Phonon number fluctuations in Debye model of solid

Q. Chen,1 Y. Liu,2,1 and Q. H. Liu1

1School for Theoretical Physics, School of Physics and Electronics, Hunan University, Changsha 410082, China
2International Department, Yali High School, Changsha, 410007, China

(Dated: February 1, 2019)

In statistical mechanics for a given system, both the particle number fluctuations and the isothermal compressibility are well-definable and in principle experimentally testable, and they are in general related to each other by the fluctuation-compressibility theorem which states that fluctuations in particle number are proportional to the isothermal compressibility. [1–4] However, it is occasionally reported that this theorem can be violated. Two known examples are BCS model of a superconductor [5] and photon gas. [6] These studies suggest that the theorem is inapplicable to all particle gases whose numbers of particle are indefinite. The present paper studies that phonon number fluctuations in Debye model of solid. This model is fundamental in understanding of the excitons and it was the first model to introduce the concept exciton/quasi-particle into physics, giving the correct $1/4$ law (where $T$ is the temperature) of the heat capacity of solid at low temperature $T \to 0$.

In the Debye model of the solid, the thermal properties are determined by the solid lattice vibrations. The vibrational frequencies form a continuous spectrum with a cut off at an upper limit $\omega_D$ of normal modes of vibration is $3N$ of which $N$ are the number of the solid atoms which can harmonically displaced from lattices. The Debye spectrum $g(\omega)$ or density of states in frequency interval $\omega \to \omega + d\omega$ is, [1–4]

$$g(\omega) = \begin{cases} \frac{2N}{\omega_D^3} \omega^2, & \omega \leq \omega_D \\ 0, & \omega > \omega_D \end{cases},$$

where symbols $c$ and $V$ denote the effective speed of sound within the solid and its volume, respectively. Two quantities $g(\omega)$ and $\omega_D$ are related by the requirement that total number of normal modes of vibration $3N$,

$$\int_0^{\omega_D} g(\omega) d\omega = 3N.$$  (2)

Assuming that there are $n_i$ phonons in the $i$th frequency $\omega_i$ whose unit energy quantum is $\hbar \omega_i$, we have the energy in a microstate $\{n_i\}$,

$$E\{n_i\} = \sum_{i=1}^{3N} n_i \hbar \omega_i.$$  (3)

The partition function is, [1–4]

$$Q = \sum_{\{n_i\}} e^{-\beta E\{n_i\}} \prod_{i=1}^{3N} \sum_{n_i=0}^{\infty} e^{-n_i \beta \hbar \omega_i} = \prod_{i=1}^{3N} \frac{1}{1 - e^{-\beta \hbar \omega_i}}.$$  (4)

where $\beta = 1/kT$, and $\hbar$ and $k$ are, respectively, Planck’s constant and Boltzmann’s constant. The average number $\langle n_i \rangle$ of phonon of energy quantum $\hbar \omega_i$ is,

$$\langle n_i \rangle = \frac{\sum_{\{n_i\}} n_i e^{-\beta E\{n_i\}}}{Q} = \frac{\sum_{n_i=0}^{\infty} n_i e^{-n_i \beta \hbar \omega_i}}{\sum_{n_i=0}^{\infty} e^{-n_i \beta \hbar \omega_i}} = \frac{1}{e^{\beta \hbar \omega_i} - 1} = -kT \frac{\partial}{\partial \beta \hbar \omega_i} \ln Q.$$  (5)
The internal energy is,
\[ U = \sum_{i=1}^{3N} \langle n_i \rangle \hbar \omega_i = \sum_{i=1}^{3N} \frac{\hbar \omega_i}{e^{\beta \hbar \omega_i} - 1} = \int_0^{\omega_D} \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} g(\omega) d\omega. \] (6)

A more detailed discussion of this integral can be given shortly. However, the internal energy can be greatly simplified in limits of high or low temperatures, [1–4]
\[ U \approx 3NkT \begin{cases} 1, & T \gg T_D \\ \frac{4\pi}{3} \left( \frac{T}{T_D} \right)^3, & T \ll T_D \end{cases}, \] (7)
where \( T_D \) is the Debye temperature defined by,
\[ kT_D = \hbar \omega_D. \] (8)

The heat capacity \( C = \partial U / \partial T \) in two opposite limits is,
\[ C \approx 3Nk \begin{cases} 1, & T \gg T_D \\ \frac{4\pi}{3} \left( \frac{T}{T_D} \right)^3, & T \ll T_D \end{cases}. \] (9)

This equation is significant for it in high temperature limit gives the Dulong–Petit law, and in low temperature limit yields the \( T^3 \) law.

