}_n = \tilde{d}_0$. In this situation all the matrices would be the same,

$$\begin{pmatrix} \tilde{c}_0^2 & \tilde{c}_0 \tilde{d}_0 \\ \tilde{c}_0 \tilde{d}_0 & \tilde{d}_0^2 \end{pmatrix} \rightarrow \begin{pmatrix} \tilde{c}_0^2 + \tilde{d}_0^2 & 0 \\ 0 & 0 \end{pmatrix}, \quad (4.34)$$

with eigenvectors:

$$|\tilde{c}_0^2 + \tilde{d}_0^2\rangle = \frac{1}{\sqrt{\tilde{c}_0^2 + \tilde{d}_0^2}} \begin{pmatrix} \tilde{c}_0 \\ \tilde{d}_0 \end{pmatrix} ; \quad |0\rangle = \frac{1}{\sqrt{\tilde{c}_0^2 + \tilde{d}_0^2}} \begin{pmatrix} \tilde{d}_0 \\ -\tilde{c}_0 \end{pmatrix}. \quad (4.35)$$

The problem it is that the basis of eigenvectors depends on the couplings. Since we wish to find a basis that also diagonalizes \hat{K} , having the eigenvectors depending on the couplings will force us to choose our internal coupling based on the coupling to the bath.

Probably the simplest way to bypass this problem is to impose that the scaled couplings are the same for all system particles, that is $\tilde{c}_n = \tilde{d}_n$, which is equivalent to say that the ratio of coupling strengths must be the same as the inverse of the square root of the ratio of masses $c_n/d_n = \sqrt{M_2/M_1}$. Because of that we can conclude that the simplest possible situation would be where the coupling strengths are identical to both system oscillators ($c_n = d_n$) and that the system masses are the same ($M_1 = M_2 = M$).

The damping kernel operator becomes

$$\hat{\Gamma}\mathbf{f}(t) = \int_0^t ds \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \gamma(t-s)\mathbf{f}(s), \quad (4.36)$$

leaving us to diagonalize

$$\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \rightarrow \begin{pmatrix} 2 & 0 \\ 0 & 0 \end{pmatrix}. \quad (4.37)$$

The eigenvector basis is composed of the center of mass and the relative motion:

$$|M\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} ; \quad |\mu\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}. \quad (4.38)$$

Within this restrictions we are free to define any spectral density $J(\omega)$ but must also have that \hat{K} can be diagonalized on the coordinates of the center of mass and the relative

motion so it is possible to uncouple the degrees of freedom.

4.1.3 Extension for N_S Degrees of Freedom

Using the vectorial notation we can extend our calculation from 2 to N_S system oscillators. We start by redefining the coordinate vectors:

$$\tilde{\mathbf{q}} = \begin{pmatrix} \tilde{q}_1 \\ \tilde{q}_2 \\ \vdots \\ \tilde{q}_{N_S} \end{pmatrix} ; \quad \tilde{\mathbf{p}} = \begin{pmatrix} \tilde{P}_1 \\ \tilde{P}_2 \\ \vdots \\ \tilde{P}_{N_S} \end{pmatrix}. \quad (4.39)$$

The internal coupling between system degrees of freedom can be expressed generically using the matrix \tilde{K} as:

$$\begin{pmatrix} \frac{1}{\sqrt{M_1}} & 0 & \cdots & 0 \\ 0 & \frac{1}{\sqrt{M_2}} & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \frac{1}{\sqrt{M_{N_S}}} \end{pmatrix} \begin{pmatrix} M_1\Omega_1^2 + K_1 & -K_{12} & \cdots & -K_{1N_S} \\ -K_{12} & M_2\Omega_2^2 + K_2 & \cdots & -K_{2N_S} \\ \vdots & \vdots & \ddots & \vdots \\ -K_{1N_S} & -K_{2N_S} & \cdots & M_{N_S}\Omega_{N_S}^2 + K_{N_S} \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{M_1}} & 0 & \cdots & 0 \\ 0 & \frac{1}{\sqrt{M_2}} & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \frac{1}{\sqrt{M_{N_S}}} \end{pmatrix}. \quad (4.40)$$

It is convenient to define a new vector with N_S components that represents the coupling between the system and bath variables:

$$\mathbf{c}_n = \begin{pmatrix} c_n^{(1)} \\ c_n^{(2)} \\ \vdots \\ c_n^{(N_S)} \end{pmatrix} ; \quad \tilde{\mathbf{c}}_n = \begin{pmatrix} \sqrt{M_1}c_n^{(1)} \\ \sqrt{M_2}c_n^{(2)} \\ \vdots \\ \sqrt{M_{N_S}}c_n^{(N_S)} \end{pmatrix} = \begin{pmatrix} \tilde{c}_n^{(1)} \\ \tilde{c}_n^{(2)} \\ \vdots \\ \tilde{c}_n^{(N_S)} \end{pmatrix}, \quad (4.41)$$

with the scaled version obeying:

$$\mathbf{c}_n \mathbf{q} = \tilde{\mathbf{c}}_n \tilde{\mathbf{q}}. \quad (4.42)$$

We are taking $c_n^{(m)}$ to represent the coupling between the n -th bath oscillator and the m -th system oscillator.

Using these definitions allows us to write the Hamiltonians as:

$$H_S = \frac{1}{2} \{ \tilde{\mathbf{p}} \tilde{\mathbf{p}} + \tilde{\mathbf{q}} \hat{K} \tilde{\mathbf{q}} \}, \quad (4.43)$$

$$H_{SB} + H_B = \sum_{n=1}^{\infty} \left\{ \frac{p_n^2}{2m_n} + \frac{m_n \omega_n^2}{2} (x_n - \tilde{\mathbf{c}}_n \tilde{\mathbf{q}})^2 \right\}. \quad (4.44)$$

Previously we decided to introduce the vectorial notation to simplify the work with the Langevin equations, here we use the vectorial notation to rewrite the Hamiltonian, and then proceed to obtain the Langevin equations already in vector form. Using this notation, the calculations are very similar to the ones in chapter 2. We start from the bath equations of motion:

$$\ddot{x}_n + \omega_n^2 x_n = \frac{\tilde{\mathbf{c}}_n \tilde{\mathbf{q}}}{m_n}, \quad (4.45)$$

solved as:

$$x_n(t) = x_n(0) \cos(\omega_n t) + \frac{p_n(0)}{m_n \omega_n} \sin(\omega_n t) + \int_0^t \frac{\tilde{\mathbf{c}}_n \tilde{\mathbf{q}}(s)}{\omega_n} \sin(\omega_n(t-s)) ds. \quad (4.46)$$

Using (2.12) in last equation we obtain that:

$$\begin{aligned} \sum_{n=1}^{\infty} \tilde{\mathbf{c}}_n x_n &= \sum_{n=1}^{\infty} \tilde{\mathbf{c}}_n \left\{ \left(x_n(0) - \frac{\tilde{\mathbf{c}}_n \tilde{\mathbf{q}}(0)}{m_n \omega_n^2} \right) \cos(\omega_n t) + \frac{p_n(0)}{m_n \omega_n} \sin(\omega_n t) + \right. \\ &\quad \left. + \frac{\tilde{\mathbf{c}}_n \tilde{\mathbf{q}}}{m_n \omega_n^2} - \int_0^t \frac{\tilde{\mathbf{c}}_n \dot{\tilde{\mathbf{q}}}(s)}{m_n \omega_n^2} \cos(\omega_n(t-s)) ds \right\}, \end{aligned} \quad (4.47)$$

defining also the vectorial expression for the fluctuating force:

$$\xi = \begin{pmatrix} \xi_1 \\ \xi_2 \\ \vdots \\ \xi_{N_S} \end{pmatrix}; \quad \xi_i(t) = \tilde{c}_n^{(i)} \left(x_n(0) - \frac{\tilde{\mathbf{c}}_n \tilde{\mathbf{q}}(0)}{m_n \omega_n^2} \right) \cos(\omega_n t) + \frac{p_n(0)}{m_n \omega_n} \sin(\omega_n t) \quad (4.48)$$

and $\hat{\Gamma}$:

$$\hat{\Gamma} f(t) = \int_0^t ds \frac{\cos(t-s)}{m_n \omega_n^2} \begin{pmatrix} \left(\tilde{c}_n^{(1)} \right)^2 & \tilde{c}_n^{(1)} \tilde{c}_n^{(2)} & \dots & \tilde{c}_n^{(1)} \tilde{c}_n^{(N_S)} \\ \tilde{c}_n^{(1)} \tilde{c}_n^{(2)} & \left(\tilde{c}_n^{(2)} \right)^2 & \dots & \tilde{c}_n^{(2)} \tilde{c}_n^{(N_S)} \\ \vdots & \vdots & \ddots & \vdots \\ \tilde{c}_n^{(1)} \tilde{c}_n^{(N_S)} & \tilde{c}_n^{(2)} \tilde{c}_n^{(N_S)} & \dots & \left(\tilde{c}_n^{(N_S)} \right)^2 \end{pmatrix} f(s). \quad (4.49)$$

The vectorial equations of motion for the system become:

$$\left\{ \frac{d^2}{dt^2} + \hat{K} \right\} \tilde{\mathbf{q}} = \sum_{n=1}^{\infty} \tilde{\mathbf{c}}_n x_n \quad (4.50)$$

$$\left\{ \frac{d^2}{dt^2} + \hat{\Gamma} \frac{d}{dt} + \hat{K} \right\} \tilde{\mathbf{q}} = \xi. \quad (4.51)$$

This is the same expression that we obtained before, only that now we are dealing with higher dimensions.

