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Third law of thermodynamics in the presence of a heat flux

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Following a maximum entropy formalism, we study a one-dimensional crystal under a heat flux. We obtain the phonon distribution function and evaluate the nonequilibrium temperature, the specific heat, and the entropy as functions of the internal energy and the heat flux, in both the quantum and the classical limits. Some analogies between the behavior of equilibrium systems at low absolute temperature and nonequilibrium steady states under high values of the heat flux are shown, which point to a possible generalization of the third law in nonequilibrium situations.

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I. INTRODUCTION

Planck statistics, i.e., Bose-Einstein statistics with zero chemical potential, is a standard ingredient in the analysis of phonons and photons. Einstein's application of Planck statistics to oscillators in crystals provided the first theory of specific heats compatible with the third law of thermodynamics. Planck statistics succesfully describes equilibrium situations. To obtain nonequilibrium distribution functions, one usually starts from suitable kinetic equations, which are relatively easy to solve when the heat flux or the electric current are low, but which are almost intractable or rather cumbersome for the analysis of high values of the heat flux.

The aim of this paper is to search for generalizations of Planck statistics in nonequilibrium situations characterized by a nonvanishing heat flux. In particular, we are interested in the situation when the heat flux is large. As we will see, the behavior of the system under high values of the heat flux bears some interesting analogies with the behavior of equilibrium systems at low absolute temperature. In particular, the heat flux reduces the disorder of the system and, therefore, reduces its entropy. Furthermore, the generalized temperature defined as the inverse of the derivative of the nonequilibrium entropy with respect to the energy tends to zero for high heat fluxes, and so does the specific heat.

Therefore, the analysis of the generalizations of Planck statistics may be useful, besides its standard academic interest, to open the question of whether the third law of thermodynamics could be generalized to deal not only with equilibrium systems in the low temperature limit, but also with nonequilibrium steady states under high values of the heat flux.

Let us finally note that the use of generalized entropies dependent on the fluxes besides on the classical variables for the description of nonequilibrium steady states is standard in recent developments of nonequilibrium thermodynamics [1] which, however, are usually restricted to second-order corrections in the heat flux. This work may also be useful in this context, by pointing out generalizations valid to any order when the heat flux is high; other examples of developments valid for high heat fluxes can be found in Refs. [2–5].

The plan of the paper is as follows. In Sec. II, we find the phonon distribution function in a one-dimensional crystal crossed by a heat flux using information theory, and evaluate the Lagrange multipliers in terms of the internal energy and the heat flux both in the quantum and the classical limits. Section III analyzes the behavior of the thermodynamic quantities in situations where the heat flux takes high values. Section IV is devoted to some concluding remarks.

II. INFORMATION THEORY AND HEAT FLOW

We start by applying the scheme of information theory [6] to obtain the phonon statistics for a one-dimensional lattice in which the energy density and the heat flux are specified. For the sake of simplicity, we will assume the Debye approximation, i.e., a linear dispersion relation $\omega = c|k|$ for all the spectrum, with ω the phonon frequency, k the wave vector, and c the (constant) sound speed. This approximation is expected to be exact in the limit of low temperatures, since then only phonons of low energy (low wave vector) are excited, and for them the dispersion relation is approximately linear. For high temperatures, however, it is only a rough approximation that, as we will see, provides qualitative good results.

We must thus maximize the entropy density for a boson gas, namely [7]

$$s = k_B \int_{-\pi/l}^{\pi/l} \frac{dk}{2\pi} \left[(f+1)\ln(f+1) - f\ln f\right], \tag{1}$$

with $f(k)$ the phonon distribution function, under the constraints of fixed energy density,

$$\epsilon = \int_{-\pi/l}^{\pi/l} \frac{dk}{2\pi} f\,\hbar\omega = \frac{\hbar c}{2\pi} \int_{-\pi/l}^{\pi/l} dk f\,|k|, \tag{2}$$

and fixed heat flux

$$q = \int_{-\pi/l}^{\pi/l} \frac{dk}{2\pi} f\,\hbar\omega \frac{d\omega}{dk} = \frac{\hbar c^2}{2\pi} \int_{-\pi/l}^{\pi/l} dk f\,k; \tag{3}$$

l denotes the cell size, and $\hbar$ the Planck constant h divided by 2π.

