PHYSICAL REVIEW E **77**, 023101 (2008)

Comment on "Analytical and numerical verification of the Nernst theorem for metals"

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(Received 25 June 2007; revised manuscript received 5 September 2007; published 8 February 2008)

Recently, Høye, Brevik, Ellingsen, and Aarseth [Phys. Rev. E **75**, 051127 (2007)] claimed that the use of the Drude dielectric function leads to zero Casimir entropy at zero temperature in accordance with Nernst's theorem. We demonstrate that their proof is not applicable to metals with perfect crystal lattices having no impurities. Thus there is no contradiction with previous results in the literature proving that the Drude dielectric function violates the Nernst theorem for the Casimir entropy in the case of perfect crystal lattices. We also indicate that the approximation of temperature independent relaxation frequency used in the paper leads to incorrect values of numerical coefficients in the obtained asymptotic expressions for metals with impurities.

DOI: 10.1103/PhysRevE.77.023101 PACS number(s): 05.30.−d, 42.50.Nn, 12.20.Ds, 65.40.G−

As correctly mentioned in the Introduction of Ref. [1], the relaxation frequency of a metal $\nu(T)$ goes to zero in accordance with the Bloch-Grüneisen law, $\nu(T)\sim T^5$, when temperature T goes to zero. It should be particularly emphasized that the Bloch-Grüneisen law is true for metals with perfect crystal lattices having no impurities. This law is also valid for metals with impurities at temperatures larger than 3–4 K but smaller than $T_D/4$, where T_D is the Debye temperature. As all real metals have a small fraction of impurities, at T well below 3–4 K the relaxation parameter instead of zero goes to some residual value ν_0 when T vanishes.

It has been known that there is a discussion in the literature on how to describe real metals in the theory of the thermal Casimir force. All sides participating in this discussion agree that the correct approach must be in agreement with the Nernst heat theorem. The question arises whether or not some theoretical approach is acceptable if it agrees with the Nernst theorem only when impurities are taken into account and disagrees otherwise. The answer is that such an approach is not acceptable. This is because the perfect crystal lattice is a truly equilibrium system with a nondegenerate dynamical state of lowest energy. At zero temperature any part of the system must be in a single ground quantum state [2]. The entropy is the logarithm of the number of states. As a result, the Casimir entropy, computed for a perfect crystal lattice, must be equal to zero. This is a direct consequence of quantum statistical physics. If one admits violation of the Nernst theorem for perfect crystal lattice, this would lead to the eventual abandonment of much of theoretical condensed matter physics, including the theory of electron-phonon interactions.

The analytical derivation of the thermal correction to the Casimir energy in Ref. [1] is performed for two Au plates with account of impurities. It is based on the Drude model and uses the condition

$$\zeta_m(T) \ll \nu(T). \tag{1}$$

This condition should be satisfied by sufficient number of Matsubara frequencies ζ_m with $m=1,2,3,\ldots$ [see Eqs. (5) and (9) in Ref. [1]; note that Ref. [1] omits the lower index m and the argument T]. Here $\zeta_m(T)=2\pi kmT/\hbar$, k is the Boltzmann constant and $m=0,1,2,\ldots$.

It is easily seen that in the case of perfect crystal lattice the condition (1) does not hold for any nonzero Matsubara frequency. In fact, according to Ref. [1], for Au $\nu(T=300\text{ K})=34.5$ meV whereas $\zeta_1(T=300\text{ K})=161.9$ meV. Thus $\nu(T=300\text{ K})<\zeta_1(T=300\text{ K})$ in contradiction with assumption (1). Taking into account that $\zeta_m=m\zeta_1$, the same inequality is valid for all nonzero Matsubara frequencies. When T decreases from room temperature up to approximately $T_D/4$ ($T_D=165$ K for Au [3]), $\nu(T)\sim T$, i.e., decreases with decreasing temperature following the same law as ζ_m. This preserves the inequality