The equation of state in terms of pressure \( p \) and energy \( U \) is similar to that for photon gas
\[ p = \frac{1}{3} \frac{U}{V}. \] (10)

This is the explicitly form of applying the following general relationship between equation of macroscopic state and the partition function to the phonon gas,
\[ p = kT \frac{\partial}{\partial V} \ln Q. \] (11)

With the isothermal compressibility defined by,
\[ \kappa_T \equiv -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T. \] (12)

the fluctuation-compressibility theorem suggests [1–4]
\[ \frac{\langle n^2 \rangle - \langle n \rangle^2}{\langle n \rangle^2} = \frac{kT}{V} \kappa_T, \] (13)
where,
\[ \langle n^2 \rangle = \left\langle \sum_{r} n_r \sum_{s} n_s \right\rangle, \quad \text{and} \quad \langle n \rangle = \sum_{i=1}^{3N} \langle n_i \rangle. \] (14)

For photon gas, it is recently shown [6] that the fluctuation-compressibility theorem does not hold for the compressibility \( \kappa_T \) does not exist, but the \( \langle n^2 \rangle - \langle n \rangle^2 \) and the relative fluctuation \( \left( \langle n^2 \rangle - \langle n \rangle^2 \right) / \langle n \rangle^2 \) are both well-definable.

There is a close analogy between photons and phonons, sharing at least eight properties in common. [7] Whether the fluctuation-compressibility theorem holds true for phonons in the Debye model of solid is worthy of investigation, and results turn out to be that both sides of the equation (13) exist, but the equality between two sides does not hold.

In section II, for the phonon gas, we present the mean numbers, corresponding fluctuations. In section III, we will further examine the internal energy, pressure, and the isothermal compressibility and show how the theorem (13) breaks down. In section IV, brief concluding remarks are given.

The Debye integral \( D_n(x) \) [8] is elementary in our analysis,
\[ D_n(x) \equiv \int_0^x \frac{\Gamma(n)}{e^t - 1} dt, \] (15)
which has simple expressions in limits of large and small \( x \) with \( \zeta \) denoting the Riemann zeta function
\[ D_n(x) \approx \begin{cases} n!\zeta(n+1) - x^n e^{-x} + O(x^n e^{-2x}), & x \to \infty \\ x^n/n + O(x^{n+1}), & x \to 0. \end{cases} \] (16)
II. THE MEAN NUMBERS AND THE NUMBER FLUCTUATIONS

The mean numbers for phonons in the Debye model of solid is from, (5)

$$\langle n \rangle = \sum_{i=1}^{3N} \langle n_i \rangle$$

$$= \int_{0}^{\omega_D} \frac{1}{e^{\beta \hbar \omega} - 1} \varrho(\omega) d\omega$$

$$= \frac{9N}{\omega_D} \int_{0}^{\omega_D} \frac{\omega^2}{e^{\beta \hbar \omega} - 1} d\omega. \quad (17)$$

Performing a variable transformation $t = \beta \hbar \omega$ and defining,

$$t_D \equiv \frac{\hbar \omega_D}{kT} = \frac{T_D}{T}, \quad (18)$$

the mean numbers $\langle n \rangle$ (17) becomes,

$$\langle n \rangle = \frac{9N}{\omega_D} \left( \frac{kT}{\hbar} \right)^3 \int_{0}^{t_D} \frac{t^2}{e^t - 1} dt = 9N t_D^{-3} D_2(t_D). \quad (19)$$

It is thus in the opposite limits of temperature intervals from, (16)

$$\langle n \rangle \simeq 9N \left( \frac{T}{T_D} \right)^3 \left\{ \begin{array}{ll}
\frac{1}{2} \left( \frac{T}{T_D} \right)^2, & T \gg T_D \\
2\zeta(3), & T \ll T_D
\end{array} \right. = 9N \left\{ \begin{array}{ll}
\frac{1}{2} \frac{T}{T_D}, & T \gg T_D \\
2\zeta(3) \left( \frac{T}{T_D} \right)^3, & T \ll T_D
\end{array} \right. \quad (20)$$