Returning to the configuration where all the coupling strengths are the same ($c_n^{(i)} = c_n$) and all the system masses are the same ($M_k = M$), $\hat{\Gamma}$ becomes:

$$\hat{\Gamma}f(t) = \int_0^t ds \frac{\tilde{c}_n^2}{m_n \omega_n^2} \cos(t-s) \begin{pmatrix} 1 & 1 & \dots & 1 \\ 1 & 1 & \dots & 1 \\ \vdots & \vdots & \ddots & \vdots \\ 1 & 1 & \dots & 1 \end{pmatrix} f(s). \quad (4.52)$$

The center of mass is clearly an eigenvector with eigenvalue N_S :

$$\begin{pmatrix} 1 & 1 & \dots & 1 \\ 1 & 1 & \dots & 1 \\ \vdots & \vdots & \ddots & \vdots \\ 1 & 1 & \dots & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 1 \\ \vdots \\ 1 \end{pmatrix} = N_S \begin{pmatrix} 1 \\ 1 \\ \vdots \\ 1 \end{pmatrix}, \quad (4.53)$$

and since all the lines are equal, its null space has a dimension of $N_S - 1$. For instance, the relative motion of consecutive components is a complete basis for the null space:

$$\mathbf{v}_1 = \begin{pmatrix} 1 \\ -1 \\ 0 \\ \vdots \\ 0 \\ 0 \end{pmatrix}; \quad \mathbf{v}_2 = \begin{pmatrix} 0 \\ 1 \\ -1 \\ \vdots \\ 0 \\ 0 \end{pmatrix}; \quad \dots; \quad \mathbf{v}_{N_S} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \vdots \\ 1 \\ -1 \end{pmatrix}. \quad (4.54)$$

This is just an example. The most important information here is that it is necessary to have at least one eigenvector of \hat{K} to be the center of mass. There is no restriction on the other eigenvectors since the null space of Γ can be represented using any basis (we use another one at 4.2).

4.2 A Few Examples

Without Internal Coupling ($\hat{K} = 0$)

The idea of solving for a system without any internal coupling may seem trivial, but it will allow us to isolate the contribution of the indirect coupling.

Considering a system with two degrees and same mass, we have the Hamiltonian:

$$H = \frac{\tilde{P}_1^2}{2} + \frac{\tilde{P}_2^2}{2} + \sum_{n=1}^{\infty} \left\{ \frac{p_n^2}{2m_n} + \frac{m_n \omega_n^2}{2} \left(x_n - \frac{\tilde{c}_n}{m_n \omega_n^2} (\tilde{q}_1 + \tilde{q}_2) \right)^2 \right\}. \quad (4.55)$$

We have already discovered in the previous section that for a case of $N_S = 2$ and identical coupling with the bath, the eigenvectors are the center of mass and the relative motion. We transform our variables:

$$\bar{q}_M = \frac{1}{\sqrt{2}}(\tilde{q}_1 + \tilde{q}_2) \quad ; \quad \bar{q}_\mu = \frac{1}{\sqrt{2}}(\tilde{q}_1 - \tilde{q}_2). \quad (4.56)$$

With this transformation we obtain that the degree of freedom associated with the relative motion is a free particle *uncoupled* to the bath, while the degree of freedom associated with the center of mass is a free particle *coupled* to the bath:

$$H = \frac{\hat{P}_\mu^2}{2} + \left\{ \frac{\hat{P}_M^2}{2} + \sum_{n=1}^{\infty} \left(\frac{p_n^2}{2m_n} + \frac{m_n \omega_n^2}{2} \left(x_n - \frac{\sqrt{2}c_n}{m_n \omega_n^2} \bar{q}_M \right)^2 \right) \right\}. \quad (4.57)$$

Assuming our system is inside a box of length L , the partition function of the reduced becomes the product of the uncoupled (subscript u) and the coupled (subscript c) free particle:

$$Z = \left(\frac{L}{\hbar} \sqrt{\frac{2\pi M}{\beta}} \right) \left\{ \frac{L}{\hbar} \sqrt{\frac{2\pi M}{\beta}} \prod_{n=1}^{\infty} \frac{\nu_n}{\nu_n + \hat{\gamma}(\nu_n)} \right\} = Z_u Z_c. \quad (4.58)$$

The specific heat is calculated:

$$\frac{C}{k_B} = \beta^2 \frac{d^2}{d\beta^2} \ln(Z_u Z_c) = \beta^2 \frac{d^2}{d\beta^2} (\ln Z_u + \ln Z_c) = C_u + C_c. \quad (4.59)$$

We can obtain in textbooks the specific heat of the free quantum particle:

$$\frac{C_u}{k_B} = \frac{1}{2}, \quad (4.60)$$

and we have already calculated for the case the free particle in chapter 2. Let us consider the Drude bath:

$$2\hat{\gamma}(z) = 2\gamma \frac{\omega_D}{z + \omega_D} = \gamma' \frac{\omega_D}{z + \omega_D}. \quad (4.61)$$

The factor 2 appears naturally at (4.53) since $N_S = 2$. That is no problem since we can scale $\gamma = \gamma'/2$. Using the change in spectral density (2.114) and expression (2.36) we conclude:

$$\begin{aligned} \frac{C_c}{k_B} &= \int_0^{\infty} \left\{ \frac{\omega_1}{\omega_1^2 + \omega^2} + \frac{\omega_2}{\omega_2^2 + \omega^2} - \frac{\omega_D}{\omega_D^2 + \omega^2} \right\} C_{\text{ho}}(\omega) d\omega \geq \\ &\geq \int_0^{\infty} \frac{-\omega_D}{\omega_D^2 + \omega^2} d\omega = -\frac{1}{2}. \end{aligned} \quad (4.62)$$

With this restriction we obtain that the specific heat will always be positive:

$$\frac{C_u}{k_B} + \frac{C_c}{k_B} \geq 0. \quad (4.63)$$

Figure (4.2) aims to illustrate the behaviour of the specific heat in a few cases.

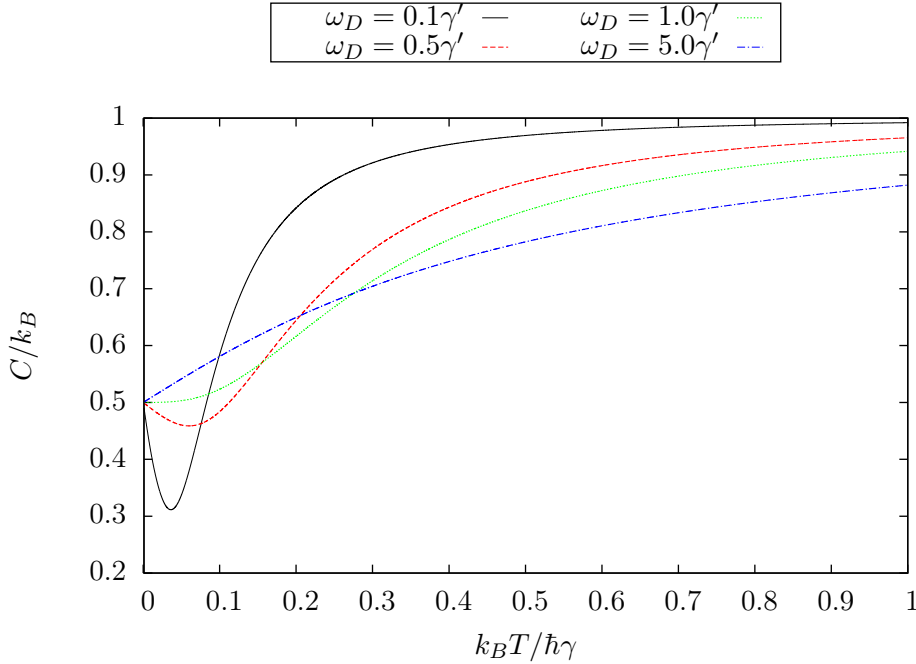


FIGURE 4.2: A simple figure showing the behaviour of $C_u/k_B + C_c/k_B$ for different values of ω_D . Note how the specific heat consists on the damped free particle translated by $+k_B/2$ by the influence of the uncoupled free particle.

Oscillator Ring

The Oscillator Ring is a model with the same internal coupling as the $N_S + N_B$ model in chapter 3. Because of that, most of the calculations have already been made so that we only need to adjust them for our model. Let us show that the discrete Fourier transform used at (3.10) is a basis of eigenvectors of $\hat{\Gamma}$:

$$\tilde{Q}_k = \frac{1}{\sqrt{N_S}} \sum_{i=1}^{N_S} \tilde{q}_i e^{2\pi i k i / N_S} \quad ; \quad \tilde{q}_i = \frac{1}{\sqrt{N_S}} \sum_{k=1}^{N_S} \tilde{Q}_k e^{-2\pi i k i / N_S}. \quad (4.64)$$

In vectorial form the transformation becomes:

$$\tilde{\mathbf{Q}} = \hat{A} \tilde{\mathbf{q}} \quad ; \quad (\hat{A})_{i,j} = \frac{1}{\sqrt{N_S}} e^{2\pi i k i / N_S}. \quad (4.65)$$

We can show that the transformation is also a basis of $\hat{\Gamma}$ since:

$$\hat{A}^* \begin{pmatrix} 1 & 1 & \dots & 1 \\ 1 & 1 & \dots & 1 \\ \vdots & \vdots & \ddots & \vdots \\ 1 & 1 & \dots & 1 \end{pmatrix} \hat{A} = \begin{pmatrix} 0 & 0 & \dots & 0 \\ 0 & 0 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & N_S \end{pmatrix}. \quad (4.66)$$

The system matrix will be the same as (3.18) with the coupling and bath Hamiltonians becoming:

$$\sum_{n=1}^{\infty} \left\{ \frac{p_n^2}{2m_n} + \frac{m_n \omega_n^2}{2} \left(x_n - \frac{\sqrt{N_S} c_n}{m_n \omega_n^2} \tilde{Q}_{N_S} \right)^2 \right\}, \quad (4.67)$$

we need to scale the damping kernel like we did in previous example:

$$\gamma'(t) = N_S \gamma(t). \quad (4.68)$$

Only the degree of freedom of the center of mass is coupled to the bath, all others are uncoupled harmonic oscillators. Unlike in chapter 3, the uncoupled harmonic oscillators do not have their potentials renormalized. The partition function of an uncoupled harmonic oscillator can be obtained in textbooks of statistical mechanics:

$$Z_u(\omega) = \frac{1}{2 \sinh(\hbar\beta\omega/2)}. \quad (4.69)$$

Our reduced partition function will be composed of a product of the uncoupled harmonic oscillators with the coupled one ((2.40)):

$$Z = \prod_{i=1}^{N_S-1} Z_u(\Omega_i) \left\{ \frac{1}{\hbar\beta\Omega_{N_S}} \prod_{n=1}^{\infty} \frac{\nu_n^2}{\nu_n^2 + \nu_n \hat{\gamma}(\nu_n) + \Omega_{N_S}^2} \right\}. \quad (4.70)$$

We remind the reader that Ω_i is defined by expression (3.19). Note that this definition for the reduced partition function is only true if $\Omega_{N_S} \neq 0$. In the case of the Drude bath, the specific heat becomes:

$$\frac{C}{k_B} = \sum_{i=1}^{N_S-1} C_{\text{ho}}(\Omega_i) + \frac{C_2}{k_B} \quad (4.71)$$

where C_2 is defined at (2.124) and is always positive, as we have demonstrated in chapter 2. We conclude then that the specific heat is positive for $\Omega_{N_S} \neq 0$ in the Drude bath, Figure 4.3 has a few examples.

