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Finite quantum dissipation: the challenge of obtaining specific heat

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Abstract. We consider a free particle coupled with finite strength to a bath and investigate the evaluation of its specific heat. A harmonic oscillator bath of Drude type with cutoff frequency ω_D is employed to model an ohmic friction force with dissipation strength γ . Two scenarios for obtaining specific heat are presented. The first one uses the measurement of the kinetic energy of the free particle, while the second one is based on the reduced partition function. Both descriptions yield results which are consistent with the Third Law of thermodynamics. Nevertheless, the two methods produce different results that disagree even in their leading quantum corrections at high temperatures. We also consider the regime where the cutoff frequency is smaller than the friction strength, i.e. $\omega_D < \gamma$. There, we encounter puzzling results at low temperatures where the specific heat based on the thermodynamic prescription becomes negative. This anomaly is rooted in an ill-defined density of states of the damped free particle, which assumes unphysical negative values when $\gamma/\omega_D > 1$.

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1. Introduction

While some physical disciplines such as classical mechanics and electrodynamics underwent profound changes with the birth of quantum mechanics and relativity, thermodynamics proved impressively robust over the last century. The main reason is that the formulation of thermodynamics rests on a few pillars only, such as entropy, temperature and the three Laws relating these state variables. The grandness of thermodynamics is that these concepts hold independently of the details of the corresponding total system dynamics. Nonetheless, the statistical mechanical foundation of thermodynamics strongly relies on the quantum mechanical properties of matter, in particular what concerns the low-temperature behaviour.

Statistical mechanics gives rise to some subtle issues when going from a closed description of all degrees of freedom, including those of large environments, to a reduced description of an *open* system where all bath degrees of freedom are traced over. Generally, no problems arise in the weak-coupling limit where the system–bath interaction tends to zero. This is the situation typically assumed explicitly, or at least implicitly, in the majority of textbooks. Even in this limit, however, pitfalls can arise in the quantum case, as recently elucidated in [1]. Generally, care must also be taken in defining correctly the expression for (Gibbs) work in the First Law, as recent debates on the validity of nonlinear fluctuation theorems have shown [2, 3].

In this work, we emphasize the *finiteness* of the coupling between the open quantum system and an environment of temperature $k_B T = 1/\beta$. The finite coupling will be modelled in terms of a generalized quantum Langevin equation (GLE) with a velocity-proportional memory friction, i.e. ohmic damping. An equivalent microscopic approach is provided by a bilinear coordinate–coordinate coupling between system degrees of freedom and environmental degrees of freedom, see e.g. in [1] and references cited therein.

The ohmic friction kernel involves two parameters that characterize the role of the environment. These are the frictional coupling strength γ and the (Drude)-frequency ω_D of the largest bath frequency. In typical situations, this Drude frequency markedly exceeds the friction strength; i.e. $\omega_D \gg \gamma$. Quantum dissipation with an unconventional environment is obtained, however, when $\omega_D < \gamma$. This situation arises, for example, for suitably tailored thermal baths or for molecular electron transfer systems which are exposed to polar solvents [4].

The presence of an ohmic friction term leads to an irreversible motion with a unique stationary state. Already at this level, prominent differences with the classical situation emerge. As is well known, the classical canonical thermal equilibrium probability assumes the familiar Gibbs–Boltzmann expression $\propto \exp(-\beta H_S)$, with H_S being the bare system Hamiltonian in the absence of interaction. Most remarkably, this classical result holds true independently of friction strength. In striking contrast, the equilibrium density operator of an open quantum system becomes a function of the friction strength [1, 5], thus exhibiting a dependence on the coupling to the environmental degrees of freedom. This feature can explicitly be inspected for an ohmic-like, damped harmonic quantum oscillator [1, 6, 7]: only in the weak-coupling limit does the canonical density operator reduce to the common Gibbs state, where H_S then represents the operator-valued system Hamiltonian.

Given this observation in the preceding paragraph it should not come as too big a surprise that the evaluation of thermodynamic quantities for an open quantum system, such as its specific heat, is also plagued with subtleties. These difficulties all originate from the assumed finite system–bath interaction. For the case of specific heat of a linear quantum oscillator of finite friction strength, this was explicitly demonstrated in a recent work [8]. While in the absence of damping, zero entropy is approached exponentially fast, this approach is weakened with finite friction to a power law dependence in friction strength and temperature [8, 9]. The Third Law has also been validated for the quantum dissipative oscillator in the presence of velocity–coordinate and velocity–velocity couplings [10] as well as for a charged oscillator in a magnetic field [11]. The main finding is that the thermodynamic entropy of the open system vanishes according to a power law in temperature with the same exponent that characterizes the frequency dependence of the memory friction in the limit of vanishing frequency.

It was remarked in [8], however, that the definition of the specific heat is ambiguous and may lead to pronouncedly different values. Therefore, the relation to experimental observations needs scrutiny, in particular in the study of nanosystems whose behaviour is quantum in nature but that are still coupled with finite strength to an environment. Another surprising observation is that the familiar von-Neumann entropy for a quantum dissipative oscillator *fails* to approach zero for vanishing bath temperature [12].

In the following, we elucidate in detail the complications that arise when evaluating thermodynamic quantities of open quantum systems whose dissipation strength is finite. A most suitable test bed is the case of a *free quantum particle* [5, 8]. It is our working hypothesis that this simple system better be understood first before daring to embark on more complex physical situations. As is well known, a classical free particle does not obey the Third Law. Surprisingly, the coupling to a heat bath renders the system more quantum thereby helping to restore the Third Law [8].

