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Thermodynamics of a subensemble of a canonical ensemble

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Two approaches to describing the thermodynamics of a subsystem that interacts with a thermal bath are considered. Within the first approach, the mean system energy E_S is identified with the expectation value of the system Hamiltonian, which is evaluated with respect to the overall (system+bath) equilibrium distribution. Within the second approach, the system partition function Z_S is considered as the fundamental quantity, which is postulated to be the ratio of the overall (system+bath) and the bath partition functions, and the standard thermodynamic relation $E_S=-d(\ln Z_S)/d\beta$ is used to obtain the mean system energy. Employing both classical and quantum-mechanical treatments, the advantages and shortcomings of the two approaches are analyzed in detail for various different systems. It is shown that already within classical mechanics both approaches predict significantly different results for thermodynamic quantities provided the system-bath interaction is not bilinear or the system of interest consists of more than a single particle. Based on the results, it is concluded that the first approach is superior.

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I. INTRODUCTION

Let us consider a system in equilibrium at fixed volume and temperature described by a canonical ensemble. If the partition function Z for the corresponding canonical distribution is known, all thermodynamic quantities, such as the internal energy, the entropy, and the specific heat, can be calculated by simple differentiations of $\ln Z$ with respect to the temperature T. In many situations it is of interest to consider a subsystem of the overall system, e.g., a smaller system that interacts with its environment (in the following referred to as the bath). The question arises as to how to describe the thermodynamics of the subsystem.

If the system-bath coupling is weak, then [to leading (zero) order in the system-bath coupling] the system can be described by a canonical distribution determined by the corresponding system Hamiltonian. This finding builds the basis of standard statistical thermodynamics. If the coupling is not weak, however, the interaction with the bath affects the system density matrix, the system partition function Z_S, and all thermodynamic quantities [1–5]. Furthermore, new interesting effects arise due to the system-bath entanglement [4–10]. In such a case, it is not straightforward, e.g., to define the energy of the system unambiguously. Different definitions are possible which incorporate, to a certain extent, the system-bath interaction into the system energy.

There exist two major approaches to describing the thermodynamics of a subsystem (strongly) coupled to a bath. The first approach (in the following referred to as approach I) considers the mean energy of the system as fundamental quantity and assumes that it is given by the expectation value of the system Hamiltonian which is evaluated with respect to the total (system+bath) canonical equilibrium distribution [11–13]. The second approach (approach II), on the other hand, is based on the partition function of the system, Z_S, and postulates it to be given as the ratio of the total (system+bath) and the bath partition functions. Based on the thus defined partition function of the system, the standard relations of thermodynamics are invoked to calculate the internal energy, the entropy, and the specific heat by differentiations of $\ln Z_S$ with respect to the temperature T [14–16].

In recent work [4,12,13], it was shown that the two approaches give different results for the specific heat of a quantum-mechanical point particle or a harmonic oscillator bilinearly coupled to a harmonic bath, despite the fact that the results are identical in the classical case. In the present work, we analyze the two approaches and assess their validity in detail for several different systems including several quantum and classical point particles and nonlinear system-bath coupling.

Our main findings are summarized as follows. If approach I is employed, then the knowledge of the system partition function Z_S alone is not sufficient to describe the thermodynamics of the system and the standard procedure calculating the thermodynamic quantities by differentiations of $\ln Z_S$ with respect to T is not valid. Additional knowledge of a bath-induced interaction operator Δ_S (see below) is required. We derive general expressions for the mean system energy, the entropy, and the specific heat in terms of Z_S and Δ_S.

If, on the other hand, the strategy of approach II is followed to define the partition function of the system Z_S, then obtaining the internal energy, the entropy, and the specific heat by differentiations of $\ln Z_S$ with respect to T cannot be justified by referring to the standard thermodynamic machinery. The so-obtained expressions must be regarded as the definitions of the corresponding quantities, whose validity must be proven *a posteriori*.

We also show that the differences between the two approaches are not of purely quantum origin. The approaches predict significantly different results already within classical mechanics, provided the system-bath interaction is not bilinear and/or the system of interest consists of more than a single particle. The general results are illustrated by explicit calculations of thermodynamic quantities for several classical and quantum model systems. Based on the thus obtained results, we conclude that approach I is clearly superior to approach II, on both physical and logical grounds.

II. THERMODYNAMICS OF A CANONICAL ENSEMBLE

Let us consider a canonical ensemble which is kept in constant volume L at fixed temperature T. The corresponding equilibrium distribution (density matrix) reads

$$\rho = Z^{-1} \exp\{-\beta H\}, \quad Z = \mathrm{Tr}(\exp\{-\beta H\}). \tag{1}$$

Here H is the Hamiltonian, Z is the partition function, $\beta \equiv 1/k_B T$ (k_B being the Boltzmann constant), and $\mathrm{Tr}(\cdots)$ denotes the integration over phase-space variables in case of a classical ensemble or taking the trace in case of a quantum ensemble. We further define the (information) ensemble entropy operator as

$$S \equiv -k_B \ln \rho = \frac{1}{T}(H - F) \tag{2}$$

and the free energy as

$$F \equiv -\frac{1}{\beta} \ln Z, \tag{3}$$

so that canonical distribution (1) can alternatively be written as

$$\rho = \exp\{-\beta(H - F)\}. \tag{4}$$

Averaging Eq. (2) over canonical distribution (4), we obtain the following expression for the ensemble-averaged entropy:

