

Quantum effects in a system of Boltzmann hard spheres

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Abstract. The quantum contribution to the energy of a ‘Boltzmann’ gas consisting of hard spheres proves to be virtually constant up to very high temperatures where the thermal de Broglie wavelength constitutes only a small proportion of the hard sphere diameter. Consequently, the heat capacity of the system barely differs from the classical value of $(3/2)k_B$ everywhere except in the lowest temperature region, where heat capacity as a function of temperature has the ‘Debye’ form but with a very low Debye temperature, of the order of several degrees. The line of equilibrium between a quantum crystal and liquid for a ‘Boltzmann’ system of hard spheres coincides with the classical one, with the exception of the very-low-temperature region. High-temperature quantum effects are revealed in the system under consideration in a kind of ‘bare’ form, while in the case of more realistic systems or models they can be masked by the complex behavior of other components of the total energy.

Keywords: quantum hard sphere system, thermal wavelength, Boltzmann gas

1. Introduction

At sufficiently high temperatures or in systems with a strong repulsive interaction, when the exchange of particles is almost impossible, the effects of Bose and Fermi statistics can be disregarded. Nevertheless, the system can be quantum-mechanical because of ‘diffraction effects’ connected with the wave nature of particles. Moreover, the effects of quantum statistics decay exponentially with an increase in temperature, while ‘diffraction effects’ decrease according to an inverse power law at $T \rightarrow \infty$.

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Thus, in a quantum system of hard spheres there is a significant temperature range in which the effects of quantum statistics play only an insignificant role [1]. A system of hard spheres is the simplest nontrivial system with interaction of the form (Fig. 1)

$$\Phi(r) = 0, \quad r > \sigma, \quad \Phi(r) = \infty, \quad r < \sigma. \quad (1)$$

The model of hard spheres was widely used to describe strongly interacting systems. Let us recall the van der Waals theory of critical phenomena, in which the interparticle repulsive interaction is described by the potential of hard spheres.

Subsequently, many efforts were made to build a theory of systems of hard spheres and a theory of liquids that use the model of hard spheres as the zero approximation within the framework of the perturbation theory [2]. The quantum model of hard spheres was a highly useful approximation in the analysis of the behavior of quantum systems with a short-

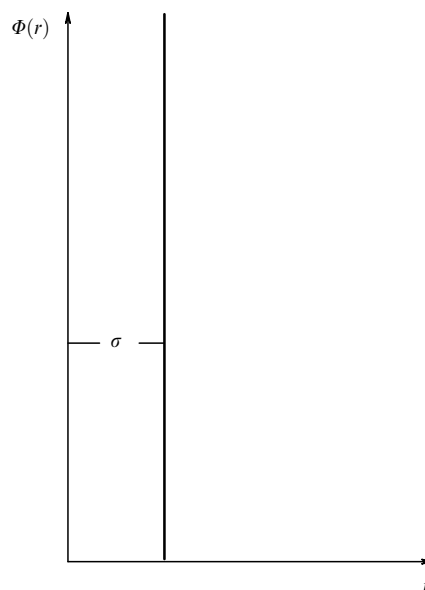


Figure 1. Potential of hard spheres.

range interaction, in particular, helium [3, 4]. Below, a situation is examined in which the quantum effects in the system are determined exclusively by the wave nature of particles and by the Heisenberg uncertainty principle.

2. Quantum harmonic oscillator

For the purpose of a comparative analysis, let us first examine the standard problem of a quantum harmonic oscillator. As follows from the quantum theory, the average energy of a quantum harmonic oscillator is written as follows [5] (Fig. 2):

$$E = \frac{1}{2} \hbar\omega + \frac{\hbar\omega}{\exp[\hbar\omega/(k_B T)] - 1}, \quad (2)$$

where the quantity $\hbar\omega/2$ is the famous ‘zero-point’ energy. Let us show that the existence of the zero-point energy directly follows from the Heisenberg uncertainty principle [6–8]

$$\Delta x \Delta p = \frac{\hbar}{2}, \quad (3)$$

where Δx and Δp are the uncertainties of the coordinate and momentum, respectively. According to principle (3), the minimum energy of a quantum harmonic oscillator can be written as follows:

$$E = \frac{(\Delta p)^2}{2m} + \frac{1}{2} m\omega^2 (\Delta x)^2, \quad (4)$$

or, using relationship (3), as

$$E = \frac{\hbar^2}{8m(\Delta x)^2} + \frac{1}{2} m\omega^2 (\Delta x)^2. \quad (5)$$

