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Entropy of a Quantum Oscillator coupled to a Heat Bath and implications for Quantum Thermodynamics

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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 we obtain explicit results both for the case of an Ohmic heat bath and a radiation heat bath. More general heat bath models are also examined. This enables us to determine the entropy at zero temperature in order to check the third law of thermodynamics in the quantum regime.

1. Introduction

The widespread interest in recent years in (a) mescoscopic systems [1,2,3,4,5,6,7] and (b) fundamental quantum physics and quantum computation [8,9,10,11,12,13,14,15,16] 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 see if it vanishes as $T \to 0$, in conformity with Nernst's law [17].

The first question which arises is how to calculate S. The von Neumann result for S involves $\rho \log \rho$, where ρ is the density matrix for the whole system, a non-trivial quantity to calculate. As a result, one's first thought is perhaps to make use of the Wigner distribution function W corresponding to ρ. This has led some authors to simply replace ρ with W in the von Neumann result but, unfortunately, this is not correct because the W corresponding to $\log \rho$ is not the log of the W corresponding to ρ and, as a consequence, one is led to misleading conclusions. A way out of this impasse is to use the method which we introduced in 1985, in collaboration with J.T. Lewis [18], in order to calculate the free energy F. Then, using a familiar thermodynamic relation, the result for S readily follows. In addition, the result for the total energy U follows in a similar manner. In Section 2, we review this method and write down the results for F, S, and U 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 for an arbitrary T. This enables us to show that $S \to 0$ as $T \to 0$, in conformity with Nernst's law. A similar 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

A very general model for the motion of a quantum particle in an arbitrary heat bath is the independent-oscillator model [14,18], which is described by the Hamiltonian

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

Here m is the mass of the quantum particle while m_j and ω_j refer to the mass and frequency of heat-bath oscillator j. In addition, x and p are the coordinate and momentum operators for the quantum particle and q_j and p_j are the corresponding quantities for the heat-bath oscillators. The infinity of choices for the m_j and ω_j give this model its great generality. Moreover, as emphasized in [14], the most general coupling of a quantum particle to a linear passive heat bath is equivalent with an independent oscillator model, which is described by the Hamiltonian given in (1).

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

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

where $V'(x) = \mathrm{d}V(x)/\mathrm{d}x$ is the negative of the time-independent external force and $\mu(t)$ 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.

In the particular case of an oscillator potential

$$V(x) = \frac{1}{2} K x^2 = \frac{1}{2} m \omega_0^2 x^2. \quad (3)$$

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

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

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

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

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

$$\alpha(z) = \frac{1}{-mz^2 - iz\tilde{\mu}(z) + K}. \quad (6)$$

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

$$\tilde{\mu}(z) = \int_0^{\infty} \mathrm{d}t \mu(t) e^{izt}. \quad (7)$$

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 only one of interest here and is given by the relation

$$S = -\left(\frac{\partial F}{\partial T} \right)_V. \quad (8)$$

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"

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

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

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

where the zero-point contribution $(\hbar\omega/2)$ has been omitted. Thus, all that remains is to specify $\tilde{\mu}(z)$ which characterizes the heat bath. In the remaining sections, we consider various heat bath models. In the low temperature case ($kT << \hbar\omega_0$), explicit results may be obtained by noting that $f(\omega, T)$ vanishes exponentially for large $(\hbar\omega/kT)$. Hence, the integrand in (9) is confined to small $(\hbar\omega/kT)$ so that the factor multiplying $f(\omega, T)$ can be expanded in powers of ω.