$$\nu(T) < \zeta_m(T), \quad m = 1,2,3, \ldots , \tag{2}$$

which is the opposite to Eq. (1). At $T<T_D/4$ the relaxation frequency decreases even more rapidly than ζ_m with decreasing T (i.e., as $\sim T^5$ according to the Bloch-Grüneisen law due to electron-phonon collisions and as $\sim T^2$ at liquid helium temperatures due to electron-electron scattering). As a result, at arbitrary low temperatures for perfect crystal lattices it holds

$$\nu(T) \ll \zeta_m(T), \quad m = 1,2,3, \ldots . \tag{3}$$

From this inequality, it follows [4] that the Casimir free energy at low T contains a term that is linearly dependent on T. This leads to a nonzero entropy at $T=0$, i.e., to a violation of Nernst's theorem, as was discussed in Ref. [4].

Inequality (3) is just the opposite of the inequality (1) used in the derivation of Ref. [1]. Thus, all the results obtained in Ref. [1] are inapplicable to perfect crystal lattices. According to Ref. [1] "the Nernst theorem is not violated when using the realistic Drude dispersion model" and this conclusion "is clearly in contrast to that presented in various earlier works [4–8]". These formulations are, however, misleading. References [4–8] deal with perfect crystal lattices and prove that for such lattices the use of the Drude model leads to the violation of the Nernst heat theorem. As explained above, the derivation in Ref. [1] is not applicable to perfect crystal lattices because it uses the inequality (1) which is just the opposite to the inequality (3) satisfied for perfect lattices. Thus there is no contradiction between the results of Ref. [1] and Refs. [4–8].

What is in fact found in Ref. [1] [see Eq. (31)] is the analytic behavior of the low-temperature thermal correction to the Casimir energy using the Drude model for crystal lattices with impurities:

$$\Delta F = C_1 T^2 (1 - C_2 T^{1/2} + \cdots), \tag{4}$$

where C_1 and C_2 are constants. According to this correction, at very low temperatures the Casimir entropy abruptly jumps to zero starting from negative values. Thus formally the Nernst heat theorem is satisfied when impurities are present. This result is not new. It was first demonstrated numerically in Ref. [9] and has been acknowledged in Refs. [4–8]. Reference [1] provides an analytical proof.

However, the values of numerical coefficients C_1 and C_2 for Au in Eq. (4) are determined in Ref. [1] incorrectly. The reason is that the dependence of ν on the temperature has been neglected in Ref. [1]. To calculate these coefficients, Ref. [1] uses the Au relaxation frequency $\nu(T=300\text{ K}) = 34.5$ meV and the inequality (1). However, as explained above, at room temperature and also at much lower temperatures in the application range of the Bloch-Grüneisen law, the inequality (1) is violated and exactly the opposite inequality (3) is valid. The inequality (1) used in Ref. [1] becomes valid only for imperfect lattices at very low T when, due to the presence of impurities, the relaxation frequency deviates from the Bloch-Grüneisen law and takes a nonzero T-independent residual value ν_0. For typical Au samples the residual relaxation frequency is approximately equal to $\nu_0 \approx 34.5 \times 10^{-3}$ meV, and for the best samples which are most close to the perfect crystal it is even three orders of magnitude lower: $\nu_0 \approx 34.5 \times 10^{-6}$ meV [3]. In order that at least the first ten Matsubara frequencies satisfy the inequality

$$\zeta_m(T) \ll \nu_0, \tag{5}$$

the temperature must be $T < 10^{-3}$ K for typical Au samples and $T < 10^{-6}$ K for the best Au samples. For the applicability of asymptotic expression (4) [Eq. (31) in Ref. [1]] temperatures must be additionally at least one order of magnitude less.