By minimizing the energy (5) with respect to Δx , we have

$$-\frac{\hbar^2}{4m(\Delta x)^3} + \frac{1}{2} m\omega^2 (\Delta x) = 0. \quad (6)$$

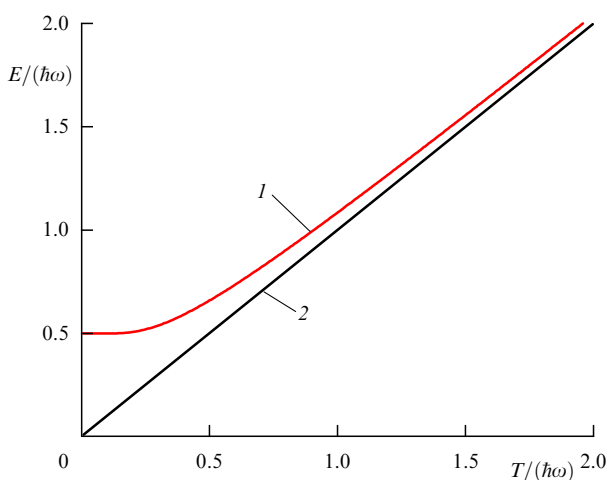


Figure 2. Temperature dependences of the energy of quantum (curve 1) and classical (curve 2) oscillators. The energy and the temperature are expressed in $\hbar\omega$ units; the latter, in the case of physical systems, is a quantity of the order of 10^2 K.

From (6), we obtain

$$\Delta x = \sqrt{\frac{\hbar}{2m\omega}}. \quad (7)$$

Finally, substituting (7) into expression (5), we find the value of the energy of the ground state of the quantum harmonic oscillator:

$$E_0 = \frac{\hbar^2}{8m(\Delta x)^2} + \frac{1}{2} m\omega^2 (\Delta x)^2 = \frac{\hbar\omega}{4} + \frac{\hbar\omega}{4} = \frac{\hbar\omega}{2}. \quad (8)$$

As can be seen from Fig. 2, the quantum contribution to the energy of the oscillator is not additive. The excessive kinetic energy connected with the uncertainty principle decreases with increasing temperature and tends to zero at $T \rightarrow \infty$, which is determined by the decrease in the thermal de Broglie wavelength, which has the form

$$\lambda_T = \sqrt{\frac{2\pi\hbar^2}{mk_B T}}. \quad (9)$$

Relationship (9) indicates that a decaying of the wave properties of particles occurs with an increase in the temperature; in this case, the motion of the oscillator acquires a more determinate nature; the uncertainty of the coordinate disappears, which entails the disappearance of the zero-point energy. However, all this occurs in the limit of high temperatures. In a real situation, the λ_T/a ratio (a is the amplitude of vibration) is always finite, which does not make it possible to ignore quantum effects, even at sufficiently high temperatures.

3. Energy and heat capacity of a system of Boltzmann hard spheres

The situation that appears in the case of an anharmonic quantum system, a clear representative of which is the quantum system of hard spheres, differs significantly from that examined in Section 2. Let us consider the results of a calculation of the thermodynamic properties of the system of hard spheres by the Monte Carlo method performed in [9]. Note that, in contrast to the classical system of hard spheres, in the quantum case there is an interparticle repulsion (which appears in the system because of the uncertainty principle), which ensures the existence of a ‘restoring’ force with respect to long-wave acoustic deformations [1].