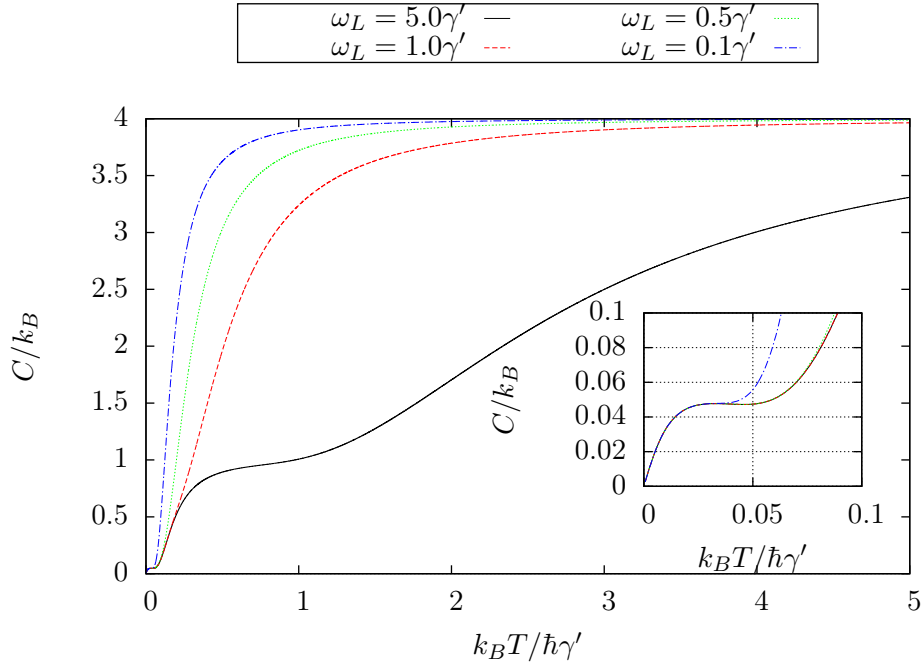


FIGURE 4.3: A figure showing the behaviour of C when $\Omega_{N_S} = 0.5\gamma'$ and $\omega_D = 0.1\gamma'$. Here we have that $N_S = 4$ and we define $\omega_L = \sqrt{K/M}$. The plot is made for different values of internal coupling. Note that it is possible to obtain more than one temperature window where the specific heat decreases (*dip*) or increases at a lesser rate.

If we've had that $\Omega_{N_S} = 0$, the partition function would need to be re-written with the coupled harmonic oscillator replaced with the coupled free particle:

$$Z = \prod_{i=1}^{N_S-1} Z_u(\Omega_i) \left\{ \frac{L}{\hbar} \sqrt{\frac{2\pi M}{\beta}} \prod_{n=1}^{\infty} \frac{\nu_n}{\nu_n + \hat{\gamma}(\nu_n)} \right\}. \quad (4.72)$$

Like for the harmonic oscillator, the resulting specific heat will be composed of the sum of each individual specific heat:

$$\frac{C}{k_B} = \sum_{i=1}^{N_S-1} C_{\text{ho}}(\Omega_i) + \frac{C_1}{k_B}. \quad (4.73)$$

We know from Chapter 2 that the specific heat of the damping free particle is negative for low values of temperature, therefore let us use definition (2.107) of C_1 to calculate:

$$\left. \frac{d}{dT} \left(\frac{C_1}{k_B} \right) \right|_{T=0} = \frac{\pi k_B}{3\hbar} \frac{1 + \hat{\gamma}'(0)}{\hat{\gamma}(0)}, \quad (4.74)$$

and using (2.32) we can also calculate:

$$\left. \frac{d}{dT} C_{\text{ho}} \right|_{T=0} = 0. \quad (4.75)$$

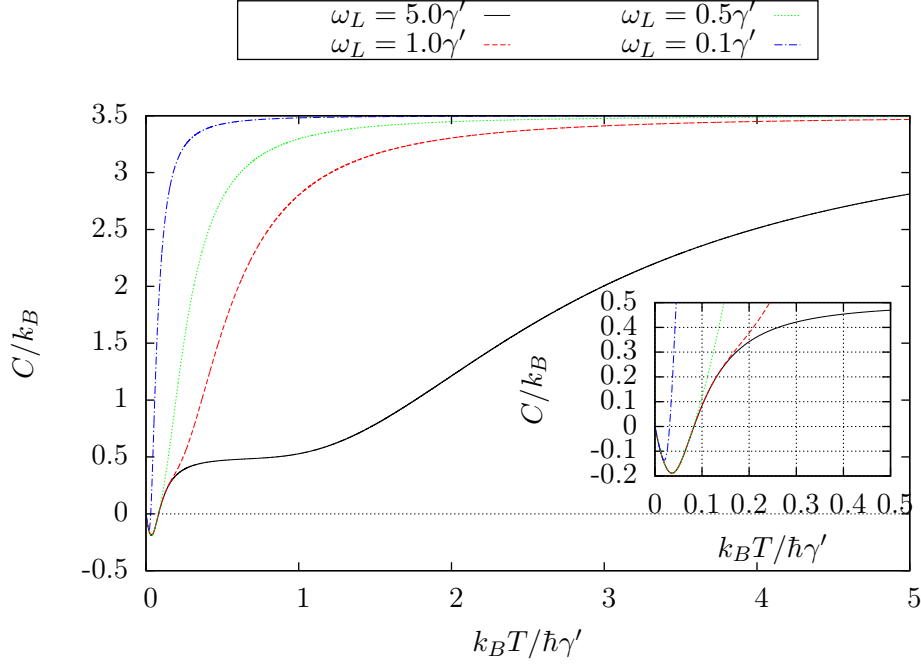


FIGURE 4.4: A figure showing the behaviour of C when $\Omega_{N_S} = 0.5\gamma'$ and $\omega_D = 0.1\gamma'$. Here we have that $N_S = 4$ and we define $\omega_L = \sqrt{K/M}$. The plot is made for different values of internal coupling. Note that the influence of the specific heat of the damped particle is dominant for low values of temperature.

For the entire specific heat, we can obtain the behaviour for low temperatures:

$$\frac{C}{k_B} \approx \frac{\pi}{3} \frac{1 + \hat{\gamma}'(0)}{\hat{\gamma}(0)} \left(\frac{k_B T}{\hbar} \right) + O(T^3), \quad (4.76)$$

therefore, if the specific heat associated with the coupled free particle is negative, the complete specific heat will also be negative, since for lower values of T it has dominant values over C_{ho} . Figure 4.4 has a few examples.

4.3 System Coupled to Independent Baths

Another possibility when dealing with systems with several degrees of freedom is to couple each degree of freedom to independent baths. For instance for a system with two degrees of freedom, the bath and coupling Hamiltonians are going to be written as:

$$\begin{aligned} H_B + H_{SB} = & \sum_{n=1}^{\infty} \left\{ \frac{p_n^2}{2m_n} + \frac{m_n \omega_n^2}{2} \left(x_n - \frac{\tilde{c}_n}{m_n \omega_n^2} \tilde{q}_1 \right)^2 + \frac{k_n^2}{2\mu_n^2} + \right. \\ & \left. + \frac{\mu_n \nu_n^2}{2} \left(y_n - \frac{\tilde{d}_n}{\mu_n \nu_n^2} \tilde{q}_2 \right)^2 \right\} \end{aligned} \quad (4.77)$$

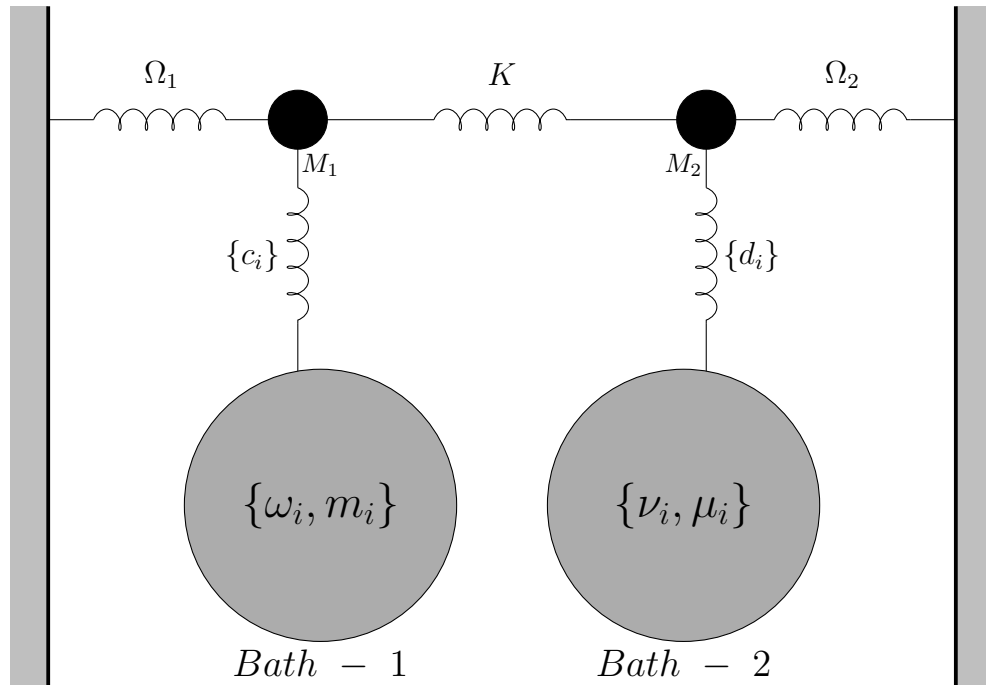


FIGURE 4.5: We aim to represent a model consisting of two system degrees of freedom coupled to each other, represented by the spring K , and each coupled to its own independent bath. The collections of different couplings are represented by $\{c_i\}$ and $\{d_i\}$

where we have already scaled out the masses M_1 and M_2 . We are taking $\{x_n, p_n\}$ and $\{y_n, k_n\}$ as the coordinates of the two baths, their respective couplings are: $\tilde{c}_n = c_n/\sqrt{M_1}$ and $\tilde{d}_n = d_n/\sqrt{M_2}$. Figure 4.5 represents this model.