The work is organized as follows. In the next section, we couple a free quantum particle to a heat bath which exerts a finite dissipation on the free particle. We then focus on the evaluation of thermal equilibrium quantities, in particular the specific heat. In section 3, we introduce two definitions of the specific heat which *a priori* both seem physically well motivated. Their properties are investigated in sections 4 and 5. The emerging results cause worrisome ‘baffling’, which we attempt to resolve by inspecting more closely the underlying density of states of a dissipative free particle. Some conclusions and consequences are given in our final section.

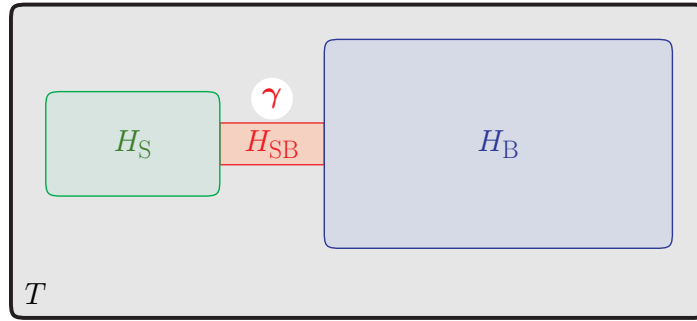


Figure 1. The setup of an open nanosystem with Hamiltonian H_S which is coupled with finite strength γ through an interaction H_{SB} to a bath described by a Hamiltonian H_B . The total system composed of system plus bath is weakly coupled to a super-bath which provides the working temperature T in thermal equilibrium.

2. Coupling a free particle to a heat bath

2.1. Dissipation and the corresponding quantum Langevin equation

As mentioned in the introduction, a free particle, or more generally, an ensemble of non-interacting, distinguishable particles fails to approach zero entropy at accessible temperatures. This classical behaviour is modified when the particle is able to exchange energy with a heat bath. We therefore focus on the simplest situation of a free quantum particle of mass M that is coupled to a heat bath made up of harmonic oscillators. The total Hamiltonian of particle plus bath thus reads (see figure 1)

$$H = H_S + H_B + H_{SB}, \quad (1)$$

where

$$H_S = \frac{p^2}{2M} \quad (2)$$

describes the free particle with momentum operator p , and

$$H_B = \sum_{i=1}^N \left(\frac{p_i^2}{2m_i} + \frac{m_i}{2} \omega_i^2 x_i^2 \right) \quad (3)$$

represents a set of harmonic oscillators constituting the heat bath which is bilinearly coupled to the free particle via its position operator q by

$$H_{SB} = \sum_{i=1}^N \frac{m_i \omega_i^2}{2} (-2qx_i + q^2). \quad (4)$$

Here, the coupling constants have been chosen without loss of generality in such a way that the ensemble of free particles and heat bath is translationally invariant so that the damped particle can still be considered as free [5].

Elimination of the heat bath leads to an effective equation of motion for the position operator of the damped free particle, the quantum Langevin equation of a free particle, reading

$$M \frac{d^2}{dt^2} q + M \int_{t_0}^t ds \gamma(t-s) \frac{d}{ds} q = \xi(t). \quad (5)$$

The coupling to the heat bath results in a damping kernel

$$\gamma(t) = \frac{1}{M} \sum_{i=1}^N m_i \omega_i^2 \cos(\omega_i t) \quad (6)$$

and an operator-valued noise term

$$\xi(t) = -M\gamma(t-t_0)q(t_0) + \sum_{i=1}^N [m_i \omega_i^2 x_i(t_0) \cos(\omega_i(t-t_0)) + \omega_i p_i(t_0) \sin(\omega_i(t-t_0))], \quad (7)$$

which depends on the initial conditions of free particle and heat bath. The sum of the second and third contributions of this expression, i.e.

$$\eta(t) = \xi(t) + M\gamma(t-t_0)q(t_0), \quad (8)$$

only depends on the initial positions and momenta of the heat bath and is characterized by a vanishing first moment,

$$\langle \eta(t) \rangle_B = 0, \quad (9)$$

while the symmetrized correlation function obeys

$$\frac{1}{2} \langle \eta(t)\eta(s) + \eta(s)\eta(t) \rangle_B = \frac{\hbar}{2} \sum_{i=1}^N m_i \omega_i^3 \cos(\omega_i(t-s)) \coth\left(\frac{\hbar\omega_i}{2k_B T}\right). \quad (10)$$

Here, $\langle \dots \rangle_B$ denotes an expectation value with respect to the equilibrium density matrix $\exp(-\beta H_B)/\text{Tr}[\exp(-\beta H_B)]$ of the isolated bath. The temperature T is imposed on the heat bath via the weak coupling to a super-bath (see figure 1). The commutator of the noise is non-vanishing, reading

$$[\eta(t), \eta(s)] = -i\hbar \sum_{i=1}^N m_i \omega_i^3 \sin(\omega_i(t-s)), \quad (11)$$

and guarantees that the familiar commutator-relation between position q and momentum p is obeyed at all times, as required by quantum mechanics.

