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Entropy of a quantum oscillator coupled to a heat bath and implications for quantum thermodynamics

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Abstract

The free energy of a quantum oscillator in an arbitrary heat bath at temperature T is given by a "remarkable formula" which involves only a single integral. This leads to a corresponding simple result for the entropy. The low-temperature limit is examined in detail and explicit results are obtained both for the case of an Ohmic heat bath and a radiation heat bath. More general heat bath models are also examined. In all cases it is found that the entropy vanishes at zero temperature, in conformity with the third law of thermodynamics (Nernst's theorem).

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1. Introduction

The widespread interest in recent years in (a) mesoscopic systems [1–7] and (b) fundamental quantum physics and quantum computation [8–16] has highlighted the critical role which dissipative environments play in such studies. This has led to a critical examination of many results that were derived for macroscopic systems. In particular, there has been considerable interest in the area of quantum and mesoscopic thermodynamics, the subject of this conference. In particular, in some instances questions have been raised about the validity of the fundamental laws of thermodynamics. Whereas many interesting new facets of old results have emerged, it is important to exercise caution before questioning the validity of fundamental laws (especially the three laws of thermodynamics), since many subtle issues arise.

Here, we examine the third law of thermodynamics in the quantum regime by calculating the entropy S for a quantum oscillator in an arbitrary heat bath at temperature T and checking to verify that it vanishes as $T \to 0$, in conformity with Nernst's law [17].

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The first question which arises is how to calculate S. The von Neumann formula for the entropy, $S = -k\mathrm{Tr}\{\rho \log \rho\}$, applies only when $\rho = \mathrm{e}^{-H/kT}/\mathrm{Tr}\{\mathrm{e}^{-H/kT}\}$ is the density matrix for a non-interacting system in its equilibrium state. For the system of oscillator coupled to a heat bath, a system with an infinite number of degrees of freedom, this is a non-trivial quantity to calculate. As a result, one's first thought is perhaps to make use of the reduced Wigner distribution function W corresponding to ρ. This has led some authors to simply replace ρ with W in the von Neumann expression but, unfortunately, this is not correct. We also emphasize that the von Neumann formula can only be applied to the entire system and not to the reduced system. A way out of this impasse is to use the method which we introduced in 1985, in collaboration with Lewis [18], in order to calculate the free energy F. Then, using a familiar thermodynamic relation, the result for S readily follows. In Section 2, we review this method and write down the results for F and S in the case of a quantum oscillator in an arbitrary heat bath at temperature T. All of these results involve just a single integral. In Section 3, we evaluate the relevant integral for the case of an Ohmic heat bath and low temperature. This enables us to show that $S \to 0$ as $T \to 0$, in conformity with Nernst's law. The same result is obtained in Section 4 for the case of a blackbody radiation heat bath and in Section 5 for an arbitrary heat bath. Our conclusions are given in Section 6.

2. Fundamentals

The most general coupling of a quantum particle coupled to a linear passive heat bath is equivalent to an independent-oscillator model [14,18], which is described by the Hamiltonian

$$H = \frac{p^2}{2m} + V(x) + \sum_j \left(\frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 (q_j - x)^2 \right). \tag{1}$$

Here x and p are the particle coordinate and momentum operators and $V(x)$ is the potential energy of an external force. The jth independent oscillator has coordinate q_j and momentum p_j and the generality of the model arises from the infinity of oscillators with an arbitrary choice of the mass m_j and frequency ω_j for each.

Use of the Heisenberg equations of motion leads to the quantum Langevin equation

$$m\ddot{x} + \int_{-\infty}^{t} \mathrm{d}t' \mu(t - t')\dot{x}(t') + V'(x) = F(t), \tag{2}$$

where $\mu(t)$ is the so-called memory function. $F(t)$ is the random (fluctuation or noise) operator force with mean $\langle F(t) \rangle = 0$. The quantities $\mu(t)$ and $F(t)$ describe the properties of the heat bath and are independent of the external force.

In the particular case of an oscillator potential

$$V(x) = \tfrac{1}{2}Kx^2 = \tfrac{1}{2}m\omega_0^2 x^2. \tag{3}$$

Substituting Eq. (3) into Eq. (2) enables us to obtain the explicit solution

$$\tilde{x}(\omega) = \alpha(\omega)\tilde{F}(\omega), \tag{4}$$

where the superposed tilde is used to denote the Fourier transform. Thus, $\tilde{x}(\omega)$ is the Fourier transform of the operator $x(t)$:

$$\tilde{x}(\omega) = \int_{-\infty}^{\infty} \mathrm{d}t x(t)\, \mathrm{e}^{\mathrm{i}\omega t}, \tag{5}$$

and similarly for $\tilde{F}(\omega)$. Here $\alpha(z)$ is the familiar response function (generalized susceptibility)

$$\alpha(z) = \frac{1}{-mz^2 - \mathrm{i}z\tilde{\mu}(z) + K}, \tag{6}$$

and $\tilde{\mu}(z)$ is the Fourier transform of the memory function:

$$\tilde{\mu}(z) = \int_0^{\infty} \mathrm{d}t \mu(t)\, \mathrm{e}^{\mathrm{i}zt}. \tag{7}$$