Before computing the particle number fluctuations, we need to deal statistical correlation $\langle n_r n_s \rangle$ of the particle number. If $r \neq s$, we have,

$$\langle n_r n_s \rangle \equiv \frac{\sum_{(n_i)} n_r n_s e^{-\beta E(n_i)}}{Q}$$

$$= \sum_{n_r=0}^{\infty} \sum_{n_s=0}^{\infty} n_r n_s e^{-(n_r \beta \hbar \omega_r + n_s \beta \hbar \omega_s)}$$

$$= \sum_{n_r=0}^{\infty} \frac{e^{-n_r \beta \hbar \omega_r}}{\sum_{n_s=0}^{\infty} e^{-n_s \beta \hbar \omega_s}} \sum_{n_s=0}^{\infty} n_s e^{-n_s \beta \hbar \omega_s}$$

$$= \langle n_r \rangle \langle n_s \rangle. \quad (21)$$

The minus of the particle number fluctuations in the $r$th vibration mode are,

$$- \left( \langle n_r^2 \rangle - \langle n_r \rangle^2 \right) = \frac{\partial}{\partial \beta \hbar \omega_r} \sum_{n_r=0}^{\infty} n_r e^{-n_r \beta \hbar \omega_r} \sum_{n_r=0}^{\infty} e^{-n_r \beta \hbar \omega_r}. \quad (22)$$

The right-handed side of this equation becomes from, (5)

$$\frac{\partial}{\partial \beta \hbar \omega_r} \frac{1}{e^{\beta \hbar \omega_r} - 1} = \frac{e^{\beta \hbar \omega_i}}{(e^{\beta \hbar \omega_i} - 1)^3}$$

$$= - \frac{e^{\beta \hbar \omega_i} - 1 + 1}{(e^{\beta \hbar \omega_i} - 1)^3}$$

$$= - \left( \langle n_r \rangle^2 + \langle n_r \rangle \right) \quad (23)$$

Combining two results (22)-(23), we reach a remarkable result,

$$\langle n_r^2 \rangle - \langle n_r \rangle^2 = \langle n_r \rangle^2 + \langle n_r \rangle. \quad (24)$$
The fluctuations in phonon number are,
\[
\langle \Delta n^2 \rangle \equiv \langle n^2 \rangle - \langle n \rangle^2 \\
= \left( \sum_r n_r \sum_s n_s \right) - \left( \sum_r n_r \right) \left( \sum_s n_s \right) \\
= \sum_{r=1}^{3N} \left( \langle n_r^2 \rangle - \langle n_r \rangle^2 \right) \\
= \sum_{r=1}^{3N} \left( \langle n_r \rangle^2 + \langle n_r \rangle \right),
\]
(25)

which can be transformed into an integral,
\[
\langle \Delta n^2 \rangle = \frac{9N}{(\omega D)^3} \int_0^\infty \omega^2 e^{\beta\omega} \left( e^{\beta\omega} - 1 \right)^2 d\omega \\
= 9Nt_D^{-3} \int_0^t \frac{4e^t}{(e^t - 1)^2} dt \\
= 9Nt_D^{-3} \left( 2D_1(t_D) - \frac{t_D^2}{e^{t_D} - 1} \right).
\]
(26)

In limits of high and low \( T \), Eq. (26) becomes with \( \zeta(2) = \pi^2/6 \),
\[
\langle \Delta n^2 \rangle \simeq 9N \left( \frac{T}{T_D} \right)^3 \left\{ \begin{array}{ll}
T_D, & T \gg T_D \\
\pi^2/3, & T \ll T_D
\end{array} \right.
\]
(27)

The relative fluctuations are,
\[
\frac{\langle \Delta n^2 \rangle}{\langle n \rangle^2} \simeq \frac{1}{9N \left( \frac{T}{T_D} \right)^3} \left\{ \begin{array}{ll}
\frac{4 \left( \frac{T}{T_D} \right)^3}{\pi^2/3 \zeta(3)}, & T \gg T_D \\
0.569 \left( \frac{T}{T_D} \right)^3, & T \ll T_D
\end{array} \right.
\]
(28)