4.3.1 The System Perspective

We now proceed with eliminating the baths dependency. Starting from the equations of motion:

$$\ddot{x}_n + \omega_n^2 x_n = \frac{\tilde{c}_n}{m_n} q_1, \quad (4.78)$$

$$\ddot{y}_n + \nu_n^2 y_n = \frac{\tilde{d}_n}{\mu_n} q_2, \quad (4.79)$$

with solutions:

$$\begin{aligned} x_n(t) &= \left(x_n(0) - \frac{\tilde{c}_n^2}{m_n \omega_n^2} \tilde{q}_1(0) \right) \cos(\omega_n t) + \frac{p_n(0)}{m_n \omega_n} \sin(\omega_n t) + \\ &+ \frac{\tilde{c}_n}{m_n \omega_n^2} - \int_0^t \frac{\tilde{c}_n}{m_n \omega_n^2} \cos(\omega_n(t-s)) \dot{q}_1(s) ds, \end{aligned} \quad (4.80)$$

$$y_n(t) = \left(y_n(0) - \frac{\tilde{d}_n^2}{\mu_n \nu_n^2} \tilde{q}_2(0) \right) \cos(\nu_n t) + \frac{k_n(0)}{\mu_n \nu_n} \sin(\nu_n t) \quad (4.81)$$

$$+ \frac{\tilde{d}_n}{\mu_n \nu_n^2} \tilde{q}_2 - \int_0^t \frac{\tilde{d}_n}{\mu_n \nu_n^2} \sin(\nu_n(t-s)) \dot{q}_2(s) ds \quad (4.82)$$

where we have already used (2.12). Replacing in the equations of motion for the system coordinates

$$\ddot{\tilde{q}}_1 + \tilde{K}_1 \tilde{q}_1 - \tilde{K}_0 \tilde{q}_2 = \sum_{n=1}^{\infty} \tilde{c}_n x_n \quad (4.83)$$

$$\ddot{\tilde{q}}_2 + \tilde{K}_2 \tilde{q}_2 - \tilde{K}_0 \tilde{q}_1 = \sum_{n=1}^{\infty} \tilde{d}_n y_n \quad (4.84)$$

we obtain the Langevin equations:

$$\ddot{\tilde{q}}_1 + \int_0^t ds \gamma_1(t-s) \dot{\tilde{q}}_1(s) + \tilde{K}_1 \tilde{q}_1 - \tilde{K}_0 \tilde{q}_2 = \xi_1(t), \quad (4.85)$$

$$\ddot{\tilde{q}}_2 + \int_0^t ds \gamma_2(t-s) \dot{\tilde{q}}_2(s) + \tilde{K}_2 \tilde{q}_2 - \tilde{K}_0 \tilde{q}_1 = \xi_2(t). \quad (4.86)$$

where:

$$\gamma_1(t) = \sum_{n=1}^{\infty} \frac{\tilde{c}_n^2}{m_n \omega_n^2} \cos(\omega_n t) \quad ; \quad \gamma_2(t) = \sum_{n=1}^{\infty} \frac{\tilde{d}_n^2}{\mu_n \nu_n^2} \cos(\nu_n t), \quad (4.87)$$

and:

$$\xi_1(t) = \left(x_n(0) - \frac{\tilde{c}_n^2}{m_n \omega_n^2} \tilde{q}_1(0) \right) \cos(\omega_n t) + \frac{p_n(0)}{m_n \omega_n} \sin(\omega_n t), \quad (4.88)$$

$$\xi_2(t) = \left(y_n(0) - \frac{\tilde{d}_n^2}{\mu_n \nu_n^2} \tilde{q}_2(0) \right) \cos(\nu_n t) + \frac{k_n(0)}{\mu_n \nu_n} \sin(\nu_n t). \quad (4.89)$$

Note that, if we turn off the internal coupling ($K = 0$), the two equations will become completely independent, the term of "indirect" interaction is lost when we choose to consider more than one bath.

4.3.2 The Vectorial Equation

It is once again possible to express both equations using a vectorial notation. The coordinate vector $\tilde{\mathbf{q}}$, the internal coupling matrix \hat{K} and the fluctuating force vector ξ are defined at (4.27), (4.28) and (4.29) respectively.

The vectorial equation will be the almost identical to (4.31), with the only difference being the definition of the damping operator. It will no longer couple indirectly the system coordinates, meaning that $\hat{\Gamma}$ is diagonal in the basis of \mathbf{q} :

$$\hat{\Gamma} f(t) = \int_0^t ds \sum_{n=1}^{\infty} \begin{pmatrix} \frac{\tilde{c}_n^2}{m_n \omega_n^2} \cos(\omega_n(t-s)) & 0 \\ 0 & \frac{\tilde{d}_n^2}{\mu_n \nu_n^2} \cos(\nu_n(t-s)) \end{pmatrix} f(s). \quad (4.90)$$

We can simplify the expression further by introducing the spectral density of eigenstates for each bath:

$$J_1(\omega) = \sum_{n=1}^{\infty} \frac{\tilde{c}_n^2}{m_n \omega_n} \delta(\omega - \omega_n) \quad ; \quad J_2(\omega) = \sum_{n=1}^{\infty} \frac{\tilde{d}_n^2}{\mu_n \nu_n} \delta(\omega - \nu_n). \quad (4.91)$$

Because we wish the spectral density of eigenstates to be independent of the system, we have to reverse our transformation to re-introduce the system masses. The alternative version of $\hat{\Gamma}$ becomes:

$$\hat{\Gamma} f(t) = \int_0^t ds \int_0^{\infty} d\omega \frac{2}{\pi\omega} \begin{pmatrix} \frac{J_1(\omega)}{M_1} & 0 \\ 0 & \frac{J_2(\omega)}{M_2} \end{pmatrix} \cos(\omega t) f(s). \quad (4.92)$$

Despite being much simpler than the operator $\hat{\Gamma}$ that we used when there was only one bath, we still need to make severe restrictions to ensure that in the final problem the degrees of freedom can be uncoupled. We have to, once again, consider that the parameters are the same for both baths: $\tilde{c}_n = \tilde{d}_n$, $\omega_n = \nu_n$ and $m_n = \mu_n$, this makes $\hat{\Gamma}$ proportional to the identity, \hat{I} ,

$$\hat{\Gamma} f(t) = \int_0^t ds \sum_{n=1}^{\infty} \frac{\tilde{c}_n^2}{m_n \omega_n^2} \cos(\omega_n(t-s)) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} f(s) = \int_0^t ds \gamma(t-s) \hat{I} f(s), \quad (4.93)$$

allowing us to perform any transformation in order to diagonalize \hat{K} :

$$\left\{ \left(\frac{d^2}{dt^2} + \Gamma \frac{d}{dt} \right) \hat{I} + \hat{K} \right\} \mathbf{q} = \xi. \quad (4.94)$$

The extension for systems with N_S degrees of freedom is very intuitive, the definition on equation (4.92) can be easily extended to

$$\hat{\Gamma}f(t) = \int_0^t ds \int_0^\infty d\omega \frac{2}{\pi\omega} \begin{pmatrix} \frac{J_1(\omega)}{M_1} & 0 & \dots & 0 \\ 0 & \frac{J_2(\omega)}{M_2} & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \frac{J_{N_S}(\omega)}{M_{N_S}} \end{pmatrix} f(s) \quad (4.95)$$

while \hat{K} goes from a 2×2 symmetrical matrix to a $N_S \times N_S$ symmetrical matrix where the component K_{ij} represents the internal interaction between the i -th and the j -th component.

4.4 A Few Examples

General Harmonic Coupling

Considering a system with N_S degrees of freedom with same masses ($M_1 = M_2 = \dots = M_{N_S} = M$), whose coupling with each other and the "ground" can be represented by \hat{K} , all of which are also equally coupled to an individual bath, also with identical frequencies, the Langevin vectorial equation would read

$$\left\{ \left(\frac{d^2}{dt^2} + \Gamma \frac{d}{dt} \right) \hat{I} + \hat{K} \right\} \mathbf{q} = \xi. \quad (4.96)$$

We have the freedom to perform any sort of linear transformation in \mathbf{q} in order to diagonalize \hat{K} . Consider the eigenvector basis \mathbf{v}_i where

$$\hat{K}\mathbf{v}_i = k_i\mathbf{v}_i, \quad (4.97)$$

where k_i is the eigenvalue associated with the eigenvector \mathbf{v}_i . The Langevin equation, expressed in this basis becomes the system

$$\left\{ \frac{d^2}{dt^2} + \Gamma \frac{d}{dt} + k_i \right\} \mathbf{q} = \xi, \quad (4.98)$$

with N_S independent equations, the eigenvector basis uncouples the Langevin equations.

Noting that \hat{k} represents the harmonic interactions between the system particles, we can conclude that $k_i \geq 0$. Let us consider the possibility that some eigenvalues can be zero, thus describing free particles, and define the degeneracy of the the eigenvalue as N_F .