Therefore, one must find the $f(k)$ functional satisfying the extremal condition

$$ds - k_B\beta d\epsilon - k_B\gamma dq = 0, \tag{4}$$

β and γ standing for the Lagrange multipliers assigned, respectively, to the energy and heat flux constraints. One finally obtains the following expression for the number of phonons with wave vector k at the given macrostate:

$$f_0(k;\beta,\gamma) = \frac{1}{\exp(\beta\hbar c|k| + \gamma\hbar c^2 k) - 1}. \tag{5}$$

A similar expression can also be obtained without using a maximum entropy formalism, as an approximation in pure dielectrics at low temperatures, with $\beta = (k_B T)^{-1}$, and $\gamma = -(k_B T)^{-1} v/c^2$, k_B being the Boltzmann constant, and v the drift velocity of the phonon gas [4, 8].

The connection between the Lagrange factors and thermodynamic quantities becomes apparent after (4), from which one immediately reads

$$k_B\beta = \left.\frac{\partial s}{\partial \epsilon}\right|_q, \qquad \text{and} \qquad k_B\gamma = \left.\frac{\partial s}{\partial q}\right|_\epsilon .$$

By comparison with the equilibrium thermodynamic relation, one can thus identify the generalized temperature, $\theta = (k_B\beta)^{-1}$, dependent not only on the energy density ϵ but also in the heat flux q; the parameter γ has no analog in equilibrium and must be regarded as a purely nonequilibrium quantity describing how an increment in the heat flux modifies the entropy. The purpose of this section is to obtain explicit expressions for both parameters in terms of the macroscopic variables, ϵ and q.

To do that, we perform the integrals appearing in (2)–(3) to find

$$\epsilon = \frac{\hbar c}{2\pi}\left(\frac{I_+}{a_+^2} + \frac{I_-}{a_-^2}\right), \tag{6}$$

and

$$q = \frac{\hbar c^2}{2\pi}\left(\frac{I_+}{a_+^2} - \frac{I_-}{a_-^2}\right), \tag{7}$$

where we have defined the parameters

$$a_\pm = \hbar c(\beta \pm \gamma c), \qquad y_\pm = a_\pm \pi/l = \varepsilon_D(\beta \pm \gamma c),$$
$$I_\pm = \int_0^{y_\pm} dx \frac{x}{\exp(x) - 1}, \tag{8}$$

$\varepsilon_D \equiv \hbar c\pi/l$ denoting the Debye energy. Equation (6) expresses that the internal energy at a given "volume" element is the sum of the energy of the phonons moving to the right plus the energy of the phonons traveling to the left; Eq. (7) is interpreted analogously. In the next subsections, expressions (6) and (7) are evaluated in two limit cases, namely the quantum and the classical limits.

A. Quantum limit

We will call the quantum limit to the range in which condition $y_\pm \gg 1$ is satisfied, as one would get by making $h \to \infty$; in equilibrium it corresponds to the low-temperature limit. In this range, expressions (6)–(7) yield, after some direct calculations

$$\beta = \frac{1}{2}\left(\frac{\pi}{6\hbar}\right)^{1/2}\left[\frac{1}{\sqrt{\epsilon c + q}} + \frac{1}{\sqrt{\epsilon c - q}}\right]$$
$$= \frac{1}{2k_B T}\left[\frac{1}{\sqrt{1+x}} + \frac{1}{\sqrt{1-x}}\right], \tag{9}$$

$$\gamma = \frac{1}{2c}\left(\frac{\pi}{6\hbar}\right)^{1/2}\left[\frac{1}{\sqrt{\epsilon c + q}} - \frac{1}{\sqrt{\epsilon c - q}}\right]$$
$$= \frac{1}{2ck_B T}\left[\frac{1}{\sqrt{1+x}} - \frac{1}{\sqrt{1-x}}\right], \tag{10}$$

with $T(\epsilon) \equiv (6\hbar c\epsilon/k_B^2\pi)^{1/2}$, the local-equilibrium temperature, and $x = q/c\epsilon$, the reduced heat flux; the integral is solved with the use of formula 3.411-1 of Ref. [9].