In the following, we will restrict ourselves to the so-called Drude model of quantum dissipation where the damping kernel describes exponential memory on the timescale ω_D^{-1} . For positive arguments $t > 0$, the damping kernel assumes the form:

$$\gamma(t) = \gamma \omega_D \exp(-\omega_D t), \quad (12)$$

while for negative times we formally obtain $\gamma(t < 0) = \gamma(|t|)$. This in turn assures that the symmetrized correlation function of the time-homogeneous noise correlation in (10) obeys a generalized Einstein relation [1]. The value γ yields the damping strength according to

$$\int_0^\infty dt \gamma(t) = \gamma. \quad (13)$$

For later use, we will also need the Laplace transform of the damping kernel, which is given by

$$\hat{\gamma}(z) = \int_0^\infty dt \gamma(t) \exp(-zt) = \frac{\gamma \omega_D}{z + \omega_D}. \quad (14)$$

The total mass of the heat bath can be expressed via the appealing formula [5]

$$\sum_{i=1}^N m_i = M \lim_{z \rightarrow 0} \frac{\hat{\gamma}(z)}{z}. \quad (15)$$

As a consequence of the fact that the Drude model behaves ohmically for low frequencies, i.e. $\hat{\gamma}(z)$ goes to a positive constant γ for $z \rightarrow 0$, this heat bath behaves non-ballistically in the sense that it assumes an infinite mass.

The Drude model is typically employed for regularization purposes. As an example, we mention that in the case of strict ohmic dissipation, i.e. memoryless damping where $\gamma(t) = 2\gamma\delta(t)$, the second moment $\langle p^2 \rangle$ of the momentum p with respect to the equilibrium density matrix of system plus bath exhibits an ultraviolet divergence. For the purposes of the regularization of such a quantity, it is assumed that ω_D^{-1} is by far the shortest timescale in the problem apart possibly from the thermal timescale $\hbar\beta$. For a free particle subject to Drude damping, one therefore typically assumes $\gamma \ll \omega_D$. In this paper, we drop the requirement of a high-frequency cutoff, which in turn enables us to study also structured, uncommon environments that may contain a low-frequency cutoff ω_D , even smaller than the damping strength γ .

The Drude model represents the simplest reservoir with memory in the sense that the memory effect can be described by a single additional degree of freedom. In fact, the deterministic equation of motion (5), i.e. where $\xi(t)$ is set to zero, is equivalent to

$$\begin{aligned} \dot{q} &= v, \\ \dot{v} &= z, \\ \dot{z} &= -\omega_D z - \gamma \omega_D v. \end{aligned} \quad (16)$$

This system of differential equations contains a zero-frequency mode because system plus bath is translationally invariant. The remaining two eigenfrequencies are obtained from the second and third equations which describe a damped harmonic oscillator with damping strength ω_D and oscillator frequency $(\gamma\omega_D)^{1/2}$. For $\omega_D > 4\gamma$, one finds exponentially damped motion which for very large cutoff frequencies contains the timescales γ and ω_D as expected. However, for sufficiently small cutoff frequency, where $\omega_D < 4\gamma$, the eigenvalues become complex and one observes a damped oscillation. This makes the Drude model more interesting than one might initially expect.

2.2. Thermodynamics of a dissipative free particle

We note that a thermodynamic description of a free particle can be meaningful only if the particle is confined to stay within a box of finite size. The presence of the box leads to the quantization of the energy levels with the typical excitation energy $\Delta E = \hbar^2\pi^2/2ML^2$ between the first excited state and the ground state for a one-dimensional box of length L with reflecting walls. This system in isolation (i.e. in the absence of dissipation) approaches zero entropy only at extremely low temperatures when the thermal energy is comparable with or below the energy difference between the first excited and the ground state.

Remarkably, although the case of a free particle is of comparably simple structure as that of a harmonic oscillator, the thermodynamic properties of the free particle are more intriguing and cannot be obtained as the limiting case of a harmonic oscillator with a vanishing oscillation frequency, ω_0 [8]. This limiting procedure would yield a free particle dynamics

without a spatially confining box. Such a confinement is intrinsically essential, however, for the existence of a thermodynamic description in terms of a partition function and its corresponding thermodynamic functions, see below.

We shall restrict our investigations to temperatures which are high enough such that the discreteness of the spectrum of a single free particle can be ignored even in the weak-coupling limit, i.e. we will always assume that $\beta\Delta E \ll 1$. For a helium atom at a temperature of approximately 500 pK, which is the lowest temperature that can be reached today in the laboratory, the thermal energy and the excitation energy are equal for a cavity of linear size of the order of 30 μm . Even for such extremely low temperatures, a handy box of linear size of, say, 1 cm would suffice to meet the required condition with $\beta\Delta E \approx 10^{-5}$. In order that any quantum effects can survive under thermal conditions rendering the discreteness of the particle spectrum practically invisible, the bath must provide relevant energy scales that are large compared with the thermal energy. In the case of a bath with a Drude cutoff, these relevant energies are given by the damping constant and the cutoff frequency. Hence, a regime of low temperatures with $\Delta E \ll k_B T \ll \hbar\gamma, \hbar\omega_D$ exists where quantum effects can be expected to become relevant.

3. Free quantum Brownian motion: two routes for calculating specific heat

We are interested in the specific heat of a free damped particle. The volume in which the particle can move, will be assumed very large but fixed. In this case, the specific heat is obtained from the internal energy U by taking the derivative with respect to the temperature T , i.e.

$$C = \frac{\partial U}{\partial T}. \quad (17)$$

Usually, it is supposed that the coupling of the system to the heat bath defining the temperature can be treated in the limit of vanishing coupling strength. However, here we are interested in the case of finite coupling where the meaning of the system's internal energy is no longer obvious. In the following, we will study two different approaches.

One possibility is to replace U by the energy E defined as expectation value of the system Hamiltonian H_S

$$E = \langle H_S \rangle, \quad (18)$$

where

$$\langle H_S \rangle = \frac{\text{Tr}_{S+B}[H_S \exp(-\beta H)]}{\text{Tr}_{S+B}[\exp(-\beta H)]}, \quad (19)$$

with $\beta = 1/k_B T$ being the inverse temperature. This leads to our *first* definition of a specific heat

$$C^E = \frac{\partial E}{\partial T}. \quad (20)$$

This definition is based on the system Hamiltonian H_S and includes the interaction of the system with the bath only via the density matrix of the total system.