$$\langle S \rangle = \frac{1}{T}(\langle H \rangle - F), \tag{5}$$

where we have used the notation $\langle \cdots \rangle \equiv \mathrm{Tr}(\rho \cdots)$. The specific heat is determined as

$$C = \frac{d\langle H \rangle}{dT}. \tag{6}$$

Using Eqs. (1) and (4) we can express the internal energy, the entropy, and the specific heat through the free energy:

$$\langle H \rangle = -\frac{d(\ln Z)}{d\beta} = F - T\frac{dF}{dT}, \tag{7}$$

$$\langle S \rangle = -\frac{dF}{dT}, \tag{8}$$

$$C = T\frac{d\langle S \rangle}{dT} = -T\frac{d^2 F}{dT^2}. \tag{9}$$

We emphasize that Eqs. (7)–(9) are a direct consequence of the explicit form and temperature dependence of canonical operator (1).

The second law of thermodynamics in differential form then reads

$$T d\langle S \rangle = d\langle H \rangle. \tag{10}$$

III. THERMODYNAMICS OF A REDUCED CANONICAL ENSEMBLE

A. General expressions

The expressions for the thermodynamical observables of a canonical ensemble listed above can be found in any textbook on statistical thermodynamics. To study the thermodynamics of a subensemble, let us now consider a system that is interacting with its environment (in the following referred to as the bath). We assume that the Hamiltonian H can be split into the system (S) Hamiltonian, the bath (B) Hamiltonian, and their coupling,

$$H = H_S + H_B + H_{SB}. \tag{11}$$

Here H_S depends solely on the system degrees of freedom and H_B depends exclusively on the bath degrees of freedom.

To calculate an observable which depends on the system degrees of freedom only, it is expedient to introduce the reduced density matrix of the system, ρ_S, which is defined by averaging the total density matrix ρ over the bath degrees of freedom,

$$\rho_S \equiv Z^{-1} \mathrm{Tr}_B[\exp\{-\beta(H_S + H_B + H_{SB})\}]. \tag{12}$$

Following Kirkwood [17], Eq. (12) can equivalently be rewritten as [11]

$$\rho_S = Z_S^{-1} \exp\{-\beta(H_S + \Delta_S)\}, \quad Z_S \equiv Z. \tag{13}$$

Here, we have defined the bath-induced interaction operator

$$\Delta_S \equiv -\frac{1}{\beta} \ln \mathrm{Tr}_B[\exp\{-\beta(H_S + H_B + H_{SB})\}] - H_S, \tag{14}$$

which, in general, depends on the system degrees of freedom and on the temperature T.

If the system-bath coupling is weak ($\|H_{SB}\| \ll \|H_S\|, \|H_B\|$), then, to the leading (zero) order in the system-bath coupling, the interaction operator is given by $\Delta_S = -\ln(Z_B)/\beta$. Here Z_B is the partition function of the bath canonical distribution

$$\rho_B = Z_B^{-1} \exp\{-\beta H_B\}, \quad Z_B \equiv \mathrm{Tr}_B(\exp\{-\beta H_B\}). \tag{15}$$

In this weak-coupling case, the overall partition function factorizes, $Z = Z_{S,c} Z_B$ (the subscript "c" stands for "canonical"), and the reduced density matrix (12) is determined by the canonical distribution for the system alone,

$$\rho_{S,c} = Z_{S,c}^{-1} \exp(-\beta H_S), \quad Z_{S,c} = \mathrm{Tr}_S(\exp\{-\beta H_S\}). \tag{16}$$

In general, however, H_{SB} cannot be neglected in Eq. (14) and the simple expression (16) is not valid.

Analogously to Eq. (2), we introduce the system free energy

$$F_S \equiv -\frac{1}{\beta} \ln Z_S, \tag{17}$$

so that distribution (13) can equivalently be rewritten as

$$\rho_S = \exp\{-\beta(H_S + \Delta_S - F_S)\}. \tag{18}$$

Distributions (13) and (18) can be used for calculating the expectation value of any operator Y_S which depends only on the system degrees of freedom [18],

$$\langle Y_S\rangle \equiv \langle Y_S\rangle_S, \quad \langle \cdots\rangle_S \equiv \mathrm{Tr}_S(\rho_S \cdots) \equiv \mathrm{Tr}_{S+B}(\rho \cdots). \quad (19)$$

B. Approach I (mean energy approach)

In approach I, the mean system energy E_S is associated with the expectation value of the system Hamiltonian $\langle H_S\rangle$ [11–13]. Accordingly, the system contribution to the specific heat is determined as

$$C_S = \frac{d\langle H_S\rangle}{dT}. \quad (20)$$

To obtain an expression for the entropy of the system, we follow the presentation in Sec. II and define the information system entropy as

$$S_S \equiv - k_B \ln \rho_S = \frac{1}{T}(H_S + \Delta_S - F_S). \quad (21)$$

Averaging the expression over distribution (13), we obtain the analog of Eq. (5),

$$\langle S_S\rangle = \frac{1}{T}(\langle H_S\rangle + \langle \Delta_S\rangle - F_S). \quad (22)$$

In passing, we note that there exists a controversy in the literature whether the so-defined $\langle S_S\rangle$ can indeed be considered as a proper thermodynamic entropy of the reduced system [4,19,20]. For the purpose of this paper, Eqs. (21) and (22) can merely be considered as intermediate mathematical expressions, which allow us to conveniently derive the formulas discussed below.