In equilibrium ($q = 0$), one has $\gamma = 0$ and $\beta = (k_B T)^{-1}$, so that (5) reduces to the equilibrium Bose-Einstein distribution. Equation (9) also provides the equation of state

$$\epsilon = \frac{k_B^2\pi^2}{3\hbar c}T^2, \tag{11}$$

in agreement with the result found by Landsberg and De Vos for photons in one-dimensional systems [10], where the corresponding Stefan-Boltzmann law is found to be $\psi = \frac{k_B^2\pi^2}{3h}T^2$, with ψ the energy radiated per unit time in each extreme of the solid; in order to show it, one simply realizes that the energy flow at a given point of the system comes described by $\psi = 2\frac{1}{2}\epsilon c$, the factor 1/2 expressing the fact that in a differential volume element of the unidimensional system one half of the photons travel in every sense, and the factor 2 coming from the two possible polarizations of photons.

Outside equilibrium, we notice that the generalized temperature only takes real positive values, since the inequality $|q| < \epsilon c$ holds from the definitions of ϵ and q, and that asymptotically approaches to zero as $|q| \to \epsilon c$, in contrast to the local-equilibrium temperature T, which is independent of the heat flux. On the other hand, a simple inspection of Eq. (10) shows that γ has the sign of $-q$, thus indicating that an increase in the heat flux carries a reduction in the entropy density, as one expects intuitively.

Finally, it is interesting to find an expression for the quantum condition out of equilibrium, thus generalizing the equilibrium low-temperature condition to nonequilibrium situations. With the help of (9)–(10), condition $y_\pm \gg 1$ is equivalent to $\epsilon + |q|/c \ll hc/l^2$. By taking into account that $|q| < \epsilon c$, it is straightforward to obtain for the quantum limit the condition

$$\varepsilon \ll \varepsilon_D, \tag{12}$$

i.e., the energy per particle, $\varepsilon = \epsilon l$, is much smaller than the Debye energy.

We could as well have defined the quantum limit so that y_+ *or* $y_- \gg 1$, then the quantum limit condition would read $\theta \ll T_D$, with $T_D \equiv \varepsilon_D/k_B$ the Debye temperature, in a stronger analogy with the equilibrium condition; nevertheless, we have preferred the former more restrictive definition because it allows one to write explicit expressions for β and γ.

B. Classical limit

On the opposite limit, we define the classical range so that $y_\pm \ll 1$; in equilibrium, this corresponds to the high-temperature limit. In this limit, one can approximate integrals $I_\pm$ simply as $I_\pm \simeq y_\pm$, and (6)–(7) yield

$$\beta = \frac{c}{2l}\left[\frac{1}{\epsilon c+q}+\frac{1}{\epsilon c-q}\right] = \frac{1}{\varepsilon}\frac{1}{1-x^2}, \tag{13}$$

$$\gamma = \frac{1}{2l}\left[\frac{1}{\epsilon c+q}-\frac{1}{\epsilon c-q}\right] = -\frac{1}{\varepsilon c}\frac{x}{1-x^2}. \tag{14}$$

In equilibrium, Eq. (13) provides the equipartition of energy, namely $\varepsilon = k_B T$, as corresponds to the classical limit in one dimension. In a nonequilibrium situation, on the other hand, the generalized temperature can be written, after (13), as

$$\theta = T(1-x^2), \tag{15}$$

where $T \equiv \varepsilon/k_B$ denotes the local-equilibrium temperature. Therefore, the existence of a heat flux leads to a reduction in the value of the generalized temperature. Nevertheless, this generalized temperature cannot take arbitrarily small values due to the classical (high-temperature) condition, as we see below, Eq. (17). The γ parameter, on the other hand, turns to be proportional to $-q$, showing again that the heat flux makes the entropy decrease, and though it seems to reach very high values as x tends to 1, the classical limit condition, Eq. (16), provides an upper limit for it, namely $\gamma \ll (\varepsilon_D c)^{-1}$. In the opposite limit, for small fluxes ($x \ll 1$), γ becomes linear in q, as usual in extended irreversible thermodynamics [1]. In the last section, we will compare these results with the corresponding expressions given by Miller and Larson for a linear harmonic chain using Boltzmann statistics [2].

