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Does the Third Law of Thermodynamics Hold in the Quantum Regime?[1]

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The first in a long series of papers by John T. Lewis, in collaboration with G. W. Ford and the present author, considered the problem of the most general coupling of a quantum particle to a linear passive heat bath, in the course of which they derived an exact formula for the free energy of an oscillator coupled to a heat bath in thermal equilibrium at temperature T. This formula, and its later extension to three dimensions to incorporate a magnetic field, has proved to be invaluable in analyzing problems in quantum thermodynamics. Here, we address the question raised in our title viz. Nernst's third law of thermodynamics.

KEY WORDS: Quantum thermodynamics; Entropy; Dissipation; Third Law of Thermo dynamics; Nernst's Low.
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1. INTRODUCTION

In recent years, the realization that quantum effects can play an important role in thermodynamic theory has led to an intense interest in quantum and mesoscopic thermodynamics,$^{(1-5)}$ to the extent that some authors$^{(1-4)}$ have questioned whether the fundamental laws of thermodynamics remain valid. The arguments are often very subtle and sometimes not easily dismissed. Here, our goal is not to survey the whole area but, instead, to focus in depth on questions which have been raised in relation to Nernst's third law of thermodyanmics, which states that the entropy S vanishes as the temperature $T \to 0$. Ford and the present author$^{(5)}$ already considered this question for the one-dimensional problem of a quantum oscillator

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[1] The author dedicates this paper to the memory of John T. Lewis, a collaborator over two decades and a wonderful friend. He is sorely missed.

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in an arbitrary heat bath and also briefly commented on what we considered to be the flaw in the calculations of other authors. We now expand on these remarks in Sec. 2 (where we discuss various approaches to the calculation of S), by carrying out a detailed calculation in which we demonstrate explicitly how use of approaches based on an incorrect utilization of the Wigner function formalism, and also the von Neumann formula, leads to an incorrect form of a well-known result. By contrast, the method we employed in Ref. 5 was based on calculating S from an exact expression for the free energy F calculated by us in 1985 at the start of a long collaboration with Lewis.(6) This formula for F was later extended to three dimensions to incorporate a magnetic field.(7) Thus, in Sec. 3, we review these results and explicitly write down the results for F and S in the three-dimensional case. All of these results involve just a single integral and, in Sec. 4, we evaluate this integral for the case of an Ohmic bath and low temperature. This enables us to confirm Nernst's law. Our conclusions are given in Sec. 5.

2. CALCULATION OF THE ENTROPY *S*

For a quantum particle in a heat bath, a basic quantity is the density matrix

$$\rho = e^{-H/kT}/\mathrm{Tr}\{e^{-H/kT}\}, \tag{2.1}$$

where H is the Hamiltonian for the whole system (quantum particle plus heat bath plus interaction). The question is how to calculate the entropy S from this expression. In Ref. 4, three different results for the entropy are obtained based on use of the free energy (S_p given in (3.59) of Ref. 4), the Wigner distribution (S_B given in (4.5) and (4.38) of Ref. 4 and referred to as the "Boltzmann" energy) and the von Neumann expression (S_{vN} given in (4.36) of Ref. 4). In particular, the authors of Ref. 4 argue that "—neither the von Neumann entropy nor the Boltzmann entropy vanishes when the bath temperature is zero," leading them to note "—the violation of the third law reported here for nonweak coupling." On the contrary, we argue that all such calculations should lead to the same result so we are motivated to examine the question of what went wrong. In the process, we will argue that a calculation based on the free energy is the simplest way to proceed to obtain the correct result, particularly if one uses the formula given in Ref. 6.

First, we examine the calculation of S_{vN}, which was based on applying the von Neumann formula to the *reduced* density matrix. But as we pointed out in Ref. 5, for a system with a non-negligible interaction energy, "—the von Neumann formula can only be applied to the *entire* system and not to the reduced system." At first glance, these may seem to be at variance with the fact that numerous calculations rely on the calculation of the von Neumann entropy of mixed states obtained by tracing out other variables. The answer is that this procedure is correct only when the interaction energy is negligible, as is often the case (so that the total entropy is equal to the sum of the entropies of the parts). However, this is not so in the case of heat baths (where we are dealing with *non-additivity of entropies*), as may be verified explicitly. This is what motivated our calculation with John T. Lewis, where the free energy F of the electron in the presence of the heat bath was calculated by first using the von Neumann formula to calculate the free energy of the *entire interacting* system and then subtracting the well-known free energy of the heat bath itself. Simply differentiating $-F$ with respect to T [see (2.10) below] leads to the correct result S_p. The authors of Ref. 4 used our procedure in their calculation of S_p [their Eq. (3.59)], obtaining a correct result in agreement with our previous calculation of this quantity,(5) but in disagreement with their result [given in their Eq. (4.36)] for S_{vN} (which was obtained assuming additivity of entropies). If, instead, one uses the density matrix of the whole system, the corresponding result will coincide with the result S_p.