We have now all the tools at our disposal necessary to obtain thermodynamic qualities for the heat bath. Our main task will be the calculation of the free energy F, which is a thermodynamic potential from which other thermodynamic functions can be obtained by differentiation. The entropy is the one of interest here and is given by the relation

$$S = -\frac{\partial F}{\partial T}. \tag{8}$$

The system of an oscillator coupled to a heat bath in thermal equilibrium at temperature T has a well-defined free energy. The free energy ascribed to the oscillator, $F(T)$, is given by the free energy of the system minus the free energy of the heat bath in the absence of the oscillator. This calculation was carried out by two different methods [18,19] leading to the "remarkable formula"

$$F(T) = \frac{1}{\pi}\int_0^\infty d\omega f(\omega, T)\,\mathrm{Im}\left\{\frac{d \log \alpha(\omega + i0^+)}{d\omega}\right\}, \tag{9}$$

where $f(\omega, T)$ is the free energy of a single oscillator of frequency ω, given by

$$f(\omega, T) = kT \log[1 - \exp(-\hbar\omega/kT)]. \tag{10}$$

Here the zero-point contribution ($\hbar\omega/2$) has been omitted. The function $f(\omega, T)$ vanishes exponentially for $\omega \gg kT/\hbar$. Therefore, as $T \to 0$ the integrand is confined to low frequencies and we can obtain an explicit result by expanding the factor multiplying $f(\omega, T)$ in powers of ω. In the next three sections we show how this works for various heat bath models.

3. Ohmic heat bath

This is an oft-studied model for which

$$\tilde{\mu}(\omega) = m\gamma, \tag{11}$$

where γ is a constant. With this the response function (6) becomes

$$\alpha(\omega) = \left[m\left(\omega_0^2 - \omega^2 - i\omega\gamma\right)\right]^{-1}, \tag{12}$$

the familiar phenomenological Drude–Lorentz model result. With this we see that at low frequency

$$\mathrm{Im}\left\{\frac{d \log \alpha(\omega)}{d\omega}\right\} = \frac{\gamma(\omega_0^2 + \omega^2)}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2} \cong \frac{\gamma}{\omega_0^2}. \tag{13}$$

Hence, using this in the remarkable formula (9) we find in the low-temperature case

$$F(T) \cong \frac{\gamma kT}{\pi\omega_0^2}\int_0^\infty d\omega \log\left[1 - \exp\left(-\hbar\omega/kT\right)\right]. \tag{14}$$

Changing the variable of integration to

$$y = \frac{\hbar\omega}{kT}, \tag{15}$$

we obtain

$$F(T) = \frac{\gamma(kT)^2}{\pi\hbar\omega_0^2}\int_0^\infty dy \log(1 - e^{-y}). \tag{16}$$

The following integral is relevant (now and later):

$$\int_0^\infty dy\, y^\nu \log(1 - e^{-y}) = -\Gamma(\nu + 1)\zeta(\nu + 2), \tag{17}$$

where Γ is the gamma function and ζ is Riemann's zeta-function,

$$\zeta(z) = \sum_{n=1}^{\infty} \frac{1}{n^z}. \tag{18}$$

If z is an even integer $\zeta(z)$ is related to the Bernoulli numbers, $\zeta(2) = \pi^2 B_1 = \pi^2/6$, $\zeta(4) = \pi^4 B_2/3 = \pi^4/90$, etc. But in Section 5 other values appear. With this we obtain the explicit results,

$$F(T) = -\frac{\pi}{6}\hbar\gamma\left(\frac{kT}{\hbar\omega_0}\right)^2, \tag{19}$$

and

$$S(T) = -\frac{\partial F}{\partial T} = \frac{\pi}{3}\gamma\frac{k^2 T}{\hbar\omega_0^2}. \tag{20}$$

We emphasize that $S(T) \to 0$ as $T \to 0$, in conformity with the third law of thermodynamics.

4. Blackbody radiation heat bath

The oscillator in a blackbody radiation heat bath was discussed by us in earlier publications [20,21]. There it was shown that in the large cut-off limit the response function is given by the simple formula

$$\alpha(\omega) = \left[-\frac{M\omega^2}{1 - i\omega\tau_e} + K\right]^{-1}, \tag{21}$$

where M is the renormalized mass and

$$\tau_e = \frac{2e^2}{3Mc^3} = 6 \times 10^{-24} s. \tag{22}$$

Thus, putting $K = M\omega_0^2$ and proceeding as in the Ohmic case, we obtain

$$\mathrm{Im}\left\{\frac{\mathrm{d}\,\log\,\alpha(\omega)}{\mathrm{d}\omega}\right\} = \frac{3\omega_0^2\tau_e\omega^2 + \tau_e^3\omega_0^2\omega^4 - \tau_e\omega^4}{\left[(\omega_0^2-\omega^2)^2 + \omega^2\omega_0^4\tau_e^2\right]\left(1+\omega^2\tau_e^2\right)} \cong \frac{3\tau_e}{\omega_0^2}\omega^2. \tag{23}$$