Finally, our purpose is to express in physical terms the condition under which the classical limit is attained, that is to say, the nonequilibrium analog to the equilibrium high-temperature limit. With the aid of Eqs. (13)–(14) the classical limit reads, after straightforward calculations

$$\varepsilon(1-|x|) \gg \varepsilon_D, \tag{16}$$

thus we have that (a) the condition of the classical limit is stronger than simply $\varepsilon \gg \varepsilon_D$, and (b) it does not make sense to study the limit $x \to 1$ in the classical limit. A more elegant expression can be reached by combining (15) and (16) to find

$$\theta \gg T_D. \tag{17}$$

Therefore, one concludes that the classical limit condition in nonequilibrium situations becomes a mere generalization of the equilibrium condition where the generalized temperature substitutes the equilibrium temperature.

III. TEMPERATURE, SPECIFIC HEAT, AND ENTROPY UNDER A HIGH HEAT FLUX

By direct inspection of Eq. (9), we have seen in Sec. II A that as x approximates one the generalized temperature θ tends to zero. Since the behavior of equilibrium systems when $T \to 0$ deserves special attention in equilibrium thermodynamics, it is natural to ask whether the situation with $x \to 1$, leading to $\theta \to 0$, should deserve also special attention in the analysis of systems under a heat flux. Some of the distinctive features when $T \to 0$ are that $S \to 0$ and, as a consequence, the specific heat $C \to 0$. In this section we will study the behavior of the specific heat and the entropy density when x tends to one, to see whether C and s tend also to zero in this case.

As we have seen, when x tends to one we are set in the quantum range (see also next section). By using Eq. (9) for the nonequilibrium temperature, one finds for the heat capacity

$$\begin{aligned} C(\epsilon,q) &= \left.\frac{\partial\epsilon}{\partial\theta}\right|_q \\ &= \frac{4\epsilon^{3/2}}{k_B\theta^2}\left(\frac{6\hbar c}{\pi}\right)^{1/2}\frac{(1-x^2)^{3/2}}{(1+x)^{3/2}+(1-x)^{3/2}}. \end{aligned} \tag{18}$$

Note that we have defined the specific heat as $C \equiv \partial\epsilon/\partial\theta$ rather than $C \equiv \partial\epsilon/\partial T$. The reason for this is that, according to macroscopic nonequilibrium thermodynamics, in a nonequilibrium steady state it is θ rather than T that is directly measured by a thermometer [12].

From (18) and (9), finally, one realizes that $C \propto (1-x)^{1/2} \to 0$ as $x \to 1$. Then we find a third-law-like behavior for steady nonequilibrium systems in situations where the heat flux approaches its maximum value.

The next step is to analyze the behavior of the entropy at high heat fluxes. In order to do so we could simply integrate the expressions found for β and γ. Instead, we calculate it from the definition itself of the entropy density, Eq. (1), and afterwards we check that the results thus obtained coincide with the ones obtained by direct integration.

Equation (1) is rearranged to give

$$s(\beta,\gamma) = \frac{k_B}{2\pi a_+}\int_0^{y_+} g(t)dt + \frac{k_B}{2\pi a_-}\int_0^{y_-} g(t)dt, \tag{19}$$

with

$$\begin{aligned} g(t) &\equiv [f(t)+1]\ln[f(t)+1] - f(t)\ln f(t), \\ f(t) &\equiv [\exp(t)-1]^{-1}. \end{aligned} \tag{20}$$

In the quantum limit ($y_\pm \gg 1$) the integrals appearing in (19) become pure numbers, with no dependence in β or γ, so that the entropy density reduces to

$$s = \frac{k_B}{2\pi}A\left(\frac{1}{a_+}+\frac{1}{a_-}\right), \tag{21}$$

where $A = \int_0^\infty g(t)dt = \pi^2/3$, as can be found through the change of variables $x = \exp(-t)$ and the help of formula 4.231-2 of Ref. [9]. By using (9) and (10), one finally gets

$$s(\epsilon,q) = \frac{k_B}{c}\left(\frac{\pi}{6\hbar}\right)^{1/2}\left[\sqrt{\epsilon c+q}+\sqrt{\epsilon c-q}\right]$$
$$= \frac{1}{2}s_{eq}(\epsilon)\left[\sqrt{1+x}+\sqrt{1-x}\right], \tag{22}$$