Alternatively, one can start from the well-known and widely used expression for the partition function of the reduced system: It is defined in terms of the partition functions of the coupled system and of the uncoupled bath as [5, 6, 8, 9], [13]–[20]

$$Z = \frac{\text{Tr}_{S+B}[\exp(-\beta H)]}{\text{Tr}_B[\exp(-\beta H_B)]}, \quad (21)$$

where the total Hamiltonian H consists of contributions from the system, the bath and the coupling according to (1). Employing the standard relation between partition function and internal energy

$$U = -\frac{\partial}{\partial\beta} \ln(Z), \quad (22)$$

equation (21) implies that the internal energy is defined as

$$\begin{aligned} U &= \langle H \rangle - \langle H_B \rangle_B \\ &= E + [\langle H_{SB} \rangle + \langle H_B \rangle - \langle H_B \rangle_B]. \end{aligned} \quad (23)$$

While the internal energy U and the system energy E agree in the absence of a coupling between system and bath, this is no longer the case at finite coupling. Particularly disturbing is the observation that this difference is not solely given by the expectation value of the interaction Hamiltonian H_{SB} , but still contains the difference of the bath energies caused by the interaction with the system.

We can now proceed and define a *second* specific heat, reading

$$C^Z = \frac{\partial U}{\partial T}. \quad (24)$$

The partition function (21) also allows us to define an entropy

$$S = k_B \left[\ln(Z) - \beta \frac{\partial}{\partial\beta} \ln Z \right]. \quad (25)$$

This results from the thermodynamic relation

$$S = -\frac{\partial F}{\partial T} \quad (26)$$

with the free energy $F = -(1/\beta)\ln(Z)$.

Alternatively, the second specific heat (24) can as well be derived from the entropy (25); i.e. C^Z is equivalently obtained as

$$C^Z = T \frac{\partial S}{\partial T}. \quad (27)$$

Our main concern is that these two routes, (20) and (24), of obtaining a specific heat generally yield different results. This will be elucidated further by studying the dissipation model of the Drude form when applied to the simple quantum dynamics of a free particle.

4. Follow the route using energy

We start our exploration of the specific heat by employing the definition (20) based on the expectation value of the system energy

$$E = \frac{1}{2M} \langle p^2 \rangle. \quad (28)$$

Here, M denotes the mass of the particle and p the momentum operator. For a general heat bath leading to an equation of motion of the form (5) and for thermal energies β^{-1} that are large compared with the energy scale $\hbar^2\pi^2/2ML^2$, one finds [5]

$$E = \frac{1}{2\beta} \left[1 + 2 \sum_{n=1}^{\infty} \frac{\hat{\gamma}(v_n)}{v_n + \hat{\gamma}(v_n)} \right] \quad (29)$$

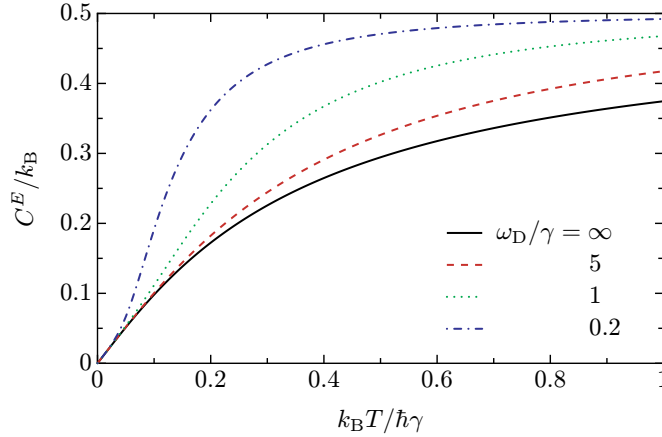


Figure 2. Energy route: the specific heat C^E is depicted as a function of dimensionless temperature for different ratios of ω_D/γ . The approach towards the classical limit $C^E = 0.5$ at low temperature is inversely proportional to friction strength γ ; it notably becomes enhanced for decreasing values of cutoff frequencies ω_D . The specific heat itself is always positive and monotonically increases with increasing temperature T .

with the Matsubara frequencies $\nu_n = 2\pi n/\hbar\beta$. In the high-temperature limit, the sum vanishes and one recovers $E = k_B T/2$, in agreement with the classical equipartition theorem. For strictly ohmic damping, $\hat{\gamma}(z) = \gamma$, the sum diverges as mentioned above and one is obliged to introduce a cutoff in the spectral density of the heat bath. From (29), we obtain by means of (20) the specific heat

$$\frac{C^E}{k_B} = \frac{1}{2} + \sum_{n=1}^{\infty} \frac{\hat{\gamma}^2(\nu_n) + \nu_n^2 \hat{\gamma}'(\nu_n)}{(\nu_n + \hat{\gamma}(\nu_n))^2}, \quad (30)$$

where the prime denotes a derivative with respect to the argument.

For strictly ohmic damping one has $\hat{\gamma}(z) = \gamma$ and therefore $\hat{\gamma}'(z) = 0$. It is tempting to drop the second term in the numerator of the sum and to evaluate the resulting sum which converges even for strict ohmic damping. However, this would yield a specific heat which diverges as the temperature approaches zero (see also the discussion after (35)). The reason for this unphysical behaviour is that for constant $\hat{\gamma}(z)$ the sum in (29) does not converge and therefore derivatives should not be taken term-by-term.