In contrast to the situation discussed in Sec. II, the system free energy F_S is no longer a universal object which determines all relevant thermodynamic quantities $\langle S_S\rangle$, $\langle H_S\rangle$, and C_S through Eqs. (7)–(9). It is the explicit dependence of Δ_S on the system degrees of freedom and the temperature which violates the standard thermodynamic expressions for the reduced system. It is straightforward, however, to generalize Eqs. (7)–(9) if we assume that operators H_S and Δ_S commute. In this case, using Eqs. (17)–(20), we obtain the expressions

$$- \frac{d(\ln Z_S)}{d\beta} = F_S - T\frac{dF_S}{dT} = \langle H_S\rangle + \langle \Delta_S\rangle - T\left\langle \frac{d\Delta_S}{dT}\right\rangle, \quad (23)$$

$$\langle S_S\rangle = \left\langle \frac{d\Delta_S}{dT}\right\rangle - \frac{dF_S}{dT}, \quad (24)$$

$$C_S = T\frac{d\langle S_S\rangle}{dT} + \left\langle \frac{d\Delta_S}{dT}\right\rangle - \frac{d\langle \Delta_S\rangle}{dT}. \quad (25)$$

It is important to note that

$$\left\langle \frac{d\Delta_S}{dT}\right\rangle \neq \frac{d\langle \Delta_S\rangle}{dT} \quad (26)$$

due to the explicit temperature dependence of ρ_S. If $H_{SB} \neq 0$, then the last two terms in Eqs. (23) and (25) give a non-negligible contribution. If the bath-induced potential Δ_S in Eq. (24) is temperature independent, then the usual formula (8) for the entropy holds, but the expressions for $\langle H_S\rangle$ [Eq. (23)] and C_S [Eq. (25)] do contain the bath-induced contributions. Furthermore, Eq. (25) shows that the second law of thermodynamics (in differential form) is modified to

$$Td\langle S_S\rangle = d\langle H_S\rangle - \langle d\Delta_S\rangle + d\langle \Delta_S\rangle. \quad (27)$$

To summarize, knowing the partition function Z_S or the free energy F_S alone is not enough to calculate $\langle S_S\rangle$, $\langle H_S\rangle$, and C_S within approach I. Instead, the more general Eqs. (23)–(27) must be used. This should be taken into account if, e.g., work theorems are employed to obtain the system partition functions beyond the weak system-bath coupling limit [21,22]. The general expressions (23)–(27) are also important for the thermodynamics of small systems [23–25].

Equations (23)–(27) have been derived assuming that H_S and Δ_S commute. This requirement is not as restrictive as it might seem at first glance and is enough for the purposes of the present paper. It is obviously fulfilled within classical mechanics. It is also fulfilled in the semiclassical limit considered below described within the Wigner function formalism, provided we start from the total (system+bath) Wigner distribution and introduce the reduced Wigner distribution of the system by averaging the total Wigner distribution over the bath degrees of freedom (see Sec. IV C).

Even in the general case, where $[H_S, \Delta_S] \neq 0$, analogs of Eqs. (7)–(9) can be derived. To this end, we first rewrite the system density matrix in the form

$$\rho_S = Z_S^{-1} \exp\{- \beta H_S\}\exp\{- \beta\tilde{\Delta}_S\} \quad (28)$$

with a slightly redefined bath-induced interaction operator

$$\tilde{\Delta}_S \equiv - \frac{1}{\beta}\ln(\exp\{\beta H_S\}\mathrm{Tr}_B[\exp\{- \beta(H_S + H_B + H_{SB})\}]). \quad (29)$$

Second, we replace $H_S \to \gamma H_S$ in Eq. (28) (with γ being a numerical parameter) but keep $\tilde{\Delta}_S$ unchanged, so that distribution (28) becomes

$$\rho_{\gamma,S} = Z_{\gamma,S}^{-1} \exp\{- \beta\gamma H_S\}\exp\{- \beta\tilde{\Delta}_S\}, \quad (30)$$

$$Z_{\gamma,S} = \mathrm{Tr}_S(\exp\{- \beta\gamma H_S\}\exp\{- \beta\tilde{\Delta}_S\}). \quad (31)$$

Then $Z_{\gamma,S}$ and $F_{\gamma,S}=-\ln(Z_{\gamma,S})/\beta$ become γ dependent and, we obtain the expressions

$$\langle H_S\rangle = - \frac{1}{\beta}\frac{d(\ln Z_{\gamma,S})}{d\gamma} = \left.\frac{dF_{\gamma,S}}{d\gamma}\right|_{\gamma=1}, \quad (32)$$

$$C_S = \left.\frac{d^2F_{\gamma,S}}{d\gamma dT}\right|_{\gamma=1}. \quad (33)$$

C. Approach II (partition function approach)

The reduced distribution (13) remains unchanged if we introduce a certain (possibly temperature-dependent) function $\Upsilon(T)$ and redefine the system partition function and the bath-induced operators as

$$Z_S \to \frac{Z_S}{\Upsilon(T)}, \quad \Delta_S \to \Delta_S + \frac{1}{\beta}\ln \Upsilon(T). \tag{34}$$

The analogous transformation for distribution (18) reads

$$F_S \to F_S - \frac{1}{\beta}\ln \Upsilon(T), \quad \Delta_S \to \Delta_S + \frac{1}{\beta}\ln \Upsilon(T). \tag{35}$$

Transformations (34) and (35) shift the origin of the bath-induced interaction Δ_S. For example, we can take $\Upsilon(T)=Z_B$ [the bath partition function is defined via Eq. (15)]. This choice is especially reasonable for weak system-bath coupling, because it results in $\Delta_S=0$ if $H_{SB}=0$. In general, for any $H_{SB}\neq 0$, it yields the system partition function

$$Z_S = Z/Z_B. \tag{36}$$

Definition (36) is the key to approach II. According to the recipe developed in Refs. [14–16], we should identify Eq. (36) with the system partition function, and use the standard Eqs. (7)–(9) to calculate the necessary thermodynamic quantities.