$s_{eq} \equiv k_B(2\varepsilon/3\varepsilon_D)^{1/2}$ being the local-equilibrium entropy. Then, as $x \to 1$, the entropy does not go to zero, in contrast to what happens in equilibrium when $T \to 0$. This can be understood microscopically as follows: as the heat flux grows, the number of phonons moving contrary to the heat flow decreases, and in the limit $x \to 1$ they disappear (see next section), but there still exist phonons of different modes moving in the sense of the heat flux; this implies that although the entropy decreases it does not vanish when the heat flux reaches its maximum value, describing the disorder inherent to the distribution of the remaining phonons over the different modes of the spectrum that point in the sense of q.

Finally, it is interesting to study the behavior of the entropy for high heat fluxes in the classical limit. Though we have seen that this is not correct since the limit $x \to 1$ is outside the classical range, it allows one to show some analogies with respect to what happens in equilibrium. For the calculation of the entropy in the classical limit, one must keep the dominant term in the development of the function $g(t)$ for small t. Some calculations supply for this dominant term: $g(t) \simeq -\ln t$, so that its integral gives $-t(\ln t - 1) \simeq -t\ln t$, and the entropy density (19) remains

$$s = -\frac{k_B}{2\pi a_+}y_+\ln y_+ - \frac{k_B}{2\pi a_-}y_-\ln y_-. \tag{23}$$

Finally, with the help of (13)–(14), the latter expression provides for the entropy per particle, $s' \equiv sl$,

$$s' = k_B\left[\ln(\varepsilon/\varepsilon_D) + \frac{1}{2}\ln(1-x^2)\right]. \tag{24}$$

As expected, the existence of a heat flux makes the entropy decrease. The problem is that when x tends to one, the entropy diverges, in analogy with the behavior of the classical entropy for an ideal gas as $T \to 0$. Thus one finds, also in the classical limit, some similarities between the behavior at low absolute temperatures in equilibrium and at high heat fluxes (or low generalized temperatures).

In summary, one observes that as the heat flux approaches its maximum value the generalized temperature and the heat capacity go to zero while the entropy does not. This could suggest some sort of generalization of the third law of thermodynamics to nonequilibrium situations by stating that when $\theta \to 0$ the heat capacity must vanish, thus encompassing the equilibrium and the nonequilibrium behaviors.

IV. CONCLUDING REMARKS

The study developed in the previous sections can be regarded in a different way by realizing that, due to the Debye approximation, the nonequilibrium phonon distribution function, Eq. (5), can be split in two equilibrium Bose-Einstein distributions corresponding, respectively, to phonons moving to the left, with temperature $\theta_-^{-1} = k_B\hbar c(\beta-\gamma c)$, and phonons moving to the right, with temperature $\theta_+^{-1} = k_B\hbar c(\beta+\gamma c)$. Of course, if the exact dispersion relation were used instead of the linear one this picture would not hold.

In this two-temperature picture, the quantum and the classical limits read simply as $\theta_\pm \ll T_D$ and $\theta_\pm \gg T_D$, respectively, and the corresponding expressions for these temperatures are, with the aid of (9)–(10) and (13)–(14),

$$\theta_\pm = T\sqrt{1\pm x}$$

in the quantum case, and

$$\theta_\pm = T\,(1\pm x)$$

in the classical one. Then, the temperatures describing the equilibrium distributions for each family of phonons depend on the value of the heat flux. In both cases it is seen that as the heat flux grows, the temperature for the phonons moving against the heat flow decreases, and when $x \to 1$ it goes to zero, meanwhile the temperature for the phonons traveling with it increases. This gives a simple explanation for why the limit $x \to 1$ cannot be addressed classically: in this limit, the number of phonons in modes with moments pointing against the heat flux is too low so as to permit the classical limit to apply. An interesting point would be to find an experiment providing evidence of the existence of these two temperatures; this is the aim of future work.