For the Drude model, one obtains with (14) for the specific heat C^E :

$$\frac{C^E}{k_B} = \frac{x_1 x_2}{x_1 - x_2} [x_2 \psi'(x_2) - x_1 \psi'(x_1)] - \frac{1}{2}, \quad (31)$$

where $\psi'(x)$ denotes the trigamma function and

$$x_{1,2} = \frac{\hbar\beta\omega_D}{4\pi} \left(1 \pm \sqrt{1 - \frac{4\gamma}{\omega_D}} \right) \equiv \frac{\hbar\beta\omega_{1,2}}{2\pi}. \quad (32)$$

The behaviour of this result is depicted in figure 2 for differently structured ohmic baths as characterized by various ratios of cutoff ω_D over damping strength γ .

We next study some asymptotic limits more closely. For *high* temperatures T much larger than $\hbar\gamma/k_B$ and $\hbar\omega_D/k_B$, the specific heat approaches the expected classical result with the leading quantum corrections reading

$$\frac{C^E}{k_B} = \frac{1}{2} - \frac{\hbar^2\gamma\omega_D}{24(k_B T)^2} + O(T^{-3}). \quad (33)$$

At *low* temperatures, i.e. for $k_B T \ll \hbar\gamma$, $\hbar\omega_D$ but still $k_B T \gg \hbar^2\pi^2/2ML^2$, the specific heat goes to zero linearly according to

$$\frac{C^E}{k_B} = \frac{\pi k_B T}{3 \hbar\gamma} - \frac{4\pi^3}{15} \left(\frac{k_B T}{\hbar\gamma}\right)^3 \left(1 - 2\frac{\gamma}{\omega_D}\right) + O(T^5). \quad (34)$$

This behaviour is in agreement with the Third Law: Finite quantum dissipation thus restores the validity of the Third Law of a free particle already at temperatures for which the discreteness of the particle spectrum is still irrelevant. The limiting behaviour is inversely proportional to damping strength. Put differently, strong dissipation diminishes the prefactor and thereby yields a turnover to the classical behaviour at higher temperatures only. The leading low-temperature behaviour of the specific heat only depends on the low-frequency behaviour of $\hat{\gamma}(z)$. Notably, only the next-to-leading order also depends on the cutoff frequency ω_D .

In the limit of an infinite cutoff frequency $\omega_D \rightarrow \infty$ the complete temperature dependence is obtained from (31) as

$$\frac{C^E}{k_B} = \left(\frac{\hbar\gamma}{2\pi k_B T}\right)^2 \psi' \left(\frac{\hbar\gamma}{2\pi k_B T}\right) - \frac{\hbar\gamma}{2\pi k_B T} - \frac{1}{2}. \quad (35)$$

The second term would have been missed in a naive calculation where one simply sets $\gamma'(z) = 0$ and subsequently evaluates the sum in (30). This term is important because it ensures that the specific heat does not diverge for $T \rightarrow 0$.

5. Follow the route using the thermodynamic partition function

In order to obtain the specific heat from the partition function (21), one must first determine the latter quantity for the damped free particle.

We again assume that the volume available to the particle is sufficiently large so that the discreteness of the energy levels can be neglected. In the limit of vanishing coupling to the heat bath, the partition function is given by

$$Z_0 = \frac{L}{\hbar} \left(\frac{2\pi m}{\beta}\right)^{1/2}. \quad (36)$$

This result is a consequence of the density of states $\rho(E) \sim E^{-1/2}$ of a free particle in one dimension.

In the presence of a finite coupling γ to the heat bath, the partition function is modified by the ratio of the two fluctuation determinants for the free particle in the absence and presence of the dissipative coupling [5, 13, 14, 17]. We then obtain for this so defined partition function

$$Z = \frac{L}{\hbar} \left(\frac{2\pi m}{\beta}\right)^{1/2} \prod_{n=1}^{\infty} \frac{\nu_n}{\nu_n + \hat{\gamma}(\nu_n)}, \quad (37)$$

which will represent the starting point for all following calculations discussed in this section. We recall that the modifications due to the environmental coupling do not take into account the presence of confining walls. In using this expression for the partition function, we therefore assume a sufficiently large confining box so that boundary effects, which could show up in the partition function, can safely be neglected.

The specific heat can be calculated from the partition function either by means of the internal energy (24) or the entropy (27). Both routes lead to identical results. In order to stay close to the reasoning of the previous section, we choose the first alternative.

The internal energy of a damped free particle is obtained from (37) by means of (22), reading

$$U = \frac{1}{2\beta} \left[1 + 2 \sum_{n=1}^{\infty} \frac{\hat{\gamma}(v_n) - v_n \hat{\gamma}'(v_n)}{v_n + \hat{\gamma}(v_n)} \right]. \quad (38)$$

This internal energy differs from the energy (29) by the second term of the numerator appearing in the sum.

For the Drude model, the sum can be evaluated and the internal energy is obtained as

$$U = \frac{\hbar\omega_D}{2\pi} \psi\left(\frac{\hbar\beta\omega_D}{2\pi}\right) - \frac{x_1}{\beta} \psi(x_1) - \frac{x_2}{\beta} \psi(x_2) - \frac{1}{2\beta}, \quad (39)$$

where $\psi(x)$ is the digamma function and $x_{1,2}$ are defined in (32). This result should be contrasted with the energy E for which one finds from (29) for the Drude model

$$E = \frac{x_1 x_2}{\beta(x_1 - x_2)} (\psi(x_1) - \psi(x_2)) - \frac{1}{2\beta}. \quad (40)$$

It is interesting to note that the internal energy U and the energy E already differ in the high-temperature limit, i.e. $\hbar\beta\omega_D/2\pi \ll 1$; consequently leading to differing high-temperature quantum corrections to the specific heat as shown below. This disagreement even persists in the case of strict ohmic damping. Note, however, that in this limit both quantities diverge logarithmically in the cutoff frequency ω_D , so that E and U will contain an infinite energy contribution independent of temperature.