In addition we have from (26) and (19),
\[
\frac{\langle \Delta n^2 \rangle}{\langle n \rangle} = \frac{2D_1(t_D) - \frac{t_D^2}{e^{t_D} - 1}}{D_2(t_D)} \\
\simeq \left\{ \begin{array}{ll}
2T/T_D, & T \gg T_D \\
\zeta(2)/\zeta(3), & T \ll T_D
\end{array} \right.
\]
(29)

It is interesting to note that with a given large number of atoms \( N \), the relative fluctuation is not automatically less than 1 at low temperature. I.e, the following equation would be violated,
\[
\frac{\langle \Delta n^2 \rangle}{\langle n \rangle^2} \simeq \frac{0.063}{N \left( \frac{T_D}{T} \right)^3} \leq 1.
\]
(30)

The self-consistence of the statistical mechanics implies a requirement upon the temperature,
\[
T \gtrsim 0.398T_D N^{-1/3}.
\]
(31)

In other words, when temperature approaches to zero Kelvin, the thermodynamic limit requires very vast number of particles \( N \to \infty \) otherwise the low temperatures can not be properly defined in a broad sense. [9]
III. THE INTERNAL ENERGY, PRESSURE, AND THE ISOTHERMAL COMPRESSIONIBILITY

The nontrivial expression for the isothermal compressibility needs higher corrections of internal energy at low
temperatures, which is from (7),

\[ U = \int_0^{\omega_D} \frac{h\omega}{e^{h\omega/2} - 1} g(\omega) d\omega \]

\[ = \frac{9Nh}{\omega_D^3} \left( \frac{kT}{h} \right)^4 \int_0^{t_D} \frac{x^3 e^x - 1}{e^x - 1} dx \]

\[ = 9NkT_t_D^3 D_3(t_D) \]

\[ \simeq 9NkT_t_D^{-3} \left\{ \begin{array}{l}
\frac{t_D^3}{3!} / 3, T \gg T_D \\
3(4) - \frac{t_D^3 e^{-t_D}}{3}, T \ll T_D
\end{array} \right. \]

\[ = 3NkT \left\{ \begin{array}{l}
1, T \gg T_D \\
\pi t_D^3 / 5 - e^{-t_D}, T \ll T_D
\end{array} \right. \]

(32)

For obtaining the heat capacity at low temperatures, the leading term of the internal energy as \(3NkT \pi t_D^3 / 5\) suffices. We are going to show that next order term that is usually ignored as \(-3NkT e^{-t_D}\) is relevant and significant. It is
evident from the computation of the inverse of the isothermal compressibility \(1/\kappa_T\),

\[ \frac{1}{\kappa_T} = -\left( V \frac{\partial p}{\partial V} \right)_T \]

\[ = -\frac{V}{3} \left( \frac{\partial U}{\partial V} \right)_T \]

\[ = -3VkT \left( \frac{\partial}{\partial V} \frac{N}{V t_D^3} D_3(t_D) \right)_T \]

\[ = -3NkT_t_D^{-3} \left( \frac{\partial}{\partial V} D_3(t_D) \right)_T \]

\[ = -3NkT_t_D^{-3} \left( \frac{\partial t_D}{\partial V} \right)_{T} \frac{t_D^3}{e^{t_D} - 1} \]

\[ = \frac{N}{V} \frac{h\omega_D}{e^{t_D} - 1}. \]

(33)

where we used two relations,

\[ \frac{N}{V t_D^3} = \left( \frac{kT}{\hbar} \right)^3 \frac{1}{6\pi^2 c^3}, \text{ independent of } V, \]

(34)

and

\[ \left( \frac{\partial t_D}{\partial V} \right)_{T} = -\frac{h\omega_D}{3kT} \frac{1}{V}. \]

(35)

The isothermal compressibility is thus,

\[ \kappa_T = \frac{V}{N h\omega_D} \left( e^{t_D} - 1 \right) \simeq \left\{ \begin{array}{l}
\frac{V}{N h\omega_D}, T \gg T_D \\
\frac{V}{N h\omega_D} e^{t_D/T}, T \ll T_D
\end{array} \right. \]

(36)