Second, we examine the calculation of S_B of Ref. 4 which was based on writing down the von Neumann formula for the entropy, $S = -k\mathrm{Tr}\{\rho \log \rho\}$, and then making use of the *reduced* Wigner distribution function W(8) corresponding to ρ, by simply replacing ρ with W in the von Neumann expression, as may be verified by examination of Eqs. (4.3) and (4.4) of Ref. 4, leading to the authors' Eq. (4.5). The calculation within this framework is correct but, unfortunately, the framework is not correct, as we shall now demonstrate explicitly in the simplest case where the interaction energy is taken to be negligible (i.e. by letting the dissipation parameter $\gamma \to 0$), where well-known results for the entropy of a *single* oscillator in equilibrium at temperature T(9) may be used as a benchmark. For an oscillator at temperature T, we have the well-known exact result for the Wigner distribution(8)

$$W(q, p) = N \exp(-aH), \tag{2.2}$$

where

$$\frac{1}{a} = \frac{\hbar\omega}{2} \coth\left(\frac{\hbar\omega\beta}{2}\right), \tag{2.3}$$

$$N = \frac{\omega a}{2\pi} = (\pi\hbar)^{-1} \tanh\left(\frac{\hbar\omega\beta}{2}\right) \equiv (2\pi\hbar)^{-1} N_1, \tag{2.4}$$

and

$$H(q, p) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2. \tag{2.5}$$

Also, we note that

$$\int\int dq dp\ W(q, p) = 1, \tag{2.6}$$

and

$$\langle H(q,p)\rangle = \int\int dqdp\ W(q,p)\ H(q,p) = \frac{1}{a}. \tag{2.7}$$

If we now replace (incorrectly as we shall see) ρ in the von Neumann formula by $2\pi\hbar\ W$ then we obtain for the entropy (which we denote here as $S^{(W)}$, indicating that it was derived using the Wigner distribution)

$$\begin{aligned}(S^{(W)}/k) &= -\int\int dqdp\ W(q,p)\log\left[2\pi\hbar W(q,p)\right]\\ &= -\log N_1\int\int dqdp\ W(q,p) + a\int\int dqdp\ H(q,p)W(q,p)\\ &= -\log N_1 - aN\frac{\partial}{\partial a}\int\int dqdp\exp(-aH)\\ &= \log\left[\frac{1}{2}\coth\frac{\hbar\omega\beta}{2}\right] + 1.\end{aligned} \tag{2.8}$$

This result is incorrect, being in striking contrast with the correct result given by Ref. 9

$$(S/k) = -\log\left[2\sinh(\hbar\omega/2kT)\right] + \frac{\hbar\omega}{2kT}\coth(\hbar\omega/2kT). \tag{2.9}$$

Only in the high temperature classical regime do equations (2.8) and (2.9) agree, in which case the Wigner distribution function simply reduces to a classical distribution function. One of the problems with this method stems from the fact that the Wigner distribution corresponding to $\log\rho$ is not the same as the log of the Wigner distribution corresponding to ρ. Thus, we need an alternative approach.

In fact, as already noted,(5–7) the best approach is simply to calculate F from the formula

$$S(T) = -\frac{\partial F}{\partial T}, \tag{2.10}$$

and in the next section we discuss the method by which F is obtained. As we shall see, the result S_p of Ref. 4 is correct and agrees with a result previously obtained by us Ref. 5 in the case of an Ohmic heat bath in the absence of a magnetic field. However, we will also note that the method used in Ref. 4, for the calculation of F, is unnecessarily complicated and only applies to the Ohmic model whereas, by contrast, our result is expressed as a simple integral in terms of the generalized susceptibility and applies, not only for the Ohmic bath, but for an arbitrary heat bath and in the presence of a magnetic field.