Approaches I and II result in different expressions for thermodynamic quantities, provided the system-bath coupling is not weak. This will be illustrated in Sec. IV based on different examples. The validity and predictions of the two approaches are discussed in Sec. V.

IV. ANALYSIS OF THE TWO DIFFERENT APPROACHES FOR ILLUSTRATIVE EXAMPLES

A. Model system

We consider a general system-bath problem. We assume that the system [e.g., a (macro)molecule] consists of N_S point particles, X_i, P_i, and M_i being their positions, momenta, and masses. The bath comprises N_B point particles with positions x_i, momenta p_i, and masses m_i. All interactions (S-S, S-B, and B-B) are pairwise, so that the parts of the overall Hamiltonian $H=H_S+H_B+H_{SB}$ are explicitly written as follows:

$$H_S = \sum_{i=1}^{N_S}\left\{\frac{P_i^2}{2M_i} + U_S(X_i)\right\} + \sum_{i>j}^{N_S} U_{SS}(X_i - X_j), \tag{37a}$$

$$H_B = \sum_{i=1}^{N_B}\frac{p_i^2}{2m_i} + \sum_{i>j}^{N_B} U_{BB}(x_i - x_j), \tag{37b}$$

$$H_{SB} = \sum_{i=1}^{N_S}\sum_{j=1}^{N_B} U_{SB}(X_i - x_j). \tag{37c}$$

Here U_{SS}, U_{BB}, and U_{SB} are the corresponding interaction potentials (which may be different for any pair of particles i and j) and the system is allowed to be subjected to an external potential U_S. For clarity, we consider a one-dimensional ensemble. A generalization to the three-dimensional case is straightforward.

B. Classical mechanics

We first consider the two approaches to subensemble thermodynamics for a system of classical point particles. In classical mechanics, the partition function for any canonical distribution is a product of the momentum and coordinate contributions. Furthermore, the momentum contributions to reduced distribution (13) can be integrated out, so that the only nontrivial part of the distribution is the contribution of the potential energy.

1. Single Brownian particle

Let us first consider a single Brownian particle, which corresponds to $N_S=1$ in Eq. (37a). After the insertion of Hamiltonians (37a)–(37c) into Eq. (12), we can make use of the isotropy of space and change the integration variables, $x_i \to x_i - X$. This way, we obtain $\Delta_S=0$ and arrive at the standard result that reduced distribution (13) is the canonical distribution (16) determined by the system Hamiltonian,

$$\rho_S = Z_{S,c}^{-1}\exp\left\{-\beta\left(\frac{P^2}{2M} + U_S(X)\right)\right\}, \tag{38a}$$

$$Z_{S,c} = \sqrt{2\pi M/\beta}\int dX \exp\{-\beta U_S(X)\}. \tag{38b}$$

It is tempting to assume that all thermodynamic characteristics of the Brownian particle can be obtained through the bath-independent canonical system distribution (38a) or, what is equivalent, through the differentiation of partition function (38b) according to the standard Eqs. (7)–(9). This is indeed the case if we use approach I. If we follow approach II, however, we obtain

$$Z/Z_B = \eta Z_{S,c}. \tag{39}$$

Here $Z_{S,c}$ is the free-particle partition function (38b) and

$$\eta = \frac{\int dx_1 \cdots dx_{N_B}\exp\left\{-\beta\left[\sum_{i>j}^{N_B} U_{BB}(x_i - x_j) + \sum_{j=1}^{N_B} U_{SB}(x_j)\right]\right\}}{\int dx_1 \cdots dx_{N_B}\exp\left\{-\beta\left[\sum_{i>j}^{N_B} U_{BB}(x_i - x_j)\right]\right\}}. \tag{40}$$

Apparently, $\eta \neq 1$, in general. This becomes evident, e.g., if we expand the numerator in Eq. (40) in powers of U_{SB}. Symbolically, $\eta = 1 + O(\|U_{SB}\|)$. In approach II, the factor of η induces (unphysical) bath dependence of the system mean energy, entropy, and specific heat. Thus, approaches I and II lead, in general, to different predictions even for a single classical Brownian particle.

An important exception is a Brownian particle bilinearly coupled to a harmonic bath,

$$H_B = \sum_{i=1}^{N_B} \left(\frac{p_i^2}{2m_i} + \frac{m_i \omega_i^2 x_i^2}{2} \right), \tag{41a}$$

$$H_{SB} = \sum_{i=1}^{N_B} \frac{m_i \omega_i^2}{2} (X^2 - 2Xx_i), \tag{41b}$$

where ω_i denotes the frequencies of the bath oscillators. In this case, we obtain $\eta = 1$ and the two approaches give the same result. This is only the case for the simple form of the bilinear system-bath coupling.