So, it is clear that with the usual approximation of the internal energy at lower temperatures, we would recover the
conclusion that \(\kappa_T\) for the phonons does not exist. In fact, it do exist but divergent as \(T \to 0\). The fluctuation-compressibility theorem (13) suggests that we have when \(T \gg T_D\) from (28) and (36),

\[ \frac{4}{9N} \simeq \frac{kT}{V^{\kappa_T}} \simeq \frac{1}{N} \]

(37)

and when \(T \ll T_D\),

\[ \frac{0.569}{9N} \left( \frac{T_D}{T} \right)^3 \simeq \frac{kT}{V^{\kappa_T}} \simeq \frac{1}{N T_D} e^{t_D/T} \]

(38)
Quantitatively, these two relations (37) and (38) do not hold true. To illustrate in what intervals the differences become bigger and larger, let us consider a slightly different version of the fluctuation-compressibility theorem, obtained by multiplication of \( \langle n \rangle \) on both sides of (13),

\[
\frac{\langle n^2 \rangle - \langle n \rangle^2}{\langle n \rangle} = \langle n \rangle \frac{kT}{V} \kappa_T.
\]  

(39)

Once it holds exactly, we would have,

\[
\frac{2D_1(t_D) - \frac{t_D^2}{e^{t_D} - 1}}{D_2(t_D)} = 9 \frac{D_2(t_D)(e^{t_D} - 1)}{t_D^4}.
\]  

(40)

Both sides of this equation are plotted in Fig. 1, we see that when \( T > T_D \), they differ mainly in a numerical factor \( 9/4 \), i.e.,

\[
9 \left( \frac{2D_1(t_D) - \frac{t_D^2}{e^{t_D} - 1}}{D_2(t_D)} \right) \approx 9 \frac{D_2(t_D)(e^{t_D} - 1)}{t_D^4}.
\]  

(41)

When \( T \ll T_D \), the left-handed side terminates at 1.37, while the right-handed side goes to infinity as \( T^4 \exp(T_D/T) \) when \( T \to \infty \).

IV. REMARKS

Fluctuations are ubiquitous in the world and the statistical mechanics offers powerful tools to understand them. In Debye model of solid, the fluctuations in photon number and the isothermal compressibility of the solid are well-defined, but the fluctuation-compressibility theorem fails. As it was shown, [6] the theorem holds true for material gas whose chemical potential is not identically zero, but how it is violated in different systems is not clear. The theorem breaks down differently for phonons and photons, though they are quite similar in modern physics.

Acknowledgments

This work is financially supported by National Natural Science Foundation of China under Grant No. 11675051.

[1] R. K. Pathria, P. D. Beale *Statistical Mechanics*, 3rd ed. (Butterworth-Heinemann, Oxford, 1996), pp. 103–104.
[2] R. Kubo, *Statistical Mechanics* (North Holland-Interscience-Wiley, New York, 1965), pp. 398–399.
[3] K. Huang, *Statistical Mechanics*, 2nd ed. (Wiley, New York, 1986), pp. 152–153.
[4] D. Chandler, *Introduction to Modern Statistical Mechanics*, (Oxford University Press, New York, 1987), p. 71.
[5] J. S. Bell, "Fluctuation compressibility theorem and its application to the pairing model", Phys. Rev. **129**, 1896-1900 (1963).
[6] H. S. Leff, "Fluctuations in particle number for a photon gas", Am. J. Phys. **83**, 362-365 (2015).
[7] A. Kumar, *Introduction to Solid State Physics*, 2nd ed. (PHI Learning Pvt. Ltd., India, 2010), p. 140.
[8] M. Abramowitz and I. Stegun, (eds.) *Handbook of Mathematical Functions: with Formulas, Graphs, and Mathematical Tables*, (Dover Publications, Inc. New York, 1972), p. 998.
[9] X. Wang, Q. H. Liu, and W. Dong, "Dependence of the existence of thermal equilibrium on the number of particles at low temperatures", Am. J. Phys. **83**, 75, 431-(2007).
FIG. 1: Discrepancies between fluctuation and compressibility for phonon gas. Solid and dashed line shows, respectively, the right- and left-handed side of equation (40). When $T \ll T_D$, the left-handed side terminates at 1.37, while the right-handed side goes to infinity as $\sim T^3 \exp(T_D/T)$ when $T \to 0$. 