It follows that

$$F(T) = \frac{3\hbar\omega_0^2\tau_e}{\pi}\left(\frac{kT}{\hbar\omega_0}\right)^4\int_0^\infty \mathrm{d}y y^2\log(1-e^{-y}) = -\frac{\pi^3}{15}\hbar\omega_0^2\tau_e\left(\frac{kT}{\hbar\omega_0}\right)^4. \tag{24}$$

Therefore, the entropy at low temperature has the form

$$S(T) = \frac{4\pi^3}{15}k\omega_0\tau_e\left(\frac{kT}{\hbar\omega_0}\right)^3. \tag{25}$$

Once again, we see that $S\to 0$ as $T\to 0$, in agreement with Nernst's law. In this case, $S\to 0$ faster than in the Ohmic case, as a result of the fact that the right side of Eq. (22) has a factor ω^2, whereas the corresponding result on the right side of Eq. (14) is independent of ω.

5. Arbitrary heat bath

The heat bath is characterized by $\tilde{\mu}(z)$. For our purposes all we need know is that it must be what is termed a positive real function [14]. That is, $\tilde{\mu}(z)$ must be analytic with positive real part everywhere in the upper half plane and, in addition, its boundary value on the real axis, which in general may be a distribution, must satisfy the reality condition,

$$\tilde{\mu}(-\omega + \mathrm{i}0^+) = \tilde{\mu}(\omega + \mathrm{i}0^+)^*. \tag{26}$$

We investigate here a very general class of heat baths, for which in the neighborhood of the origin

$$\tilde{\mu}(z) \cong mb^{1-v}(-\mathrm{i}z)^v, \quad -1<v<1, \tag{27}$$

where b is a positive constant with the dimensions of frequency. It is easy to verify that this is a positive real function if and only if v is within the indicated range (we choose the branch with $-\pi<\arg(z)<\pi$).

The cases $v=\pm 1$ requires special treatment, since $v=1$ corresponds to a shift in mass and $v=-1$ to a shift in force constant. In either case the response function is of the form of an oscillator without dissipation,

$$\alpha(\omega) = \frac{1}{-m\omega^2 + K}. \tag{28}$$

For this case,

$$\mathrm{Im}\left\{\frac{\mathrm{d}\,\log\,\alpha(\omega+\mathrm{i}0^+)}{\mathrm{d}\omega}\right\} = \pi[\delta(\omega-\omega_0) + \delta(\omega+\omega_0)], \tag{29}$$

so

$$F(T) = f(\omega_0, T) \cong -kT\,\mathrm{e}^{-\hbar\omega/kT}, \tag{30}$$

from which it is clear that $S(T)$ vanishes exponentially as $T\to 0$.

We now turn to the general case $-1<v<1$. Then, in the neighborhood of the origin the response function is of the form

$$\alpha(z) = \frac{1}{-mz^2 + mb^{1-v}(-\mathrm{i}z)^{1+v} + m\omega_0^2}. \tag{31}$$

Then

$$\mathrm{Im}\left\{\frac{\mathrm{d}\,\log\,\alpha(\omega+\mathrm{i}0^+)}{\mathrm{d}\omega}\right\} = \mathrm{Im}\left\{\frac{2\omega + \mathrm{i}(1+v)b^{1-v}(-\mathrm{i}\omega)^v}{\omega_0^2 - \omega^2 + b^{1-v}(-\mathrm{i}\omega)^{1+v}}\right\} = \frac{b^{1-v}\omega^v\cos(v(\pi/2))[(1+v)(\omega_0^2-\omega^2) + 2\omega^2]}{\left|\omega_0^2 - \omega^2 + b^{1-v}(-\mathrm{i}\omega)^{1+v}\right|^2} \cong (1+v)\cos\left(v\frac{\pi}{2}\right)\frac{b^{1-v}}{\omega_0^2}\omega^v. \tag{32}$$

With this low-frequency form, the remarkable formula (9) gives

$$F(T) = -\Gamma(v+2)\zeta(v+2)\cos\left(v\frac{\pi}{2}\right)\frac{\hbar b^3}{\pi\omega_0^2}\left(\frac{kT}{\hbar b}\right)^{2+v}, \tag{33}$$

where we have used the integral (17) and the formula $z\Gamma(z) = \Gamma(z+1)$. It follows that

$$S(T) = \Gamma(v+3)\zeta(v+2)\cos\left(v\frac{\pi}{2}\right)\frac{kb^2}{\pi\omega_0^2}\left(\frac{kT}{\hbar b}\right)^{1+v}. \tag{34}$$

As a check, we note that for $v = 0$ and $b = \gamma$, this result reduces to the Ohmic result given in Eq. (20). Since $v + 1$ can never be negative, we conclude once again that $S(T) \to 0$ as $T \to 0$.

6. Conclusions

For the case of a quantum oscillator coupled to an arbitrary heat bath, we have shown that Nernst's third law of thermodynamics is still valid: the entropy vanishes at zero temperature. In this connection we should emphasize that the remarkable formula (9), which is the basis of our discussion, is exact and model-independent. The model appears in the form of the response function, as we have seen in the discussion.

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