In this basis we can write the complete Hamiltonian as a sum of N_S independent Hamiltonians:

$$H = \sum_{m=1}^{N_S} H_{(m)} \quad (4.99)$$

$$H_{(m)} = \sum_n \left(\frac{p_n^{(m)2}}{2m_n} + \frac{m_n \omega_n^2}{2} \left(x_n^{(m)} - \frac{c_n}{m_n \omega_n^2} v_m^2 \right)^2 \right) + \frac{P^{(m)2}}{2M} + \frac{k_m}{2} v_m^2, \quad (4.100)$$

where we use m and (m) to label the m -th degree of system freedom. Using this expression for the Hamiltonian, we obtain that the partition functions

$$\begin{aligned} Z_{S+B} &= \text{Tr} \exp(-\beta H) = \text{Tr} \exp\left(-\beta \sum_{m=1}^{N_S} H_{(m)}\right) = \text{Tr} \prod_{m=1}^{N_S} \exp(-\beta H_{(m)}) = \\ &= \prod_{m=1}^{N_S} \text{Tr}_{(m)} \exp(-\beta H_{(m)}), \end{aligned} \quad (4.101)$$

$$Z_B = \text{Tr}_B \exp(-\beta H_B) = \prod_{m=1}^{N_S} \text{Tr}_{B,(m)} \exp(-\beta H_{B,(m)}), \quad (4.102)$$

which will lead, using (2.39) and (2.40), to the ratio:

$$\begin{aligned} Z &= \prod_{m=1}^{N_S} \frac{Z_{(m)}}{Z_{B,(m)}} = \prod_{m=1}^{N_F} \left\{ \frac{L}{\hbar} \sqrt{\left(\frac{2\pi M}{\beta}\right)} \prod_{n=1}^{\infty} \frac{\nu_n}{\nu_n + \hat{\gamma}(\nu_n)} \right\} \times \\ &\times \prod_{m=1}^{N_S - N_F} \left\{ \frac{1}{\hbar \beta k_m} \prod_{n=1}^{\infty} \frac{\nu_n^2}{\nu_n^2 + \nu_n \hat{\gamma}(\nu_n) + k_m^2} \right\}. \end{aligned} \quad (4.103)$$

As an example, let us look at a system with two degrees of freedom where $M_1 = M_2$ and $\Omega_1 = \Omega_2 = 0$ for the Drude bath. Considering \tilde{K} ,

$$\tilde{K} = \begin{pmatrix} K & -K \\ -K & K \end{pmatrix}, \quad (4.104)$$

the basis of eigenvectors is:

$$|0\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \quad |2K\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}, \quad (4.105)$$

with their respective eigenvalues, the center of mass coordinate is a free particle (eigenvalue 0), and the relative motion coordinate is an harmonic oscillator of frequency

$\Omega_0 = \sqrt{2\frac{K}{M}}$ (eigenvalue $2K$). The partition function becomes:

$$Z = \left\{ \frac{L}{\hbar} \sqrt{\left(\frac{2\pi M}{\beta}\right)} \prod_{n=1}^{\infty} \frac{\nu_n}{\nu_n + \hat{\gamma}(\nu_n)} \right\} \times \left\{ \frac{1}{\hbar\beta\Omega_0} \prod_{n=1}^{\infty} \frac{\nu_n^2}{\nu_n^2 + \nu_n \hat{\gamma}(\nu_n) + \Omega_0^2} \right\}. \quad (4.106)$$

Using our findings in chapter 2, we can obtain the specific heat as:

$$\frac{C}{k_B} = \frac{C_1}{k_B} + \frac{C_2}{k_B}, \quad (4.107)$$

where $C_1(T)$ and $C_2(T)$ are defined as (2.62) and (2.68) respectively. Only for low values of temperature we may have that C_1 can become negative, therefore let us use the series expansions in (2.52) and (2.107) to obtain that:

$$\frac{C}{k_B} \approx \frac{\pi}{3\hat{\gamma}(0)\Omega_0^2} \left(\hat{\gamma}^2(0) + \Omega_0^2 (1 + \hat{\gamma}'(0)) \right) \left(\frac{k_B T}{\hbar} \right) + O(T^3), \quad (4.108)$$

which in the Drude bath becomes

$$\frac{C}{k_B} \approx \frac{\pi}{3\gamma\Omega_0^2} \left(\gamma^2 + \Omega_0^2 (1 - \gamma/\omega_D) \right) \left(\frac{k_B T}{\hbar} \right) + O(T^3). \quad (4.109)$$

In order to have negative specific heat, we must have that

$$\gamma + \Omega_0^2 \left(1 - \frac{\gamma}{\omega_D} \right) < 0 \rightarrow \omega_D \gamma^2 + \omega_D \Omega_0^2 - \Omega_0^2 \gamma < 0 \rightarrow \omega_D < \frac{\Omega_0^2 \gamma}{\gamma^2 + \Omega_0^2}. \quad (4.110)$$

Figure 4.6 illustrates a few examples.

The N -Dimensional Problem

Let us imagine a particle in an N dimensional space under the influence of a potential $V(\vec{q})$, where \vec{q} is the particles position. The system Hamiltonian is written as:

$$H_S = \frac{1}{M} \vec{P}\vec{P} + V(\vec{q}), \quad (4.111)$$

which will lead us to the equations of motion:

$$\ddot{\vec{q}} = -\vec{\nabla}V(\vec{q}), \quad (4.112)$$

where $\vec{\nabla}$ is the gradient in N dimensions.

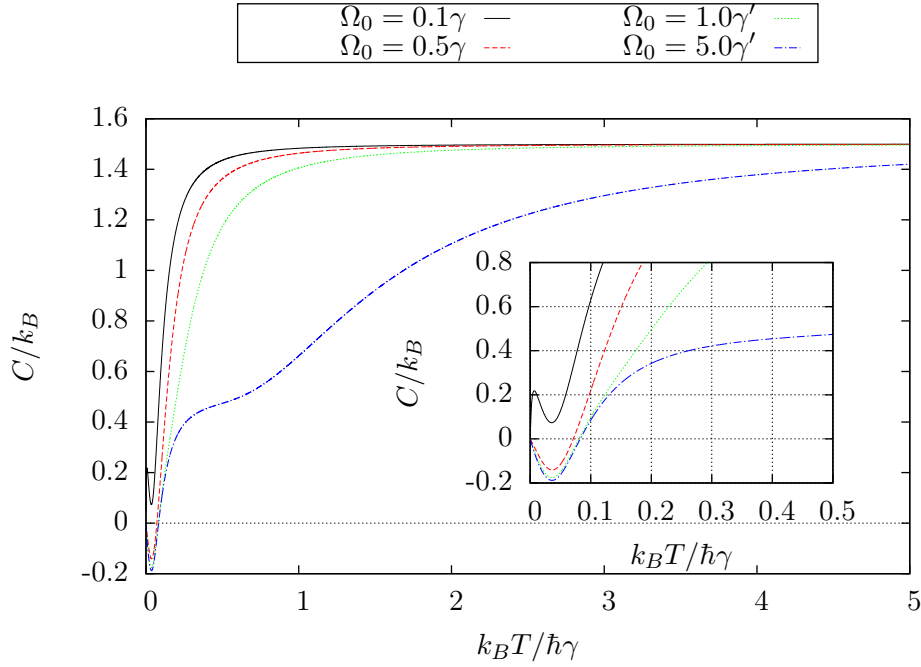


FIGURE 4.6: A few examples of specific heat where we have fixed $\omega_D = 0.1\gamma$ and allowed Ω_0 to vary.

In order to express dissipation, we will couple this system with a bath of oscillators described by the Hamiltonian

$$H_B = \sum_{n=1}^{\infty} \left\{ \frac{1}{m} \vec{p}_n \vec{p}_n + \frac{m\omega_n^2}{2} \vec{x}_n \vec{x}_n \right\}, \quad (4.113)$$

using the interaction Hamiltonian:

$$H_{SB} = \sum_{n=1}^{\infty} -c_n \vec{x}_n \vec{q} + \sum_{n=1}^{\infty} \frac{c_n^2}{2m_n \omega_n^2} \vec{q} \vec{q}. \quad (4.114)$$

The parallel becomes quite clear: the problem of a single degree of freedom in a N -dimensional space is equivalent to N degrees of freedom in one dimensional. Also note that this scenarios naturally satisfies all the restrictions imposed in this chapter ($M_i = M$, $\omega_n^{(i)} = \omega_n, \dots$).

A good example is to consider the Landau Diamagnetism [10, 12], where we an electron of mass m placed in a magnetic field $\vec{B} = B\hat{z}$ with an additional two dimensional harmonic oscillator of frequency ω_0 . The system Hamiltonian is written as:

$$H_S = \frac{1}{m} \left[\left(p_x - \frac{e}{2c} y B \right)^2 + \left(p_y + \frac{e}{2c} x B \right)^2 \right] + m\omega_0^2 (x^2 + y^2). \quad (4.115)$$

We know from textbooks that the magnetic part of the system Hamiltonian will lead to the Lorentz force:

$$\ddot{\vec{q}} = -\omega_0^2 \vec{q} - \frac{e}{mc} \left(\dot{\vec{q}} \times \vec{B} \right), \quad (4.116)$$

that we can expand to:

$$\begin{pmatrix} \ddot{q}_x \\ \ddot{q}_y \end{pmatrix} + \omega_c \begin{pmatrix} \dot{q}_y \\ -\dot{q}_x \end{pmatrix} + \omega_0^2 \begin{pmatrix} q_x \\ q_y \end{pmatrix} = 0, \quad (4.117)$$

where $\omega_c = eB/mc$. This type of internal coupling is different than the one we analysed before since it couples the velocities. The internal interaction is written as:

$$\begin{pmatrix} \omega_0^2 & \omega_c \frac{d}{dt} \\ -\omega_c \frac{d}{dt} & \omega_0^2 \end{pmatrix} \vec{q} = \hat{K} \vec{q}, \quad (4.118)$$

we can replace \hat{K} in equation (4.96):

$$\left\{ \left(\frac{d^2}{dt^2} + \Gamma \frac{d}{dt} \right) \hat{I} + \begin{pmatrix} \omega_0^2 & \omega_c \frac{d}{dt} \\ -\omega_c \frac{d}{dt} & \omega_0^2 \end{pmatrix} \right\} \vec{q} = \xi. \quad (4.119)$$

Note that we are using the arrow to represent vectors instead of the bold notation we have used throughout this chapter. We are doing this simply to differentiate when the vector is simply an abstract quantity, the bold notation, and when it actually has a physical representation, the arrow notation that here denotes the position of the electron.