3. Ohmic heat bath

This is an oft-studied model for which

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

where γ is a constant. Thus

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

is the familiar phenomenological Drude-Lorentz model result. Hence, using (12) and (10) in (9), we obtain

$$F(T) = \frac{kT}{\pi}\int_0^\infty d\omega \; \log\left[1 - \exp\left(-\hbar\omega/kT\right)\right] \times \frac{\gamma\left(\omega^2+\omega_0^2\right)}{\left[\left(\omega^2-\omega_0^2\right)^2+\gamma^2\omega^2\right]}. \tag{13}$$

Hence, in the low temperature case,

$$\text{Im} \left\{\frac{d\log\alpha(\omega)}{d\omega}\right\} = \frac{\gamma\left(\omega^2+\omega_0^2\right)}{\left(\omega_0^2-\omega^2\right)^2+\gamma^2\omega^2} \to \frac{\gamma}{\omega_0^2}. \tag{14}$$

Substituting into (13) and changing the variable of integration to

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

we obtain

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

The following integral is relevant (now and later)

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

where ζ is the Riemann 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. Thus, in particular,

$$\int_0^\infty dy \log\left(1 - e^{-y}\right) = -\frac{\pi^2}{6}, \tag{19}$$

$$\int_0^\infty dy y^2 \log\left(1 - e^{-y}\right) = -\frac{\pi^4}{45}. \tag{20}$$

Hence

$$F(T) = -\frac{\pi}{6}\hbar\gamma\left(\frac{kT}{\hbar\omega_0}\right)^2. \tag{21}$$

Also

$$S(T) = -\left(\frac{\partial F}{\partial T}\right)_V = \frac{\pi}{3}\gamma\frac{k^2 T}{\hbar\omega_0^2}. \tag{22}$$

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

4. Blackbody radiation heat bath

In this case, we obtained [20]

$$\alpha(\omega) = (1 - i\omega\tau_e)\alpha_D(\omega), \tag{23}$$

where $\alpha_D(\omega)$ is the Drude result with γ replaced by

$$\gamma_e = \omega_0^2\tau_e, \tag{24}$$

and

$$\tau_e = \frac{2e^2}{3mc^3} = 6 \times 10^{-24} s. \tag{25}$$

Thus, proceeding as in the Ohmic case and once again letting $\omega \to 0$ in order to calculate the results for small T, we obtain [21]

$$\text{Im}\left\{\frac{d\log\alpha(\omega)}{d\omega}\right\} = \frac{\gamma_e\left(\omega^2+\omega_0^2\right)}{\left(\omega_0^2-\omega^2\right)^2+\gamma_e^2\omega^2} - \frac{\gamma_e}{1+\omega^2\tau_e^2} \to \frac{3\gamma_e}{\omega_0^4}\omega^2. \tag{26}$$

It follows that

$$\begin{aligned} F(T) &= \frac{\gamma_e(kT)^2}{\pi\hbar\omega_0^2}3\left(\frac{kT}{\hbar\omega_0}\right)^2\int_0^\infty dy y^2\log(1-e^{-y}) \\ &= -\frac{\pi^3}{15}\hbar\gamma_e\left(\frac{kT}{\hbar\omega_0}\right)^4, \end{aligned} \tag{27}$$

from which it follows that

$$S = \frac{4\pi^2}{15}\hbar\gamma_e\frac{k^4T^3}{(\hbar\omega_0)^4}. \tag{28}$$

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 (25) has a factor ω^2 whereas the corresponding result on the right-side of (14) is independent of ω.

5. Arbitrary heat bath

From (3) and (6), we obtain

$$\text{Im } \alpha(\omega) = \omega|\alpha(\omega)|^2 \text{ Re } \tilde{\mu}(\omega), \tag{29}$$

$$\text{Re } \alpha(\omega) = \left\{-m\left(\omega^2 - \omega_0^2\right) -\omega \text{ Im } \tilde{\mu}(\omega)\right\}|\alpha(\omega)|^2. \tag{30}$$

Using these results in (9) leads to

$$F(T) = \tfrac{1}{\pi}\int_0^\infty d\omega f(\omega,T)|\alpha|^2 \left\{m\left(\omega^2+\omega_0^2\right) \text{Re } \tilde{\mu}(\omega) - \omega^2 \text{Re } \tilde{\mu}(\omega)\tfrac{d}{d\omega} \text{ Im } \tilde{\mu}(\omega) + \omega\left(-m\omega^2 + m\omega_0^2 + \omega \text{Im } \tilde{\mu}\right)\tfrac{d}{d\omega}\text{Re } \tilde{\mu}(\omega)\right\}. \tag{31}$$