On the other hand, a question that may bear some theoretical interest is to contrast our one-dimensional expressions in the quantum limit with the tridimensional ones, namely [4]

$$\beta \propto (\hbar c)^{-3/4}\epsilon^{-1/4}\left(\sqrt{4-3x^2}-1\right)^{-3/4}$$
$$\times\left(\sqrt{4-3x^2}+2\right)^{1/2}, \tag{25}$$

$$\gamma_i \propto -(\hbar c)^{-3/4}\epsilon^{-5/4}\left(\sqrt{4-3x^2}-1\right)^{-3/4}$$
$$\times\left(\sqrt{4-3x^2}+2\right)^{-1/2}q_i, \tag{26}$$

with $x \equiv |\mathbf{q}|/\epsilon c$.

One observes some analogies between the latter expressions and our Eqs. (9)–(10), such as the fact that in both cases the generalized temperature tends to zero as the heat flux approaches its maximum value, or that γ_i keeps the sign of $-q_i$, thus indicating that the heat flux contributes to a decrease in the entropy. But there also exist some differences. Aside from a different exponent in ϵ that is responsible for the T^4 dependence of the Stefan-Boltzmann law in three dimensions, it is observed that the reduced heat flux appears in each case differently: while in the tridimensional case x appears in terms of the type $\sqrt{4-3x^2}+d$, with d a numerical constant, in one dimension it appears in terms of the form $1 \pm x$, see Eqs. (9) and (10); obviously, the same happens with the entropy. Furthermore, similarly as the energy density appears with different exponents in each case, the way in which the generalized temperature approximates to zero as x tends to one is also different in each case, namely $\theta \propto (1-x)^{1/2}$ in one dimension, and $\theta \propto (1-x)^{3/4}$ in three dimensions.

Finally, we compare the results obtained from our information theoretic analysis of heat transport in unidimensional crystals using a quantum statistics for phonons, and a similar maximum entropy development given in the past for a linear harmonic chain by using a classical Boltzmannian statistics for the oscillators.

One expects to recover the results obtained by Miller and Larson in the classical (high-temperature) limit. Those are in our notation, for the Lagrange multipliers appearing in the classical distribution function (Eqs. (29), Ref. [2])

$$\beta' = \frac{1}{\varepsilon}\frac{1+x^2}{1-x^2}, \tag{27}$$

$$\gamma' = -\frac{2N}{\varepsilon}\frac{x}{1-x^2}, \tag{28}$$

and for the entropy per particle

$$s' = \lim_{N\to\infty}(S/N) = k_B\left[1+\ln\varepsilon+\ln(1-x^2)\right], \tag{29}$$

with S the total entropy of the system. These expressions must be compared with (13), (14), and (24), respectively. In order to accomplish this, one must realize that one cannot establish a direct connection between both pairs of Lagrange factors by expecting the quantum distribution to tend towards the classical one in the high-temperature limit. This is so because phonons, like photons, have zero chemical potential, so that in no limit the quantum statistics becomes classical, in contrast to what happens for electrons, for instance.

They become comparable through the entropy, since the maximum entropy formalism leads in the classical case to

$$dS = k_B\beta' dU + k_B\gamma' dq, \tag{30}$$

U being the total energy of the system. Dividing by the total length L and comparing with (4), one thus would expect to find $\beta' = \beta$ and $\gamma' = \gamma L$. The comparison of (13) and (27) shows similar expressions differing in a factor $1+x^2 \simeq 2$. The product γL, on the other hand, can be easily rearranged to give $-\frac{N}{\varepsilon}\frac{x}{1-x^2}$ with the help of the expression for the sound speed in a linear chain of particles of mass m, namely $c = \sqrt{\kappa/m}\,l$, κ being the elastic constant [11], and making $\kappa = m = 1$ as in Ref. [2]; in this case, one observes a discrepancy in a factor of 2 with respect to (28). Expression (29) for the entropy also differs from our Eq. (24) by a factor of 1/2. Therefore, the results obtained through both developments are similar but not the same.