It is possible to diagonalize \hat{K} in the basis:

$$\bar{q}_1 = \frac{q_y + iq_x}{\sqrt{2}}, \quad \bar{q}_2 = \frac{q_y - iq_x}{\sqrt{2}} \quad (4.120)$$

leading us to the equation:

$$\left\{ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \frac{d^2}{dt^2} + \begin{pmatrix} \Gamma_{\text{eff}} & 0 \\ 0 & \Gamma_{\text{eff}}^* \end{pmatrix} + \omega_0^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \right\} \begin{pmatrix} \bar{q}_1 \\ \bar{q}_2 \end{pmatrix} = \xi, \quad (4.121)$$

where:

$$\Gamma_{\text{eff}} f(t) = \int_0^t ds \gamma_{\text{eff}}(t-s) f(s), \quad (4.122)$$

and:

$$\hat{\gamma}_{\text{eff}}(z) = \hat{\gamma}(z) + i\omega_c. \quad (4.123)$$

Replacing these results in (4.106) we obtain the partition function ratio:

$$Z = \left(\frac{1}{\beta \hbar \omega_0} \right)^2 \prod_{n=1}^{\infty} \frac{\nu_n^2}{\nu_n^2 + \nu_n \hat{\gamma}_{\text{eff}}(\nu_n) + \omega_0^2} \prod_{n'=1}^{\infty} \frac{\nu_{n'}^2}{\nu_{n'}^2 + \nu_{n'} \hat{\gamma}_{\text{eff}}^*(\nu_{n'}) + \omega_0^2} = \quad (4.124)$$

$$= \left(\frac{1}{\beta \hbar \omega_0} \right)^2 \prod_{n=1}^{\infty} \frac{\nu_n^4}{(\nu_n^2 + \hat{\gamma}(\nu_n) \nu_n + \omega_0^2)^2 + \omega_c^2 \nu_n^2}, \quad (4.125)$$

which is the same one obtained in [10, 12].

4.5 Final Remarks

One of our motivations for this chapter was to understand how the internal coupling would affect the specific heat of our system. We managed to solve the oscillator ring from Chapter 3, using our interaction Hamiltonian, to a wider range of couplings.

Another motivation was to provide an alternative model, where the system degrees of freedom would be coupled to their own individual baths. And unlike in the single bath model, here we don't have to impose any sort of restrictions upon \hat{K} , but are still forced to impose all previous restrictions.

The coupled Langevin equations of systems with several interacting degrees of freedom, although being very compactly represented using vectorial notation, introduces us to several new problems. Whether we decide to use a single bath or several bath, the problem of diagonalizing (4.31) is not trivial. This doesn't mean that the partition function ratio can only be obtained for the very restricted conditions we discussed here. To obtain the reduced partition function would require a direct calculation using techniques like the path integral, which would be out of the scope of this dissertation.

Chapter 5

Conclusions

Our main motivation in this dissertation was to understand the model presented by H. Hasegawa [13] ($N_S + N_B$), more specifically, understand how its coupling mechanism works in order to explain the different results when compared to the Caldeira-Leggett model, as implemented, for instance, by G.-L. Ingold et al.

The comparison using minimal models in Chapter 3 lead us to conclude that the coupling with the environment in both models was intrinsically different, since the $N_S + N_B$ model would renormalize the potential of the system *and bath*. Even though using the minimal model has helped clarify the results, we need more research to understand exactly how the renormalizing terms in the $N_S + N_B$ model would behave for a general bath (nonidentical frequencies), and which physical reality it describes. We also need to investigate if the definition of the partition function ratio (1.1) (the starting point of our calculations) will leads us to results with physical meaning when we allow the coupling to shift the bath frequencies.

It is also important to note that we are not claiming that having a potential renormalization is a "problem" that could lead to wrong results. There are some occasions, like the Lamb Shift [15] where the interaction with the environment *does* cause a potential renormalization on the system potential. However, we must have our objectives clear: the Caldeira-Leggett model, as we have defined, aims to analyse systems where the environment *does not* renormalize the potential of (2.13). In the $N_S + N_B$ model the physical meaning of the potential renormalization is not clear.

In Chapter 4 we have proposed two new models for systems with interacting degrees of freedom. They were defined with a familiar coupling Hamiltonian, inspired directly by the Caldeira-Leggett model, in order to prevent problems with the potential renormalization. Many new problems appeared, the Langevin equations (4.31) could be

solved using methods like the Laplace transform or the Fourier transform. However, in order to obtain the reduced partition function it would be necessary to perform all the calculations, using path-integrals for instance. Since this was out of the scope of this dissertation, we cannot be sure on the restrictions necessary for it to be analytically solvable or even on how the final result would behave. This is an interesting direction that could be researched in the future. We only solved for restricted systems such that (4.31) could be diagonalized.

The applications of our single bath model are very intuitive since all we have done is assume that the system is composed of several oscillators that interact in a non-negligible way, a situation very simple to picture in nature. It can also be applied, for instance, to systems with several particles where the interaction with the environment does not affect the system potential. In the case of the several bath model, besides its instinctive use for problems with more dimensions, could be used to express, for instance, the vibrations of an internal degree of freedom between atoms in a molecule.¹

Another route for research, besides the one we took for systems with interacting oscillators, is to consider a general linear environment with spectral density like (2.21), i.e.,

$$J(\omega) = M\gamma\omega^s \frac{\omega_c^{2p-s+1}}{(\omega_c^2 + \omega^2)^p}$$

for $s \neq 1$. It has been discovered that the Ohmic damping stands as a the very particular case where the specific heat vanishes for $T = 0$ [16]. Regarding the Caldeira-Leggett model, it still stands as a useful tool for describing a variety of situations, e.g., ranging from the Kondo superconductor [18] to transport in proteins [17]. This, combined with the growing set of techniques, leads us to expect many other interesting results.

¹G.-L Ingold, private conversations.

Appendix A

General Demonstrations

Several calculations that did not add to the physical interpretation of the problem but where non-trivial and required demonstrations where moved here to avoid crowding the main text.

A.1 Equivalent Roots

This section contains a demonstration that the roots of the polynomial obtained from the partition function ratio:

$$p_1(x) = x^3 + \omega_D x^2 + (\gamma\omega_D + \Omega_0^2)x + \Omega_0^2\omega_D = (x + x_1)(x + x_2)(x + x_3), \quad (\text{A.1})$$

and the polynomial obtained from the denominator of the change in density of eigenfrequencies:

$$p_2(x) = x^6 + (\omega_D^2 - 2\gamma\omega_D - 2\Omega_0^2)x^4 + \left(\gamma^2\omega_D^2 + 2\gamma\Omega_D\Omega_0^2 - 2\Omega_D^2\Omega_0^2 + \Omega_0^4\right)x^2 + \omega_D^2\Omega_0^4 = (x^2 + X_1^2)(x^2 + X_2^2)(x^2 + X_3^2), \quad (\text{A.2})$$

are equivalent to:

$$\begin{aligned} x_1 &= X_1 = \omega_1, \\ x_2 &= X_2 = \omega_2, \\ x_3 &= X_3 = \omega_3. \end{aligned} \quad (\text{A.3})$$

For simplicity, since the roots are quite big, given that this is a third degree polynomial, we are going to take an alternative route. Assuming last affirmation to be true, let's

take:

$$p_1(ix) = (ix + \omega_1)(ix + \omega_2)(ix + \omega_3) = i^3(x - i\omega_1)(x - i\omega_2)(x - i\omega_3), \quad (\text{A.4})$$

$$p_1(-ix) = (-ix + \omega_1)(-ix + \omega_2)(-ix + \omega_3) = i^{-3}(x + i\omega_1)(x + i\omega_2)(x + i\omega_3), \quad (\text{A.5})$$

and from that we obtain:

$$p_1(ix)p_1(-ix) = (x^2 + \omega_1^2)(x^2 + \omega_2^2)(x^2 + \omega_3^2) = p_2(x). \quad (\text{A.6})$$

Therefore, we can bypass the long algebraic calculations that would be required by demonstrating that:

$$p_1(ix)p_1(-ix) = p_2(x). \quad (\text{A.7})$$

With the latter being easily demonstrated using the definition for $p_1(x)$ and $p_2(x)$:

$$p_1(ix) = -ix^3 - \omega_D^2 x^2 + (\omega_D + \Omega_0^2)ix + \Omega_0^2 \omega_D, \quad (\text{A.8})$$

$$p_1(-ix) = ix^3 - \omega_D^2 x^2 + (\omega_D + \Omega_0^2)ix + \Omega_0^2 \omega_D, \quad (\text{A.9})$$

so that

$$\begin{aligned} p_1(ix)p_1(-ix) &= x^6 + (\omega_D^2 - 2\gamma\omega_D - 2\Omega_0^2)x^4 + (\gamma^2\omega_D^2 + 2\gamma\Omega_D\Omega_0^2 - \\ &\quad - 2\Omega_D^2\Omega_0^2 + \Omega_0^4)x^2 + \omega_D^2\Omega_0^4 = p_2(x). \end{aligned} \quad (\text{A.10})$$

Q.E.D.

A.2 Describing the density as Lorentzians

Our objective is to prove that the change in the density of eigen-frequencies for the Drude bath can be written as a sum of Lorentzians. For the free particle the calculations are very simple, but in the case of the harmonic potential becomes impractical to demonstrate using the roots themselves, since their expressions are very long. What we are going to do is use properties obtained in Appendix A.1 to demonstrate.