If we retain the harmonic bath [Eq. (41a)] but add a nonlinear interaction term to H_{SB}, the situation differs. Let us consider, for example, the potential

$$H_{SB} = \sum_{i=1}^{N_B} \left\{ \frac{m_i \omega_i^2}{2} (X^2 - 2Xx_i) + \frac{\xi_i}{(X - x_i)^2} \right\}, \tag{42}$$

where ξ_i denote the corresponding constants. The additional term in the potential, the form of which has been chosen for demonstrative purposes, may describe repulsion of the particles at short distances. The reduced system partition function Z_S is given by Eq. (38b). Incorporating Eqs. (41a) and (42) into Eq. (40), we obtain for the factor η, which describes the deviation of the system partition function Z_S from the ratio Z/Z_B,

$$\eta = \prod_{j=1}^{N_B} \exp\{-\beta \omega_j \sqrt{2 m_j \xi_j}\}. \tag{43}$$

Thus, even for this rather simple example, the factor η can significantly differ from unity and also acquire a temperature dependence. Within approach II, this would result in incorrect predictions for $\langle S_S \rangle$, $\langle H_S \rangle$, and C_S [26].

2. Harmonic dumbbell

Let us suppose that the system (e.g., a molecule) consists of a collection of point particles. In general, the explicit evaluation of the bath-induced potential Δ_S beyond the weak system-bath coupling limit is a difficult task [11,27,28], except in the case of a harmonic bath (modeling, e.g., a Gaussian solvent) bilinearly coupled to the system. In the latter case, the integrations over x_i in Eq. (12) can easily be performed analytically. It is instructive to consider the simplest nontrivial situation, when the system consists of two identical particles ($N_S = 2$). Such a model can describe, for example, a diatomic molecule or a dumbbell. If we require the total (harmonic) Hamiltonian H [Eq. (11)] to be translationally invariant, we arrive at the expressions

$$H_S = \frac{P_1^2}{2M} + \frac{P_2^2}{2M} + \frac{M\Omega_S^2}{2}(X_1 - X_2)^2, \tag{44a}$$

$$H_{SB} + H_B = \sum_{i=1}^{N_B} \left(\frac{p_i^2}{2m_i} + \frac{m_i \omega_{1i}^2}{2}(X_1 - x_i)^2 + \frac{m_i \omega_{2i}^2}{2}(X_2 - x_i)^2 \right), \tag{44b}$$

where ω_{1i}, ω_{2i}, and Ω_S denote the corresponding oscillator frequencies [29].

For later use it is convenient to rewrite Eq. (44b) in the equivalent form

$$H_{SB} + H_B = \sum_{i=1}^{N_B} \left(\frac{p_i^2}{2m_i} + \frac{m_i}{2}(\omega_{1i}^2 + \omega_{2i}^2) \left\{ x_i - \frac{\omega_{1i}^2 X_1 + \omega_{2i}^2 X_2}{\omega_{1i}^2 + \omega_{2i}^2} \right\}^2 \right) + \frac{M\Omega_\Delta^2}{2}(X_1 - X_2)^2. \tag{45}$$

Here

$$\Omega_\Delta^2 = \sum_{j=1}^{N_B} \frac{m_j \omega_{1j}^2 \omega_{2j}^2}{M(\omega_{1j}^2 + \omega_{2j}^2)} \tag{46}$$

is the frequency of the bath-induced harmonic potential. Integrating out the bath modes, we obtain a reduced distribution ρ_S in the form of Eq. (13) with

$$\Delta_S = \frac{M\Omega_\Delta^2}{2}(X_1 - X_2)^2, \tag{47a}$$

$$Z_S = \frac{2\pi M}{\beta} L \sqrt{\frac{2\pi}{\beta M(\Omega_\Delta^2 + \Omega_S^2)}}. \tag{47b}$$

Here L is the (one-dimensional) system volume. It is seen that the influence of the bath manifests itself in the additional attractive harmonic potential Δ_S, which is coordinate dependent but temperature independent, so that $d\Delta_S/dT = 0$ [30].

For the Hamiltonians (44a) and (44b), the ratio of the total and the bath partition functions yields the system partition function, i.e., $Z/Z_B = Z_S$ [Eq. (47b)]. One might thus expect that approaches I and II give the same predictions for the thermodynamic quantities. Due to the presence of the bath-induced potential Δ_S, this is, however, not the case. Indeed, if we would follow approach II, the mean system energy is given by

$$E_S = -\frac{d(\ln Z_S)}{d\beta} = -\frac{d(\ln\{Z/Z_B\})}{d\beta} = \frac{3}{2\beta}, \tag{48}$$

which corresponds to the thermal energy of a system with 3 degrees of freedom (one for the center-of-mass translation and two for the vibration). If, on the other hand, according to approach I, we associate E_S with $\langle H_S \rangle$, then Eq. (23) yields

$$\langle H_S \rangle = -\frac{d(\ln Z_S)}{d\beta} - \langle \Delta_S \rangle = \frac{1}{2\beta}\left(3 - \frac{\Omega_\Delta^2}{\Omega_\Delta^2 + \Omega_S^2} \right). \tag{49}$$

Thus, approach II predicts for the heat capacity that $C_S = 3k_B/2$, irrespective of the strength of the dumbbell (Ω_S^2) and solvent-induced (Ω_Δ^2) potentials. This seems to be physically incorrect, given that the reduced distribution ρ_S contains the bath-induced attractive harmonic potential Δ_S [Eq. (47a)] and does not coincide with canonical distribution (16) for the dumbbell alone. Approach I, on the other hand, predicts the bath-dependent specific heat to be

$$C_S = \frac{k_B}{2}\left(3 - \frac{\Omega_\Delta^2}{\Omega_\Delta^2 + \Omega_S^2}\right). \tag{50}$$

The coupling to the solvent has the strongest influence in case of two free Brownian particles ($\Omega_S^2=0$). In this case, the actual number of degrees of freedom is reduced by 1, which is in accordance with the physical expectations.