The origin of this discrepancy relies on the Debye approximation made at the beginning of our paper, which amounts to approximate the exact dispersion relation $\omega = (2c/l)|\sin(kl/2)|$ by its linear approximation $\omega = c|k|$ [11]. It is not difficult to repeat the calculations in [2] using the linear approximation instead of the exact dispersion relation. Miller and Larson obtain the logarithm of the partition function as the integral

$$\ln Z = -\frac{N}{\pi}\int_0^{\pi/2} d\phi\,[2\ln(2\beta') + 2\ln(\sin\phi) + \ln(1-y^2\cos^2\phi)], \tag{31}$$

where $y \equiv \gamma'/(N\beta')$ and ϕ is an integration variable. It is easy to show that the linear approximation in the dispersion relation yields $\sin\phi \simeq \phi$ and $\cos\phi \simeq 1$, so that integral (31) straightforwardly yields

$$\ln Z = -N\left[\ln\beta' + \frac{1}{2}\ln(1-y^2)\right], \tag{32}$$

except from an additive constant without interest. One thus obtains

$$U = -\frac{\partial \ln Z}{\partial \beta'} = \frac{N}{\beta'}\frac{1}{1-y^2}, \tag{33}$$

$$q = -\frac{\partial \ln Z}{\partial \gamma'} = -\frac{1}{\beta'}\frac{y}{1-y^2}. \tag{34}$$

The ratio between (34) and (33) immediately supplies for the parameter $x \equiv q/c\epsilon = q/\varepsilon = -y$, which substituted in (33) and with the help of the definition of y yields precisely (13) and (14) for β' and γ', instead of (27) and (28).

The entropy per particle can be obtained classically also in the Debye approximation by using the expression (Eq. (37), Ref. [2])

$$S = k_B\left(\beta' U + \gamma' q + \ln Z\right). \tag{35}$$

Introduction of (32), and of (13)–(14) for β' and γ' into the latter equation leads, after some direct calculations, to

$$s' = \lim_{N\to\infty}\frac{S}{N} = k_B\left[1+\ln\varepsilon+\frac{1}{2}\ln(1-x^2)\right], \tag{36}$$

which aside from an additive constant coincides with our expression (24).

As we have seen in this paper, the Debye approximation allows quite a simple mathematical analysis supplying, aside from a factor of the order of 2, the exact expressions found from a much more complex calculation. Therefore, we conclude that the Debye approximation does not significantly modify the thermodynamics of the system while it greatly simplifies the mathematics.

The present quantum analysis permits, furthermore, one to know the precise conditions under which the classical limit is attained in nonequilibrium situations, a question that cannot be addressed from the classical approach. As we have seen in Sec. II B, this limit is a generalization of the equilibrium high-temperature range, namely $\theta \gg T_D$. In this nonequilibrium classical limit, the heat flux cannot take very high values because then the generalized temperature goes to zero, so that the limit $x \to 1$ cannot be taken. This solves the divergence of the entropy function and other quantities claimed by Miller and Larson when x tends to one — see, for instance, Eqs. (29) or (36). We stress again the similarity between this divergence in the nonequilibrium entropy and the one faced at equilibrium for the classical entropy of an ideal gas, both disappearing when the systems are treated using quantum mechanics.

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[1] D. Jou, J. Casas-Vázquez, and G. Lebon, *Extended Irreversible Thermodynamics* (Springer, Berlin, 1993); Rep. Prog. Phys. **51**, 1105 (1988).
[2] B.N. Miller and P.N. Larson, Phys. Rev. A **20**, 1717 (1976).
[3] G.M. Kremer and I. Muller, J. Math. Phys. **33**, 2265 (1992).
[4] W. Larecki and S. Piekarski, Nuovo Cimento D **14**, 141 (1992).
[5] J. Camacho and M. Zakari, Phys. Rev. E **50**, 4233 (1994).
[6] E.T. Jaynes, Am. J. Phys. **33**, 391 (1965); in *Frontiers of Nonequilibrium Statistical Physics*, edited by G.T. Moore and M.O. Scully (Plenum, New York, 1986).
[7] L. Landau and E. Lifshitz, *Physique Statistique* (Mir, Moscow, 1967).
[8] H. Nielsen and B.I. Shklovsky, Zh. Eksp. Teor. Fiz. **56**, 709 (1969) [Sov. Phys JETP **29**, 386 (1969)].
[9] I.S. Gradshteyn and I.M. Ryzhik, *Table of Integrals, Series and Products* (Academic Press, New York, 1965).
[10] P.T. Landsberg and A. De Vos, J. Phys. A **22**, 1073 (1989).
[11] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1976).
[12] J. Casas-Vázquez and D. Jou, Phys. Rev. E **49**, 1040 (1994); D. Jou and J. Casas-Vázquez, Phys. Rev. A **45**, 8371 (1992).