3. FUNDAMENTALS

The Hamiltonian for a charged quantum oscillator (with a force constant $K = m\omega_0^2$) moving in an external magnetic field and linearly coupled to a passive heat bath (consisting of an infinite number of oscillators) may be written as$^{(7)}$

$$H_o = \frac{1}{2m}\left[\vec{p} - \frac{e}{c}\vec{A}\right]^2 + \frac{1}{2}K\vec{r}^{\,2} + \sum_j \left[\frac{\vec{p}_j^{\,2}}{2m_j} + \frac{1}{2}m_j\omega_j^2\left(\vec{q}_j - \vec{r}\right)^2\right]. \tag{3.1}$$

This is the independent oscillator (IO) model in the presence of an external magnetic field $\vec{B}$, where e, m, $\vec{p}$, $\vec{r}$ are the charge, mass, momentum and position of the oscillator respectively and the corresponding quantities with the lower indices j refer to the jth heat bath oscillator. The vector potential $\vec{A}$ is related to the magnetic field $\vec{B}$ through the equation

$$\vec{B}(\vec{r}) = \vec{\nabla} \times \vec{A}(\vec{r})\,. \tag{3.2}$$

Next, using the Heisenberg equations of motion, the problem has been formulated exactly in terms of the quantum Langevin equation

$$m\ddot{\vec{r}} + \int_{-\infty}^{t} dt'\mu(t-t')\dot{\vec{r}}(t') - \frac{e}{c}\dot{\vec{r}} \times \vec{B} + K\vec{r} = \vec{F}(t). \tag{3.3}$$

Here $F(t)$ is the fluctuation force (whose exact form is known but is not relevant to our present discussion) and $\mu(t)$ is the so-called memory (non-Markovian) term given by Ref. 7

$$\mu(t) = \sum_j m_j\omega_j^2\,\cos(\omega_j t)\theta(t), \tag{3.4}$$

where $\theta(t)$ is the Heaviside function.

We note that $\mu(t)$ does not depend on the magnetic field. Fourier transforming (3.3), we obtain$^{(7)}$

$$\tilde{r}_\rho(\omega) = \alpha_{\rho\sigma}(\omega)\,[\tilde{F}_\sigma(\omega)]\,, \tag{3.5}$$

where

$$\alpha_{\rho\sigma}(\omega) \equiv [D(\omega)^{-1}]_{\rho\sigma} = \left[\lambda^2\delta_{\rho\sigma} - \left(\omega\frac{e}{c}\right)^2 B_\rho B_\sigma - \epsilon_{\rho\sigma\eta}B_\eta\lambda i\omega\frac{e}{c}\right]\Big/\det D(\omega)\,, \tag{3.6}$$

is the generalized susceptibility, with

$$\det D(\omega) = \lambda\left[\lambda^2 - \left(\omega\frac{e}{c}\right)^2\vec{B}^2\right]\,, \tag{3.7}$$

and

$$\lambda(\omega) \; = \; -m\omega^2 \; + \; K - i\omega\tilde{\mu}(\omega) \; \equiv \; \{\alpha^{(0)}(\omega)\}^{-1} \, . \tag{3.8}$$

Also

$$\tilde{\mu}(\omega) \equiv \int_o^\infty dt e^{i\omega t}\mu(t), \tag{3.9}$$

$$\tilde{r}_\sigma(\omega) \; = \; \int_{-\infty}^{\infty} dt e^{i\omega t} r_\sigma(t), \tag{3.10}$$

and so on, and where $\epsilon_{\rho\sigma\eta}$ is the Levi-Civita symbol, a totally antisymmetric tensor. The Greek indices stand for three spatial directions (i.e. ρ, σ, etc. = 1, 2, 3) and we adopt Einstein summation convention for repeated Greek indices. From (3.4) and (3.9), we obtain the Fourier transform of the memory function

$$\tilde{\mu}(\omega) \; = \; \frac{i}{2}\sum_j m_j\omega_j^2\left[\frac{1}{\omega-\omega_j} \; + \; \frac{1}{\omega+\omega_j}\right]. \tag{3.11}$$

We have now all the tools required in order to calculate various quantities. Here, we discuss the free energy and associated entropy.

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 is a non-trivial quantity to calculate, details of which may be found in$^{(7)}$ leading to the result

$$F_o(T,B) \; = \; \frac{1}{\pi}\int_o^\infty d\omega f(\omega,T) Im\left\{\frac{d}{d\omega}ln\left[\det\alpha(\omega+io^+)\right]\right\}, \tag{3.12}$$

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

$$f(\omega,T) = kT\log[1-\exp(-\hbar\omega/kT)]. \tag{3.13}$$

Here the zero-point contribution ($\hbar\omega/2$) has been omitted and

$$\det\alpha(\omega) = [\alpha^{(0)}(\omega)]^3\left[1-\left[\frac{eB\omega}{c}\right]^2[\alpha^{(0)}(\omega)]^2\right]^{-1}, \tag{3.14}$$

with

$$[\alpha^{(0)}(\omega)]^{-1} \; = \; -m\omega^2 \; + \; K - i\omega\tilde{\mu}(\omega). \tag{3.15}$$