C. Quantum mechanics

We next analyze the two approaches to subensemble thermodynamics for quantum-mechanical point particles. In the quantum-mechanical case, there exist pitfalls and subtleties in the calculation of the specific heat already for a single Brownian particle bilinearly coupled to a heat bath of harmonic oscillators. This was demonstrated in Refs. [4,12,13]. To elucidate the nature of these subtleties and to simplify the presentation, we restrict ourselves to a semiclassical analysis and calculate the leading-order ($\sim\hbar^2$) quantum corrections to the thermodynamic quantities. To this end, we employ the Wigner representation [31].

To simplify the notation, we introduce a collective index a which runs over all N_S+N_B system and bath particles and use a tilde to denote the corresponding positions, momenta, and masses. Thus, total Hamiltonian (11) reads

$$H = \sum_a \left\{\frac{\tilde{p}_a^2}{2\tilde{m}_a}\right\} + U(\tilde{x}_1, \ldots, \tilde{x}_{N_S+N_B}). \tag{51}$$

Within the Wigner representation, we treat $\tilde{p}_a$ and $\tilde{x}_a$ as (semi)classical phase-space variables. The Hamiltonian retains its classical form, but the canonical distribution for the overall system [Eq. (1)] is given by the corresponding Wigner distribution (denoted by the superscript W)

$$\rho^W = Z^{-1}\exp\{-\beta H + \lambda H^{(1)}\} + O(\lambda^2), \tag{52a}$$

$$Z = \mathrm{Tr}(\exp\{-\beta H + \lambda H^{(1)}\}) + O(\lambda^2), \tag{52b}$$

$$\lambda \equiv (2\pi\hbar)^2. \tag{52c}$$

Here, as in the classical case, $\mathrm{Tr}(\cdots)$ denotes the integration over the corresponding phase-space variables. The quantum correction $H^{(1)}$ is explicitly given as [31,32]

$$H^{(1)} = \sum_a \left\{-\frac{\beta^2}{8\tilde{m}_a}\frac{\partial^2 U}{\partial \tilde{x}_a^2} + \frac{\beta^3}{24\tilde{m}_a}\left(\frac{\partial U}{\partial \tilde{x}_a}\right)^2\right\} + \sum_{a,b}\frac{\beta^3\tilde{p}_a\tilde{p}_b}{24\tilde{m}_a\tilde{m}_b}\frac{\partial^2 U}{\partial \tilde{x}_a\,\partial \tilde{x}_b}. \tag{53}$$

It is noted that $H^{(1)}$ is explicitly temperature dependent and contains mixed coordinate-momenta terms.

The reduced Wigner distribution of the system, ρ_S^W, is obtained by integrating the Wigner distribution of the overall system [Eq. (52a)] over the phase-space variables of the bath. Since H and $H^{(1)}$ in Eq. (52a) are functions but not operators, expressions (12)–(27) derived in Sec. III remain also correct for the reduced Wigner distribution. In general, the Wigner transform of an operator differs from its respective classical expression, because quantum mechanically positions and momenta do not commute. However, if an operator can be split into a part which depends only on coordinates and a part which depends only on momenta, then the Wigner transform is given by the corresponding classical expression. This is the case for H_S, H_B, and H_{SB}. Therefore, we can use the classical expression for H_S while evaluating the mean system energy.

1. Quantum Brownian particle

As in Ref. [13], we consider a single Brownian particle bilinearly coupled to a heat bath of harmonic oscillators. The system Hamiltonian is given by Eq. (37a) with $N_S=1$, the bath Hamiltonian by Eq. (41a), and the system-bath coupling by Eq. (41b). Inserting the corresponding formulas into Eqs. (51) and (53), we can integrate the bath degrees of freedom out of the overall (system+bath) Wigner distribution (52a) and arrive at the system distribution

$$\rho_S^W = Z_S^{-1}\exp\{-\beta(H_S + \Delta_S)\} + O(\lambda^2). \tag{54}$$

Here $H_S = P^2/2M$ is the free-particle Hamiltonian, the bath-induced interaction operator reads

$$\Delta_S = -\lambda\frac{P^2}{2M}\frac{(\Omega\beta)^2}{12}, \quad \Omega^2 = \sum_{j=1}^{N_B}\frac{m_j\omega_j^2}{M}, \tag{55}$$

and the partition function is given by the expression

$$Z_S = L\sqrt{\frac{2\pi M}{\beta[1-\lambda(\Omega\beta)^2/12]}} = L\sqrt{\frac{2\pi M}{\beta}}\left(1 + \frac{\lambda(\Omega\beta)^2}{24}\right) + O(\lambda^2). \tag{56}$$

The bath-induced operator Δ_S is position independent, but depends on momentum and temperature.

The ratio of the total (Z) and bath (Z_B) partition functions can also be readily obtained from expressions (52a) and (53) to yield

$$\frac{Z}{Z_B} = L\sqrt{\frac{2\pi M}{\beta}}\left(1 - \frac{\lambda(\Omega\beta)^2}{24}\right) + O(\lambda^2). \tag{57}$$

A comparison of Eqs. (57) and (56) shows that the partition function of the system is not given by the ratio of the total (Z) and bath (Z_B) partition functions. The quantum corrections in the two expressions have the same magnitude but opposite signs.