We also decided to take the backwards road and from the Lorentzians prove that you will obtain the polynomials associated with the change in density:

$$\begin{aligned} & \frac{\omega_1}{x^2 + \omega_1^2} + \frac{\omega_2}{x^2 + \omega_2^2} + \frac{\omega_3}{x^2 + \omega_3^2} = \\ \frac{1}{2} \left\{ \frac{1}{\omega_1 + ix} + \frac{1}{\omega_1 - ix} + \frac{1}{\omega_2 + ix} + \frac{1}{\omega_2 - ix} + \frac{1}{\omega_3 + ix} + \frac{1}{\omega_3 - ix} \right\} = & \quad (\text{A.11}) \\ \frac{1}{2} \left\{ \frac{1}{\omega_1 + ix} + \frac{1}{\omega_2 + ix} + \frac{1}{\omega_3 + ix} + \frac{1}{\omega_1 - ix} + \frac{1}{\omega_2 - ix} + \frac{1}{\omega_3 - ix} \right\} \end{aligned}$$

$$\begin{aligned} & \frac{1}{\omega_1 + ix} + \frac{1}{\omega_2 + ix} + \frac{1}{\omega_3 + ix} = \\ & \frac{(\omega_1 + ix)(\omega_2 + ix) + (\omega_1 + ix)(\omega_3 + ix) + (\omega_2 + ix)(\omega_3 + ix)}{(\omega_1 + ix)(\omega_2 + ix)(\omega_3 + ix)} \end{aligned} \quad (\text{A.12})$$

$$\begin{aligned} & \frac{1}{\omega_1 - ix} + \frac{1}{\omega_2 - ix} + \frac{1}{\omega_3 - ix} = \\ & \frac{(\omega_1 - ix)(\omega_2 - ix) + (\omega_1 - ix)(\omega_3 - ix) + (\omega_2 - ix)(\omega_3 - ix)}{(\omega_1 - ix)(\omega_2 - ix)(\omega_3 - ix)} \end{aligned} \quad (\text{A.13})$$

Using:

$$p_1(x) = (\omega_1 + x)(\omega_2 + x)(\omega_3 + x), \quad (\text{A.14})$$

$$p_1(x) = x^3 + (\omega_1 + \omega_2 + \omega_3)x^2 + (\omega_1\omega_2 + \omega_1\omega_3 + \omega_2\omega_3)x + (\omega_1\omega_2\omega_3), \quad (\text{A.15})$$

one arrives at:

$$g_1(x) = (\omega_1 + x)(\omega_2 + x) + (\omega_1 + x)(\omega_3 + x) + (\omega_2 + x)(\omega_3 + x), \quad (\text{A.16})$$

$$q_1(x) = 3x^2 + 2(\omega_1 + \omega_2 + \omega_3)x + (\omega_1\omega_2 + \omega_1\omega_3 + \omega_2\omega_3). \quad (\text{A.17})$$

Comparing $p_1(x)$ with its initial definition (A.1) in Appendix A.1 we obtain that:

$$\omega_1 + \omega_2 + \omega_3 = \omega_D, \quad (\text{A.18})$$

$$\omega_1\omega_2 + \omega_1\omega_3 + \omega_2\omega_3 = \omega_D + \Omega_0^2, \quad (\text{A.19})$$

$$\omega_1\omega_2\omega_3 = \omega_D\Omega_0^2, \quad (\text{A.20})$$

and replace on $g_1(x)$:

$$g_1(x) = 3x^2 + 2\omega_D x + \omega_D + \Omega_0^2. \quad (\text{A.21})$$

The sum of Lorentzians becomes:

$$\frac{1}{2} \left\{ \frac{g_1(ix)}{p_1(ix)} + \frac{g_1(-ix)}{p_1(-ix)} \right\} = \frac{1}{2} \left\{ \frac{g_1(ix)p_1(-ix) + g_1(-ix)p_1(ix)}{p_1(ix)p_1(-ix)} \right\}. \quad (\text{A.22})$$

And since we have demonstrated in Appendix A.1 that $p_1(ix)p_1(-ix)$ is the denominator, we only need to prove that the numerators are the same:

$$\frac{g_1(ix)p_1(-ix) + g_1(-ix)p_1(ix)}{2} = \omega_D x^4 + (\omega_D^2 - 2\omega_D \Omega_0^2)x^2 + \omega_D^2 \Omega_0^2 + \omega_D \Omega_0^4. \quad (\text{A.23})$$

Q.E.D.

A.3 Calculating Equation (2.116)

We only need to solve for one Lorentzian:

$$C_1 = \int_0^\infty \frac{\omega_1}{\omega^2 + \omega_1^2} k_B \left(\frac{\hbar\beta\omega}{2 \sinh \frac{\hbar\beta\omega}{2}} \right)^2 d\omega. \quad (\text{A.24})$$

To simplify the problem lets change the variables to:

$$y = \frac{\hbar\beta\omega}{2} ; \quad dy = \frac{\hbar\beta}{2} d\omega \quad (\text{A.25})$$

and also, since we are integrating an even function lets also change the limits to the complete real line. That will allow us to use the residue theorem later on.

$$C_1 = \frac{k_b}{2} \int_{-\infty}^\infty \frac{1}{1 + \left(\frac{2}{\hbar\beta\omega_1} y \right)^2} \left(\frac{2}{\hbar\beta\omega_1} \right) \left(\frac{y}{\sinh y} \right)^2 dy, \quad (\text{A.26})$$

for simplicity:

$$C_1 = \frac{k_b}{2} \int_{-\infty}^\infty \frac{a}{1 + a^2 y^2} \left(\frac{y}{\sinh y} \right)^2 dy, \quad (\text{A.27})$$

$$a = \left(\frac{2}{\hbar\beta\omega_1} \right). \quad (\text{A.28})$$

The expression to be integrated has poles of order one at:

$$1 + a^2 y^2 = 0 \rightarrow y = \pm \frac{i}{a}, \quad (\text{A.29})$$

$$(\text{A.30})$$

and of order two at:

$$\sinh(y) = 0 \rightarrow y = i\pi n, \quad (\text{A.31})$$

where n is an integer number. Note that because of the term y^2 on the numerator, $n = 0$ is not a pole.

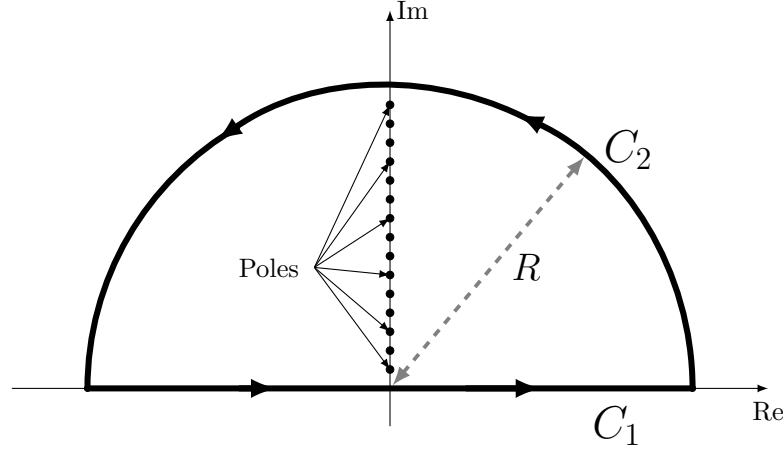


FIGURE A.1: A representation of the contours and the poles.

If we allow for our variable to become complex, $y \rightarrow z$, we can use residue theorem to calculate the integral, we define our contours as shown in figure A.1. The integral

$$\int_{C_1} f(z)dz + \int_{C_2} f(z)dz = 2\pi i \sum_i \text{Res}(f, z_i), \quad (\text{A.32})$$

where C_1 is the real line $(-\infty, \infty)$ and C_2 is a semi-circle of radius R , enclosing the upper side of the complex plane (positive imaginary numbers). Taking the limit where $R \rightarrow \infty$, the integral over C_1 becomes our objective and over C_2 is null,

$$\int_{C_2} f(z)dz = \int_0^\pi \lim_{R \rightarrow \infty} f(Re^{i\theta})i\theta Re^{i\theta} d\theta = 0. \quad (\text{A.33})$$

Calculating the residues:

$$\text{Res}\left(f, \frac{i}{a}\right) = \lim_{z \rightarrow i/a} f(z) \left(z - \frac{i}{a}\right) = -\frac{i}{2a^2 \sin^2(1/a)}, \quad (\text{A.34})$$

$$\text{Res}(f, i\pi n) = \lim_{z \rightarrow i\pi n} \frac{d}{dz} (f(z)(z - i\pi n)^2) = 2i \frac{a\pi n}{(a^2\pi^2 n^2 - 1)^2}, \quad (\text{A.35})$$

we rewrite the last expression as:

$$\frac{2ia\pi n}{(a^2\pi^2 n^2 - 1)^2} = \frac{i}{2} \frac{1}{(a\pi n - 1)^2} - \frac{i}{2} \frac{1}{(a\pi n + 1)^2} = \frac{i}{2a^2\pi^2} \left(\frac{1}{n - \frac{1}{a\pi}} - \frac{1}{n + \frac{1}{a\pi}} \right). \quad (\text{A.36})$$

Making use of the Trigamma function:

$$\psi'(z) = \sum_{n=0}^{\infty} \frac{1}{(z+n)^2}, \quad (\text{A.37})$$

and noting that we are starting from $n = 1$ rather than $n = 0$ we get:

$$\sum_{n=1}^{\infty} \frac{1}{n + \frac{1}{a\pi}} = \psi'(1 + 1/a\pi), \quad (\text{A.38})$$

$$\sum_{n=1}^{\infty} \frac{1}{n - \frac{1}{a\pi}} = \psi'(1 - 1/a\pi). \quad (\text{A.39})$$

Replacing:

$$\sum_{n=1}^{\infty} \text{Res}(f, i\pi n) = \frac{i(\psi'(1 - 1/a\pi) - \psi'(1 + 1/a\pi))}{2a^2\pi^2}. \quad (\text{A.40})$$

Using the recurrence:

$$\psi'(1 + z) = \psi'(z) - \frac{1}{z^2}, \quad (\text{A.41})$$

and the reflection propriety:

$$\psi'(1 - z) = -\psi'(z) + \frac{\pi^2}{\sin^2(\pi z)}, \quad (\text{A.42})$$

for the Trigamma function, the sum becomes:

$$\sum_{n=1}^{\infty} \text{Res}(f, i\pi n) = i \left\{ \frac{1}{2a^2 \sin^2(1/a)} + \frac{1}{2} - \frac{\psi'(1/a\pi)}{a^2\pi^2} \right\}. \quad (\text{A.43})$$

We can conclude that:

$$\sum_i \text{Res}(f, z_i) = 2\pi i \left(\text{Res}(f, i/a) + \sum_{n=1}^{\infty} \text{Res}(f, i\pi n) \right) = 2 \frac{\psi'(1/a\pi)}{a^2\pi^2} - 1. \quad (\text{A.44})$$