This enabled us to write

$$F_o(T,B) \; = \; F_o(T,0) \; + \; \Delta F_o(T,B), \tag{3.16}$$

where

$$F_o(T,0) \; = \; \frac{3}{\pi}\int_o^\infty d\omega \; f(\omega,T) Im\left\{\frac{d}{d\omega}ln\alpha^{(0)}(\omega)\right\} \tag{3.17}$$

is the free energy of the oscillator in the absence of the magnetic field (in agreement with Eq. (5) of Ref. 6, except for the extra factor of 3 which results from our consideration here of three dimensions) and the correction due to the magnetic field is given by

$$\Delta F_o(T, B) = -\frac{1}{\pi} \int_o^\infty d\omega \; f(\omega, T) Im \left\{ \frac{d}{d\omega} ln \left[1 - \left(\frac{eB\omega}{c} \right)^2 (\alpha^{(0)}(\omega))^2 \right] \right\}. \tag{3.18}$$

4. OHMIC HEAT BATH

In the case of the Ohmic heat bath, $\tilde{\mu}(\omega) = m\gamma$, a constant, which is the simplest memory function one can choose and is an oft-used[4] choice. Thus, making use of (3.7) and (3.8), (3.3) becomes

$$\begin{aligned} F_o(T, B) = \frac{1}{\pi} \int_o^\infty d\omega f(\omega, T) & \qquad (4.1) \\ \times \left\{ \frac{\gamma(\omega^2 + \omega_o^2)}{(\omega^2 - \omega_o^2)^2 + \omega^2\gamma^2} + \frac{\gamma(\omega^2 + \omega_o^2)}{(\omega^2 - \omega_o^2 + \omega_c\omega)^2 + \omega^2\gamma^2} \right. \\ \left. + \frac{\gamma(\omega^2 + \omega_o^2)}{(\omega^2 - \omega_o^2 - \omega_c\omega)^2 + \omega^2\gamma^2} \right\}, \end{aligned}$$

where $\omega_o = (K/m)^{\frac{1}{2}}$ and $\omega_c = (eB/mc)$.

We now wish to examine the low-temperature behavior of this result. First, we note that 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. Hence, in particular, we see that the terms involving the magnetic field (the ω_c terms) are negligible since they always contain an ω factor. Thus our result corresponds to the results obtained in the absence of a magnetic field,[6] except for the extra factor of 3 which results from our consideration here of three dimensions. Thus, proceeding as in Ref. 5, we obtain in the low-temperature case

$$\begin{aligned} F(T) &\cong \frac{3\gamma kT}{\pi\omega_0^2} \int_0^\infty d\omega \log\left[1 - \exp\left(-\hbar\omega/kT\right)\right] \\ &= -\frac{\pi}{2}\hbar\gamma \left(\frac{kT}{\hbar\omega_0} \right)^2, \end{aligned} \tag{4.2}$$

so that

$$S(T) = -\frac{\partial F}{\partial T} = \pi\gamma \frac{k^2 T}{\hbar\omega_0^2}. \tag{4.3}$$

Hence $S(T) \to 0$ as $T \to 0$, in conformity with the third law of thermodynamics. We also note that the result for the entropy is independent of the magnetic field B and actually corresponds (except for a factor of 3 because here we considered 3 dimensions) to the result obtained earlier by us(5) in the $B = 0$ case and also agrees with the result for S_p given in Ref. 4. The latter calculation was also based on a determination of the free energy F but this calculation was much more complicated, involving a non-trivial determination of the frequencies of the interacting system.(10) By contrast, our calculation was based on a simple integral,(6,7) given here by (3.12), and which involves only the specification of the generalized susceptibility $\alpha(\omega)$.

5. CONCLUSION

Similar results to those obtained in the Ohmic case may be obtained also in the case of a blackbody radiation heat bath and, in fact, in the case of arbitrary heat baths. Thus, we conclude that 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 basis of our discussion is the remarkably simple formula for the free energy of an oscillator, in an arbitrary heat bath at arbitrary temperature T, obtained in the 1985 paper(6) with John T. Lewis. Since the validity of the second law of thermodynamics has also been called into question,(1–4) we note that this formula for the free energy was also used in refuting speculations that quantum effects could lead to extraction of energy from a zero-temperature heat bath.(11)

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