Since the bath-induced operator Δ_S is momentum and temperature dependent, it is not expected that the differentiation of the partition function alone gives the averaged energy $\langle H_S\rangle$. Indeed, the calculation gives

$$-\frac{d(\ln Z_S)}{d\beta}=\frac{1}{2\beta}-\frac{\lambda\Omega^2}{12}\beta+O(\lambda^2). \tag{58}$$

On the other hand, if we follow approach I and use Eq. (23) or perform directly an average over distribution (54), we obtain the correct value

$$\langle H_S\rangle=\frac{1}{2\beta}+\frac{\lambda\Omega^2}{24}\beta+O(\lambda^2). \tag{59}$$

Finally, approach II predicts for the average system energy

$$E_S=-\frac{d(\ln\{Z/Z_B\})}{d\beta}=\frac{1}{2\beta}+\frac{\lambda\Omega^2}{12}\beta+O(\lambda^2). \tag{60}$$

It is noted that Eqs. (60) and (59) were derived in [13] using a different method. The results obtained for the average system energy via the different approaches, Eqs. (58)–(60), are all different, thus providing a nice example of how noncritical use of the standard thermodynamic equations (23) can lead to ambiguous results.

2. Quantum harmonic dumbbell

As a final example we consider the harmonic model of a dumbbell coupled to a bath quantum mechanically [33,34]. The thermodynamics of the quantum harmonic dumbbell can be constructed within the Wigner distribution method employing the general Eqs. (52a) and (53). The total classical dumbbell+bath Hamiltonian H in Eq. (52a) is given by Eqs. (44a) and (45). Further, H is inserted into Eq. (53) to derive the quantum correction $H^{(1)}$. The so-obtained expression is, however, quite cumbersome and is not presented. Here, we only give the results necessary for the discussion of the thermodynamic quantities.

The reduced Wigner distribution of the system is given by the general formula (54), where H_S is defined via Eq. (44a) and the bath-induced operator reads

$$\Delta_S=\Delta_S^0-\frac{\lambda\beta^2}{12}\Delta_S^1. \tag{61}$$

Here we have introduced the notation

$$\Delta_S^0=\frac{M\Omega_\Delta^2}{2}(X_1-X_2)^2, \tag{62a}$$

$$\Delta_S^1=M(\Omega_S^2+\Omega_\Delta^2)^2(X_1-X_2)^2+\frac{P_1^2}{2M}(\Omega_1^2+\Omega_S^2)$$
$$+\frac{P_2^2}{2M}(\Omega_2^2+\Omega_S^2)-\frac{P_1P_2}{M}\Omega_S^2, \tag{62b}$$

$$\Omega_1^2=\frac{1}{M}\sum_{j=1}^{N_B}m_j\omega_{1j}^2,\qquad \Omega_2^2=\frac{1}{M}\sum_{j=1}^{N_B}m_j\omega_{2j}^2. \tag{62c}$$

The frequency Ω_Δ^2 of the bath-induced harmonic potential is defined via Eq. (46). The bath-induced operator Δ_S is explicitly coordinate dependent [due to classical contribution (62a)] as well as momentum and temperature dependent [due to quantum correction (62b)]. The corresponding partition function reads

$$Z_S=Z_S^{cl}\left\{1+\frac{\lambda\beta^2}{24}(4\Omega_S^2+2\Omega_\Delta^2+\Omega_1^2+\Omega_2^2)\right\}, \tag{63}$$

where the classical system partition function Z_S^{cl} is given by Eq. (47b).

The mean energy of the dumbbell calculated via approach I [employing Eq. (54)] is given by the expression

$$\langle H_S\rangle=\langle H_S\rangle_{cl}+\lambda\langle H_S\rangle_q+O(\lambda^2). \tag{64}$$

Here the first term is the classical contribution

$$\langle H_S\rangle_{cl}=\frac{1}{\beta}\left(1+\frac{1}{2}\frac{\Omega_S^2}{\Omega_\Delta^2+\Omega_S^2}\right), \tag{65}$$

and the quantum correction reads

$$\langle H_S\rangle_q=\frac{\beta}{24}\left\{5\Omega_S^2+\Omega_1^2+\Omega_2^2+\frac{1}{2}\frac{\Omega_S^2}{\Omega_\Delta^2+\Omega_S^2}(2\Omega_S^2+\Omega_1^2+\Omega_2^2)\right\}. \tag{66}$$

In the limit $\Omega_S^2=0$, $\Omega_1^2=\Omega_2^2$; the dumbbell reduces to two noninteracting Brownian particles. Correspondingly, mean energy (64) gives twice of what is predicted by Eq. (59). The same is true for the bath-induced interaction operators Δ_S [cf. Eqs. (61) and (55)].

On the other hand, if we follow approach II, we obtain for the ratio of the partition functions of the overall system and the bath

$$\frac{Z}{Z_B}=Z_S^{cl}\left\{1-\frac{\lambda\beta^2}{24}(2\Omega_S^2+\Omega_1^2+\Omega_2^2)\right\}, \tag{67}$$

and correspondingly as prediction for the mean energy of the system

$$-\frac{d(\ln\{Z/Z_B\})}{d\beta}=\frac{3}{2\beta}+\frac{\lambda\beta}{12}(2\Omega_S^2+\Omega_1^2+\Omega_2^2)+O(\lambda^2). \tag{68}$$

The comparison with Eq. (64) shows that approaches I and II give not only different classical contributions to the mean system energy, but also very different quantum corrections. It is also interesting to note that the strength of the bath-induced potential, Ω_Δ^2, does not enter the expression for the mean energy [Eq. (68)], while the mean energy calculated via approach I [Eq. (64)] depends sensitively on this quantity.