Replacing in the original expression, remembering that we need to divide the result by 2 since we are taking only positive values of ω , and reversing the changes in variables we obtain:

$$\int_0^{\infty} \frac{\omega_1}{\omega^2 + \omega_1^2} k_B \left(\frac{\hbar\beta\omega}{2 \sinh \frac{\hbar\beta\omega}{2}} \right)^2 d\omega = \left(\frac{\hbar\beta\omega_1}{2\pi} \right)^2 \psi' \left(\frac{\hbar\beta\omega_1}{2\pi} \right) - \frac{1}{2}, \quad (\text{A.45})$$

therefore:

$$\begin{aligned} \frac{C}{k_b} &= \int_0^{\infty} \left\{ \frac{\omega_1}{\omega^2 + \omega_1^2} + \frac{\omega_2}{\omega^2 + \omega_2^2} + \frac{\omega_3}{\omega^2 + \omega_3^2} - \frac{\omega_D}{\omega^2 + \omega_D^2} \right\} \left(\frac{\hbar\beta\omega}{2 \sinh \frac{\hbar\beta\omega}{2}} \right)^2 d\omega = \\ &= \left(\frac{\hbar\beta\omega_1}{2\pi} \right)^2 \psi' \left(\frac{\hbar\beta\omega_1}{2\pi} \right) + \left(\frac{\hbar\beta\omega_2}{2\pi} \right)^2 \psi' \left(\frac{\hbar\beta\omega_2}{2\pi} \right) + \left(\frac{\hbar\beta\omega_3}{2\pi} \right)^2 \psi' \left(\frac{\hbar\beta\omega_3}{2\pi} \right) - \\ &\quad - \left(\frac{\hbar\beta\omega_D}{2\pi} \right)^2 \psi' \left(\frac{\hbar\beta\omega_D}{2\pi} \right) - 1. \end{aligned} \quad (\text{A.46})$$

A.4 Specific Heat of the Harmonic Oscillator

We wish to prove that C_2 is always positive:

$$\int_0^\infty \left\{ \frac{\hat{\omega}_1}{\hat{\omega}_1^2 + \hat{\omega}^2} + \frac{\hat{\omega}_2}{\hat{\omega}_2^2 + \hat{\omega}^2} + \frac{\hat{\omega}_3}{\hat{\omega}_3^2 + \hat{\omega}^2} - \frac{\hat{\omega}_D}{\hat{\omega}_D^2 + \hat{\omega}^2} \right\} \left(\frac{\frac{\hat{\omega}}{2\hat{T}}}{\sinh\left(\frac{\hat{\omega}}{2\hat{T}}\right)} \right)^2 d\hat{\omega} > 0, \quad (\text{A.47})$$

where $\hat{\omega} = \omega/\gamma$ and $\hat{T} = k_B T/\hbar\gamma$. Obviously, if we can show that:

$$\int_0^\infty \left\{ \frac{\hat{\omega}_i}{\hat{\omega}_i^2 + \hat{\omega}^2} - \frac{\hat{\omega}_D}{\hat{\omega}_D^2 + \hat{\omega}^2} \right\} \left(\frac{\frac{\hat{\omega}}{2\hat{T}}}{\sinh\left(\frac{\hat{\omega}}{2\hat{T}}\right)} \right)^2 d\hat{\omega} > 0, \quad (\text{A.48})$$

its true, then (A.47) is also true. We choose ω_i to be a real frequency; if ω_1 and ω_2 are complex, $\omega_i = \omega_3$.

Changing the variables to $x_i = \hat{\omega}/\hat{\omega}_i$ and $y_i = \hat{\omega}_i/2\hat{T}$, the integral becomes:

$$\int_0^\infty \frac{\hat{\omega}_i}{\hat{\omega}_i^2 + \hat{\omega}^2} \left(\frac{\frac{\hat{\omega}}{2\hat{T}}}{\sinh\left(\frac{\hat{\omega}}{2\hat{T}}\right)} \right)^2 d\hat{\omega} = \int_0^\infty \frac{1}{1 + x_i^2} \left(\frac{x_i y_i}{\sinh(x_i y_i)} \right)^2 dx_i, \quad (\text{A.49})$$

we can do the same for ω_D term. Since the integration limits are the same, we can write x_i and x_D as the same variable:

$$\int_0^\infty \left\{ \frac{\hat{\omega}_i}{\hat{\omega}_i^2 + \hat{\omega}^2} - \frac{\hat{\omega}_D}{\hat{\omega}_D^2 + \hat{\omega}^2} \right\} \left(\frac{\frac{\hat{\omega}}{2\hat{T}}}{\sinh\left(\frac{\hat{\omega}}{2\hat{T}}\right)} \right)^2 d\hat{\omega} = \int_0^\infty \frac{1}{1 + x^2} \left\{ \left(\frac{x y_i}{\sinh(x y_i)} \right)^2 - \left(\frac{x y_D}{\sinh(x y_D)} \right)^2 \right\} dx. \quad (\text{A.50})$$

Note that the derivative of the function $\left(\frac{x y_i}{\sinh(x y_i)} \right)^2$,

$$\frac{d}{dx} \left(\frac{x y_i}{\sinh(x y_i)} \right)^2 = y_i \left(\frac{x y_i}{\sinh(x y_i)} \right) (1 - x \coth(x y_i)), \quad (\text{A.52})$$

is negative for all $x > 0$, meaning that the function values always decreases as x increases for all positive x . We conclude that in order to make the integral always positive we must have that:

$$\left(\frac{x y_i}{\sinh(x y_i)} \right)^2 > \left(\frac{x y_D}{\sinh(x y_D)} \right)^2, \quad (\text{A.53})$$

which is true if, and only if:

$$xy_i < xy_D \rightarrow y_i < y_D \rightarrow \omega_i < \omega_D. \quad (\text{A.54})$$

We only need to prove that at least one real frequency is smaller than ω_D to finish the demonstration. Using (A.1):

$$p_1(x) = x^3 + \omega_D x^2 + (\Omega_0^2 + \gamma\omega_D)x + \omega_D \Omega_0^2 = (x + \omega_1)(x + \omega_2)(x + \omega_3), \quad (\text{A.55})$$

we have that:

$$p_1(0) = \omega_D \Omega_0^2 \quad \text{and} \quad p_1(-\omega_D) = -\gamma\omega_D^2. \quad (\text{A.56})$$

Since we switch values from negative to positive we conclude that in the interval $(-\omega_D, 0)$ there is a $-\omega_i$ such that $\omega_i < \omega_D$.

Q.E.D.

A.5 Sign of $G'(\omega)$

In this appendix we shall obtain the values of ω_D and Ω_0 that allow $G'(\omega)$ to be negative:

$$G'(\omega) < 0 \rightarrow 3\omega^4(\omega_D^2 - \omega_D\gamma - \Omega_0^2)\omega^2\omega_D^2\Omega_0^2 < 0, \quad (\text{A.57})$$

changing the variables $\omega^2 = x$ gives us the polynomial:

$$x^2 + (\omega_D^2 - \Omega_0^2 - \gamma\omega_D)x + \omega_D^2\Omega_0^2 < 0, \quad (\text{A.58})$$

with roots:

$$x_{1,2} = \frac{1}{6} \left(\Omega_0^2 + \gamma\omega_D - \omega_D^2 \pm \sqrt{(\Omega_0^2 + \gamma\omega_D - \omega_D^2)^2 - 12\omega_D^2\Omega_0^2} \right) \quad (\text{A.59})$$

Since the concavity is upwards, the only way to obtain negative values for the specific heat is to have two real roots. Also, since $x = \omega^2$, both roots must be positive. There restrictions are written as:

$$(\Omega_0^2 + \gamma\omega_D - \omega_D^2)^2 > 12\omega_D^2\Omega_0^2, \quad (\text{A.60})$$

$$\Omega_0^2 + \gamma\omega_D - \omega_D^2 > 0. \quad (\text{A.61})$$

Restriction (A.60) yields two equations:

$$\Omega_0^2 + \gamma\omega_D - \omega_D^2 > 2\sqrt{3}\omega_D\Omega_0, \quad (\text{A.62})$$

$$\omega_D^2 - \Omega_0^2 - \gamma\omega_D > 2\sqrt{3}\omega_D\Omega_0. \quad (\text{A.63})$$

We can use (A.61) to get rid of (A.63) leaving us with (A.62), a hyperbola centred at $\omega_D = \sqrt{3}/8$ and $\Omega_0 = 1/8$. If translated to the origin and rotated 30 degrees anti-clockwise on the plane $\omega_D\Omega_0$, the hyperbola becomes:

$$32\Omega_0'^2 - 32\omega_D'^2 = 1. \quad (\text{A.64})$$

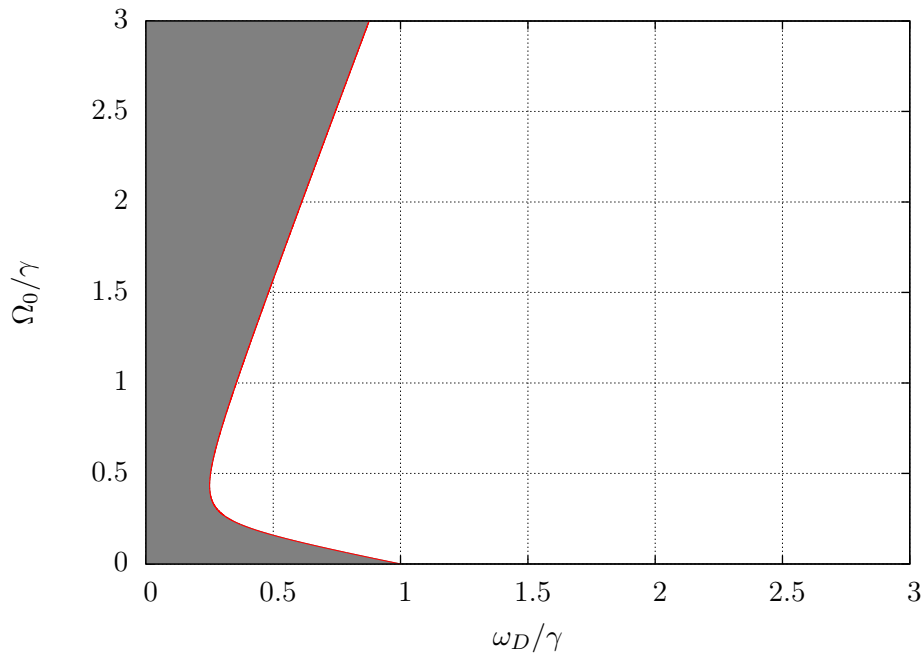


FIGURE A.2: The coloured region represents the points that allows negative values of $G'(\omega)$. The red line binding the grey region is given by: $\Omega_0^2 + \gamma\omega_D - \omega_D^2 = 2\sqrt{3}\omega_D\Omega_0$.

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