As was mentioned above, to calculate the values of the coefficients C_1 and C_2 Ref. [1] uses the value $\nu(T=300\text{ K}) = 34.5$ meV. The correct values to be used instead are $\nu_0 = 34.5 \times 10^{-3}$ meV for typical Au samples and $\nu_0 = 34.5 \times 10^{-6}$ meV for the best Au samples. As a result, Eqs. (13), (18), and (30) in Ref. [1] lead to the following values of coefficients in Eq. (4):

$$C_1 = 5.81 \times 10^{-10}\ \text{J}/(\text{m}^2\,\text{K}^2), \quad C_2 = 95.75\ \text{K}^{-1/2} \quad (\text{typical Au samples}),$$

$$C_1 = 5.81 \times 10^{-7}\ \text{J}/(\text{m}^2\,\text{K}^2), \quad C_2 = 3028.0\ \text{K}^{-1/2} \quad (\text{best Au samples}). \tag{6}$$

This should be compared with the values presented in Ref. [1]:

$$C_1 = 5.81 \times 10^{-13}\ \text{J}/(\text{m}^2\,\text{K}^2), \quad C_2 = 3.03\ \text{K}^{-1/2}. \tag{7}$$

The results of numerical computations in Ref. [1] were found to be in agreement with the asymptotic expression (4) containing the wrong coefficients (7). The reason is that in numerical computations the room temperature relaxation frequency $\nu(T=300\text{ K}) = 34.5$ meV was also used incorrectly within the wide temperature region from 0.01 K to 800 K. To obtain the correct computation results, from 4–5 K to 800 K the actual temperature dependence of the relaxation frequency on T should be employed (given by the Bloch-Grüneisen law and the linear dependence). For temperatures around zero the residual relaxation frequency for Au, ν_0, depending on the concentration of impurities, must be applied.

To conclude, Ref. [1] finds (up to incorrectly determined coefficients) the low-temperature behavior of the thermal correction to the Casimir energy in the configuration of two Au plates with impurities, using the permittivity of the Drude model. Although the results of Ref. [1] are in formal agreement with the Nernst theorem, there is no contradiction with the results of Refs. [4–8] demonstrating the violation of the Nernst theorem in the Drude model approach for perfect crystal lattices. The reason is that the condition used by the authors of Ref. [1] in their derivation is violated for perfect lattices and can be applied to only lattices with impurities.

It must be emphasized that the results of Ref. [1] do not solve the problem of inconsistency of the Drude model with basic thermodynamic principles in the application to the Casimir entropy, as the authors claim. Reference [1] recognizes that “a simple physical model of course cannot be permitted to run into conflict with thermodynamics.” However, as is seen in the above and from Refs. [4–8], the Drude model violates the Nernst heat theorem for the Casimir entropy in the case of metals with perfect crystal lattices. This alone makes the Drude model approach to the Casimir force unacceptable as being in contradiction with quantum statistical physics. According to the authors of Ref. [1], the approaches with nonzero contributions of the transverse electric term at zero frequency (recall that in the Drude model approach this term does not contribute at $\zeta = 0$) would violate the Nernst theorem. This is misinformation. As is shown in Refs. [4,10], both the plasma model approach and the impedance approach are in agreement with the Nernst theorem, and both of them include a nonzero contribution from the transverse electric term at zero frequency. Thus, although for metals with impurities the Drude model approach leads to zero Casimir entropy at zero temperature, this approach is theoretically invalid and fails to provide a consistent description of the thermal Casimir force in the framework of the Lifshitz theory. The authors of Ref. [1] underline that they “shall not be concerned with a comparison between experiment and theory.” In this respect it is pertinent to note that measurements of Refs. [11,12] exclude the Drude model approach to the thermal Casimir force at a 99.9% confidence level within the wide range of separations between the plates from 210 to 620 nm. The only theoretical approach which is consistent with both short separation [13] and long separation [5,11,12] measurements of the Casimir force is based on the use of the generalized plasmalike dielectric permittivity [8,12] which takes into account dissipation processes due to interband transitions of core electrons, but disregards dissipation due to scattering of conduction electrons. The resolution of the problem why the account of one type of dissipation in the Lifshitz theory is necessary while that of another leads to contradictions with thermodynamics and experiment is expected in near future.

The authors are grateful for helpful discussions with all coauthors of our publications on this subject, i.e., V. B. Bezerra, M. Bordag, R. S. Decca, E. Fischbach, B. Geyer, D. E. Krause, D. López, U. Mohideen, and C. Romero. This work was supported by Deutsche Forschungsgemeinschaft, Grant No. 436 RUS 113/789/0–3.

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