From (39) it is straightforward to evaluate the specific heat C^Z by means of (24); i.e.

$$\frac{C^Z}{k_B} = x_1^2 \psi'(x_1) + x_2^2 \psi'(x_2) - \left(\frac{\hbar\beta\omega_D}{2\pi}\right)^2 \psi'\left(\frac{\hbar\beta\omega_D}{2\pi}\right) - \frac{1}{2}. \quad (41)$$

In the strictly ohmic limit $\omega_D \rightarrow \infty$, this result agrees with the corresponding expression (35) for C^E . Some results obtained from (41) are depicted in figure 3.

For *high* temperatures but finite cutoff, i.e. if $\hbar\beta\gamma/2\pi, \hbar\beta\omega_D/2\pi \ll 1$, one obtains

$$\frac{C^Z}{k_B} = \frac{1}{2} - \frac{\hbar^2 \gamma \omega_D}{12(k_B T)^2} + O(T^{-3}). \quad (42)$$

While this reproduces the correct classical result, the leading correction differs by a factor of two from the high-temperature result of the specific heat (33) derived from the system energy E .

Very puzzling is the behaviour at *low* temperatures. In this limit, the specific heat behaves like

$$\frac{C^Z}{k_B} = \frac{\pi}{3} \frac{k_B T}{\hbar \gamma} \left(1 - \frac{\gamma}{\omega_D}\right) - \frac{4\pi^3}{15} \left(\frac{k_B T}{\hbar \gamma}\right)^3 \left[1 - 3\frac{\gamma}{\omega_D} - \left(\frac{\gamma}{\omega_D}\right)^3\right] + O(T^5). \quad (43)$$

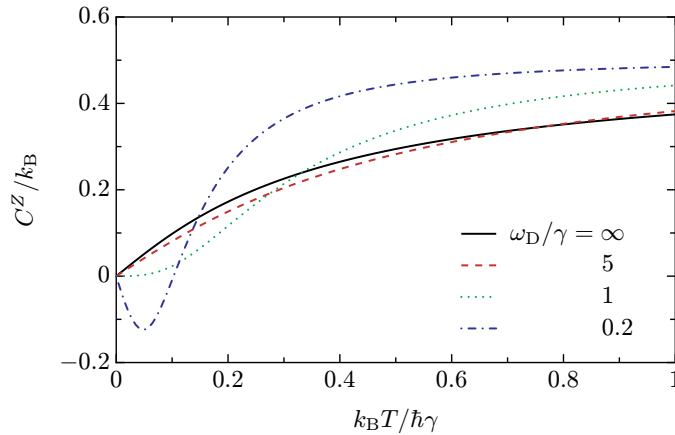


Figure 3. Partition function route: the specific heat C^Z is depicted as a function of dimensionless temperature for different ratios of ω_D/γ . In the strict ohmic limit $\omega_D \rightarrow \infty$ this result agrees with C^E , as depicted in figure 2. The behaviour as a function of finite cutoff is intriguing: while for $\omega_D > \gamma$, C^Z is monotonically growing with increasing temperature, as expected from thermodynamics, this fails to be the case when the friction strength surpasses the cutoff strength. Although still vanishing at absolute zero temperature we find at low temperatures formally negative-valued specific heats for this dissipative quantum system.

Notably this result does again obey the Third Law in the same sense as C^E does. Moreover, equation (43) agrees with (34) for $\omega_D \gg \gamma$. The big surprise surfaces, however, for small cutoff frequencies. For $\omega_D < \gamma$, the specific heat C^Z becomes negative at very low temperatures. This indicates a serious defect which must be hidden somewhere in the theory leading to (43).

The appearance of a negative specific heat is not restricted to the Drude model. This can be seen by expanding the general expression (38) for the internal energy in powers of temperature. By means of the Euler–MacLaurin summation formula, one obtains

$$U = U_0 + \sum_{n=1}^{\infty} \frac{B_{2n}}{(2n)!} \left(\frac{2\pi}{\hbar} \right)^{2n-1} (k_B T)^{2n} [f^{(2n-1)}(\infty) - f^{(2n-1)}(0)], \quad (44)$$

where B_{2n} are the Bernoulli numbers, $f^{(k)}$ denotes the k th derivative of f and the ground-state energy is given by

$$U_0 = \frac{\hbar}{2\pi} \int_0^{\infty} dx f(x). \quad (45)$$

For the free damped particle, one finds, by means of (38),

$$f(x) = \frac{\hat{\gamma}(x) - x\hat{\gamma}'(x)}{x + \hat{\gamma}(x)}. \quad (46)$$

From (44), one readily obtains the specific heat

$$\frac{C^Z}{k_B} = \sum_{n=1}^{\infty} \frac{B_{2n}}{(2n-1)!} \left(\frac{2\pi k_B T}{\hbar} \right)^{2n-1} [f^{(2n-1)}(\infty) - f^{(2n-1)}(0)]. \quad (47)$$

The leading term of this expansion yields

$$\frac{C^Z}{k_B} = \frac{\pi}{3} \frac{1 + \hat{\gamma}'(0)}{\hat{\gamma}(0)} \frac{k_B T}{\hbar} + \mathcal{O}(T^3) \quad (48)$$

in agreement with the specific heat (43) for the Drude model. This result implies that a negative specific heat will be found within the approach based on the partition function for every damping kernel with $\hat{\gamma}'(0) < -1$.