V. DISCUSSION AND CONCLUSIONS

The results presented above demonstrate that the two different approaches to describing the thermodynamics of a subsystem can predict very different results if the system-bath coupling is not weak. This was already shown earlier for a quantum harmonic oscillator [12] and for a quantum Brownian particle [13] bilinearly coupled to a harmonic bath. The results obtained here corroborate and extend these earlier findings. The study also shows that ambiguities in the description of reduced thermodynamics already occur in the classical case for more complex systems, such as an anharmonic bath (Sec. IV B 1) or if the system under study consists of more than a single point particle (Sec. IV B 2). Based on the results above we shall now analyze the two approaches and discuss their advantages and shortcomings.

The different predictions of the two approaches for the thermodynamic quantities can be related to the ambiguities in the definition of the energy of a system that is coupled to the environment. If the system-bath coupling is not negligible, the system-bath interaction H_{SB} (or a certain part of it) may be included in the system energy [35], thus resulting in a variety of definitions. Furthermore, the results for the thermodynamic quantities may depend on the particular physical quantity that is considered fundamental (e.g., the system energy or the partition function).

Approach I associates the mean system energy E_S with the expectation value of the system Hamiltonian $\langle H_S \rangle$. The definition $E_S = \langle H_S \rangle$ clearly associates the observable (E_S) with the corresponding physical operator H_S. This definition appears natural and fits into the general scheme of statistical thermodynamics and probability theory. For example, if we think of E_S as the mean internal energy (e.g., the internal energy of a molecule with several vibrational degrees of freedom), the choice $E_S = \langle H_S \rangle$ is well physically justified. As a result of the definition $E_S = \langle H_S \rangle$, the bath and the system-bath coupling influence the mean system energy E_S only indirectly, through the reduced distribution (density matrix) of the system ρ_S given by Eq. (13). It is important to note that ρ_S does not coincide with the canonical distribution for the isolated system. As a consequence, the thermodynamics of the reduced system is described by relations (23)–(27). Once the definition $E_S = \langle H_S \rangle$ is accepted, no other assumptions are necessary to construct the system thermodynamics. Corroborating the results obtained in Refs. [12,13], the present extended study shows that the use of this definition gives rise to physically and logically consistent results for both quantum-mechanical and classical systems.

The fundamental quantity of approach II, on the other hand, is the partition function of the system, Z_S. To obtain thermodynamic quantities, approach II involves two steps. First, the partition function of the system is identified as the ratio of the total and bath partition functions, Z/Z_B [Eq. (13)]. In addition to this choice, approach II assumes that the standard thermodynamical relations given by Eqs. (7)–(9) can be used to calculate thermodynamic quantities such as the mean energy, the entropy, and the specific heat. The choice $Z_S = Z/Z_B$ for the partition function of the system appears to be reasonable, notably in the limit of weak system-bath coupling. However, as discussed in Sec. III C, the partition function $Z_S = Z/Z_B$ corresponds to the reduced distribution ρ_S given in Eqs. (13) and (34), which does not coincide with the corresponding canonical distribution for the isolated system alone. Instead, ρ_S contains an additional bath-induced operator Δ_S which, in general, depends on the temperature and on the degrees of freedom of the system. In such a case, as has been shown in Sec. III A, the thermodynamic relations for a subensemble, Eqs. (23)–(27), should be employed instead of the standard thermodynamic relations (7)–(10), provided the system-bath coupling is not small. Therefore, there is no *a priori* theoretical justification for using $Z_S = Z/Z_B$ in Eqs. (7)–(10), and we have to additionally postulate that differentiations of $F_S = -\ln(Z/Z_B)/\beta$ give, according to Eqs. (7)–(9), the mean system energy, entropy, and specific heat. Thus the two fundamental assumptions of approach II, the choice of Z_S and the validity of the standard thermodynamic relations (7)–(10) even for the subensemble, cannot be proven within the approach itself.

It also worthwhile to mention another peculiarity of approach II. As was pointed out in Refs. [12,13], the mean energy of the system obtained within approach II corresponds to the definition

$$E_S = \langle H \rangle - \langle H_B \rangle_B \equiv \langle H_S \rangle + \langle H_B + H_{SB} \rangle - \langle H_B \rangle_B, \quad (69)$$

where $\langle \cdots \rangle_B$ denotes averaging over the bath distribution [Eq. (15)]. For nonvanishing system-bath interaction, the term $\langle H_B + H_{SB} \rangle - \langle H_B \rangle_B$ gives an additional contribution to E_S that is not present in approach I. As a consequence of the structure of this additional term, it is not possible to introduce an operator of the mean energy, whose average will give E_S. Furthermore, considering, for example, E_S as the mean internal energy of a molecule with several vibrational degrees of freedom, it does not appear to be consistent that definition (69) contains contributions which are explicitly determined by the bath degrees of freedom.

To summarize, although approaches I and II give identical results for the thermodynamics of a subsystem if the system-bath coupling is negligible, their predictions differ significantly for finite system-bath coupling. These differences arise because different quantities are considered as fundamental in the two approaches and are related to the different definitions of the mean energy of the system used. The results obtained above and those presented earlier [13] suggest that approach I is superior from both the physical and the logical points of view.

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