Now we make use of the fact that $\tilde{\mu}(z)$ must be a positive real function [14] and hence the boundary value of $\tilde{\mu}(z)$ on the real axis has everywhere a positive real part i.e.

$$\text{Re}\left[\tilde{\mu}\left(\omega + i0^+\right)\right] \geq 0, \quad -\infty < \omega < \infty. \tag{32}$$

Thus, in the neighborhood of the origin, a very general class of models are incorporated by writing

$$\tilde{\mu}(z) = mb^{1-\alpha}(-iz)^\alpha, \quad -1 \leq \alpha \leq 1, \tag{33}$$

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

$$\begin{aligned}\text{Re } \tilde{\mu}(\omega) &\sim \omega^\alpha \cos\left\{\alpha\left(\theta - \pi/2\right)\right\} \\ \text{Im } \tilde{\mu}(\omega) &\sim \omega^\alpha \sin\left\{\alpha\left(\theta - \pi/2\right)\right\}.\end{aligned} \tag{34}$$

As it turns out, the case $\alpha = -1$ requires special treatment so we will consider this first, obtaining $\tilde{\mu} = imb^2/z$, so that

$$\alpha(\omega) = \frac{1}{-m\omega^2 + m(b^2+\omega_0^2)}. \tag{35}$$

Thus, this corresponds to a shift in the force constant K with no dissipation. In the absence of dissipation

$$\text{Im}\left\{\frac{d\log\alpha(\omega+i0^+)}{d\omega}\right\} = \pi\left[\delta(\omega-\omega_0) + \delta(\omega+\omega_0)\right], \tag{36}$$

so

$$F(T) = f(\omega_0, T) \cong -kTe^{-\hbar\omega/kT}, \tag{37}$$

from which it is clear that $S(T) \to 0$ as $T \to 0$. We now return to the more general case $-1 < \alpha \leq 1$ and again consider the low-temperature limit. Thus, as $\omega \to 0$, the { } term in (30) reduces to

$$\{\ \} \to m\omega_0^2(1+\alpha)\text{Re } \tilde{\mu}, \tag{38}$$

and, in addition, $|\alpha(\omega)|^2 \to \left(m\omega_0^2\right)^{-2}$. It follows that

$$F(T) \to \frac{kT}{\pi m\omega_0^2} b^{(1-\alpha)}(1+\alpha)\cos\left\{\alpha\left(\theta - \frac{\pi}{2}\right)\right\} I(\omega), \tag{39}$$

where

$$\begin{aligned}I(\omega) &= \int_0^\infty d\omega\omega^\alpha \log\left[1 - \exp\left(-\hbar\omega/kT\right)\right] \\ &= \left(\tfrac{kT}{\hbar}\right)^{\alpha+1}\int_0^\infty dyy^\alpha \log\left(1-e^{-y}\right).\end{aligned} \tag{40}$$

It follows from (39), (40) and (8) that

$$S(T) = \tfrac{1}{\pi m\omega_0^2} b^{(1-\alpha)}(\alpha+1)(\alpha+2)\tfrac{k^{\alpha+2}}{\hbar^{\alpha+1}} \times T^{\alpha+1}\Gamma(\alpha+1)\xi(\alpha+2). \tag{41}$$

As a check, we note that for $\alpha = 0$ and $b = \gamma$, this result reduces to the Ohmic result given in (22). Hence, since $(\alpha+1)$ can never be negative, we conclude that

$$S(T) \sim (kT)^{\alpha+1} \longrightarrow 0 \ \ as\ T \to 0. \tag{42}$$

6. Conclusions

For the case of a quantum oscillator coupled to an arbitrary heat bath, we found that Nernst's third law of thermodynamics is still valid.

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