In contrast, for a damped harmonic oscillator with frequency ω_0 , one obtains

$$f(x) = \frac{2\omega_0^2 + x\hat{\gamma}(x) - x^2\hat{\gamma}'(x)}{\omega_0^2 + x\hat{\gamma}(x) + x^2}, \quad (49)$$

resulting in the leading low-temperature behaviour of the specific heat

$$\frac{C^Z}{k_B} = \frac{\pi}{3} \frac{\hat{\gamma}(0)}{\omega_0^2} \frac{k_B T}{\hbar} + O(T^3). \quad (50)$$

Here, the specific heat remains positive independently of the damping kernel.

6. Partition function and density of states

The theory leading to the unexpected appearance of a negative specific heat, cf (43), is based on an assumption and an approximation. The assumption is that the thermodynamic behaviour can be described by the partition function (21). The approximation concerns the calculation of this partition function and limits the validity of the specific heat (42) to sufficiently high temperatures for a fixed size of the box confining the particle. By choosing a sufficiently large box, one though can approach such low temperatures for which the specific heat C^E becomes negative but for which the approximation is still fully justified.

It is therefore the form of the partition function as the ratio of the two partition functions of the total system and the bath that deserves further scrutiny. We will analyse the situation within the Drude model. Inserting the Laplace transform (14) of the damping kernel into the general expression (37) of the partition function, one finds

$$Z = \frac{L}{\hbar} \left(\frac{2\pi m}{\beta} \right)^{1/2} \frac{\Gamma(1+x_1)\Gamma(1+x_2)}{\Gamma(1+\hbar\beta\omega_D/2\pi)}, \quad (51)$$

where $\Gamma(z)$ is the gamma function and $x_{1,2}$ are defined in (32).

Formally, the partition function can be related to a density of states $\rho(E)$ of a damped system by means of a Laplace transform [18]

$$Z(\beta) = \int_0^\infty dE \rho(E) \exp(-\beta E). \quad (52)$$

By its very definition as the number of states at energy E per unit energy, the density of states $\rho(E)$ must not assume negative values. This basic property of the density of states also restricts the admissible form of physically meaningful partition functions. In the remainder of this section, we demonstrate that the unphysical behaviour of the specific heat as given by (43) comes along with negative regions of the density of states.

In order to discuss the partition function and the density of states it is useful to shift the origin of the energy scale to the ground-state energy of the damped free particle

$$U_0 = \frac{\hbar\omega_1}{2\pi} \ln\left(\frac{\omega_D}{\omega_1}\right) + \frac{\hbar\omega_2}{2\pi} \ln\left(\frac{\omega_D}{\omega_2}\right), \quad (53)$$

where the frequencies $\omega_{1,2}$ have been defined in (32). This expression is obtained from (39) in the limit of zero temperature. Instead of the partition function Z , we thus consider $Z \exp(\beta U_0)$.

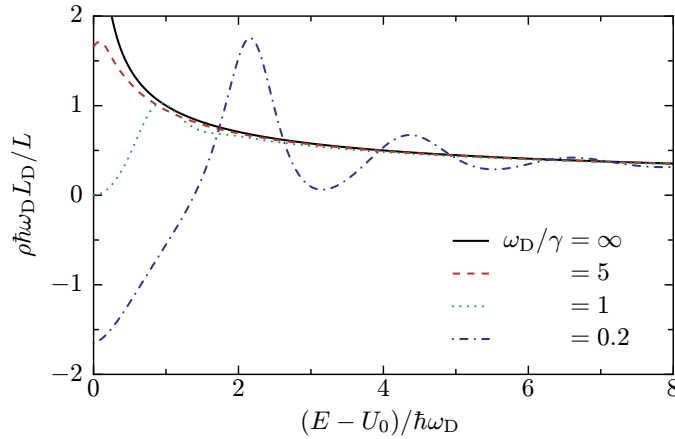


Figure 4. Energy dependence of the density of states for $\omega_D/\gamma = 0.2, 1$ and 5 . The solid line corresponds to the density of states of an undamped particle in one dimension.

As the specific heat (43) may become negative at low temperatures, we focus on the behaviour of the density of states at low energies. For $\hbar\beta\omega_D \gg 1$, one finds

$$Z \exp(\beta U_0) = \frac{L}{L_D} \left(\frac{\pi\gamma}{\omega_D} \right)^{1/2} \times \left[1 + \frac{\pi}{6\hbar\beta\omega_D} \left(\frac{\omega_D}{\gamma} - 1 \right) + \frac{\pi^2}{72(\hbar\beta\omega_D)^2} \left(\frac{\omega_D}{\gamma} - 1 \right)^2 + O(\beta^{-3}) \right], \quad (54)$$

where

$$L_D = \left(\frac{\hbar}{2m\omega_D} \right)^{1/2} \quad (55)$$

is a characteristic length related to the Drude cutoff frequency ω_D . The inverse Laplace transform of (54) yields the low-energy behaviour of the density of states

$$\rho(E) = \frac{L}{\hbar\omega_D L_D} \left(\frac{\pi\gamma}{\omega_D} \right)^{1/2} \left[\delta \left(\frac{E - U_0}{\hbar\omega_D} \right) + \frac{\pi}{6} \left(\frac{\omega_D}{\gamma} - 1 \right) + \frac{\pi^2}{72} \left(\frac{\omega_D}{\gamma} - 1 \right)^2 \frac{E - U_0}{\hbar\omega_D} + O \left(\left(\frac{E - U_0}{\hbar\omega_D} \right)^2 \right) \right]. \quad (56)$$

Except for the delta function at the ground-state energy U_0 , the low-energy behaviour of the density of states is dominated by a constant which changes sign at $\gamma = \omega_D$. If the cutoff frequency ω_D is smaller than the damping constant γ , the density of states is no longer positive everywhere. This readily explains the surprising behaviour of the specific heat found in the previous section. In figure 4, the energy dependence of the density of states is shown for $\omega_D/\gamma = 0.2, 1$ and 5 . For $\omega_D < \gamma$, the density of states starts out with negative values as expected. At larger energies, peaks of the density of states are observed which can be related to the characteristic frequencies of the equation of motion (16), which, for $\omega_D < \gamma$, give rise to

underdamped oscillations. For a sufficiently large damping constant γ , there may exist several energy regions displaying a negative density of states. For $\omega_D \gg \gamma$, one recovers the limit of vanishing damping where

$$\rho_0(E) = \frac{L}{L_D} \frac{1}{(\hbar\omega_D E)^{1/2}}. \quad (57)$$

In the previous section, we have seen that the specific heat of a damped harmonic oscillator at low temperatures is always positive. An analysis along the lines presented above for the free damped particle indeed shows that the density of states, apart from a delta-function contribution, starts out at low temperatures with a positive value. However, the positivity condition of a density of states defined by (52) is by no means obvious as we will discuss next.

By its statistical mechanical definition, the partition function is the sum over the Boltzmann factors counted with the multiplicity of the respective eigenenergies and therefore coincides with the Laplace transform of the density of states as a function of the energy. The corresponding Laplace variable is the inverse temperature β . This in particular implies that the inverse Laplace transform of any proper partition function must not assume any negative values.

Apparently, the positivity of the density of states is not automatically guaranteed by the above definition (21) as can be seen in the case of a free particle. Another example is provided by a system that is coupled to a rather trivial bath consisting of a single oscillator with angular frequency ω . In this case, one obtains for the partition function of the reduced system, according to the definition (21)

$$Z = \frac{\text{Tr}_{\text{S+osc}}[\exp(-\beta H)]}{\text{Tr}_{\text{osc}}[\exp(-\beta H_{\text{osc}})]} = \sum_n g_n e^{-\beta E_n} (e^{\hbar\beta\omega/2} - e^{-\hbar\beta\omega/2}), \quad (58)$$

where E_n denotes the eigenenergies of the system coupled to the oscillator and the positive weights g_n are the corresponding degeneracies. For a finite, spatially confined system, these eigenenergies constitute a discrete spectrum. The first factor of the right-hand side coincides with the partition function of the total system, $Z_{\text{S+B}}$, and the second term represents the inverse of the partition function of the bath consisting of a single oscillator. The inverse Laplace transform $\rho(E)$ of Z becomes

$$\rho(E) = \sum_n g_n \delta(E - E_n + \hbar\omega/2) - \sum_n g_n \delta(E - E_n - \hbar\omega/2). \quad (59)$$

It consists of two sets of delta functions, one with positive weights at the energies $E_n - \hbar\omega/2$, whereas the second set, which is located at the shifted energies $E_n + \hbar\omega/2$, possesses negative weights. Therefore, neither does $\rho(E)$ represent a physically meaningful density of states nor must its Laplace transform $Z = \int dE \exp(-\beta E) \rho(E)$ be interpreted as the partition function of the reduced system.

For reservoirs that represent true thermal baths, both the total system and the reservoir alone will have a continuous spectrum such that a more subtle compensation of the different contributions to the inverse Laplace transform may indeed lead to a positive density of states and a corresponding, physically meaningful partition function.

7. Conclusions

In this work, we compared two definitions of specific heat for a free quantum particle that interacts at a finite strength with an oscillator heat bath possessing a Drude cutoff.

The first definition was based on the assumption that the equilibrium expectation value of the Hamiltonian H_S of the system can be identified with the thermodynamic internal energy of the particle. The resulting specific heat approaches the classical result for high temperatures and goes to zero for vanishing temperature in accordance with the Third Law. The second definition is based on the ratio of the partition functions of the total system and the heat bath, which traditionally is identified as the partition function of an open quantum system [5, 6, 8, 9], [13]–[20].

The two definitions yield different results which even disagree in the high-temperature regime in terms of their quantum corrections. If one associates a free energy with each of the three partition functions of the total system, the system and the bath (as done commonly), the free energy of the open system is expressed as the difference of the free energies of the total system and the heat bath, in accordance with the ‘most remarkable formula’ of Ford *et al* [17]. We found that this definition may lead to unphysical results for the damped free particle, such as negative specific heat and negative regions of the density of states. A corresponding analysis of the respective quantities for a damped harmonic quantum oscillator though does not show any violations of their formal properties [8, 9]. This latter fact alone does not resolve the encountered baffling: the finding of a thermodynamic consistent result which is in no apparent violation with formal properties, such as a truly positive-valued density of states, does not necessarily imply that the so obtained values are physically meaningful.

The definition of the specific heat via the expectation value of the system Hamiltonian H_S leads to a quantity that can be measured in principle. In contrast, no clear scheme seems to be available for a measurement of the specific heat that derives from the partition function of the reduced system.

The conundrum of the physical meaning of a partition function of a reduced system that is coupled with finite strength to an environment thus remains. We emphasize once more that the detected difficulties all ‘evaporate’ when the dissipation can be described within the weak-coupling limit. However, the impressive experimental progress on tailored, well-defined nanosystems whose behaviour is quantum in nature but that are intrinsically in interaction with omnipresent macroscopic environments, requires us to go beyond weak coupling. It thus calls for an urgent clarification of the thermodynamics of nanosystems and related issues.

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