The author of [9] has represented the dimensionless energy $E/(k_B T)$ of the fluid state of a system as a function of the reduced density $\rho^* = \rho\sigma^3$ (σ is the diameter of the sphere) along lines with a constant λ^* ($\lambda^* = \hbar/(2\pi mk_B T\sigma^2)^{1/2}$ is the ratio of the thermal de Broglie wavelength to the diameter of the hard sphere). It is obvious that if the thermal length is less than the diameter of the hard sphere, then particle scattering on each other has a purely classical character. For this reason, it is convenient to use the ratio λ_T/σ when analyzing quantum effects in a system of hard spheres.

For the analysis, we select the results of calculations of the energy at a density $\rho^* = 0.3$, which cover the greatest interval of reduced de Broglie lengths λ^* . The corresponding data are demonstrated in Fig. 3.

As can be seen from Fig. 3 (see graph in the inset), the calculated data obviously are extrapolated at $\lambda^* \rightarrow 0$ (classical limit) to the classical value $E/(k_B T) = 1.5$, which

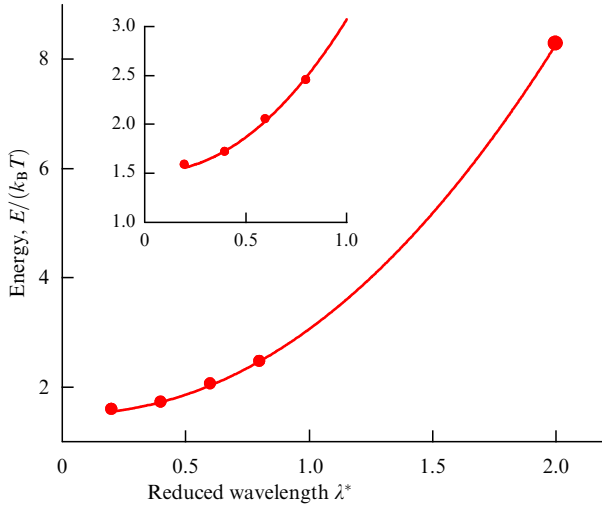


Figure 3. Dependence of the dimensionless energy $E/(k_B T)$ of the fluid of quantum hard spheres on the reduced de Broglie wavelength $\lambda^* = h/(2\pi m k_B T \sigma^2)^{1/2}$. Solid circles stand for the results of calculations [9]. The curve corresponds to the approximation of the calculation data.

verifies the calculated results. Note that the total energy of the quantum hard spheres includes only the kinetic energy of the translational motion of particles and the zero-point energy connected with the uncertainty principle. The approximation formula that describes the numerical data obtained in [9] has the following form:

$$\frac{E}{k_B T} = 1.5 + 1.5645(\lambda^*)^{2.1169}. \tag{10}$$

Substituting numerical data into the expression for λ^* ($\sigma = 3.5 \text{ \AA}$, $m = 28.0134 \text{ a.u.}$ [9]), we obtain the following expressions for the energy and heat capacity:

$$E = 1.5T + 1.395T^{-0.06}, \tag{11}$$

$$C_v = 1.5 - 0.084T^{-1.006}. \tag{12}$$

From expressions (11) and (12), there follow quite surprising results. The zero-point energy diminishes so slowly with the temperature that, in contrast to the energy in the harmonic case, it proves to be almost additive (Figs 4 and 5). However, as could be expected, the quantum contribution to the energy disappears together with the zeroing of the thermal de Broglie wavelength (Fig. 6).

The behavior of the quantum contribution to the energy of the system of hard spheres (see Figs 4, 5) confirms the conclusion made in [10] devoted to the study of the Boltzmann gas of hard spheres, in which it is noted that, in spite of naive expectations, the quantum effects prove to be very important, even when the thermal de Broglie wavelength is only a small fraction of the diameter of the hard sphere. In this connection, of interest are the results of the calculations performed in [11], which revealed the extremely slow damping of the excess kinetic (quantum) energy in the case of ‘steep’ potentials of interaction.

In connection with the almost constant value of the quantum contribution, the heat capacity of the system differs only a little from the classical value $(3/2)k_B$ everywhere except for the region of lowest temperatures, where the

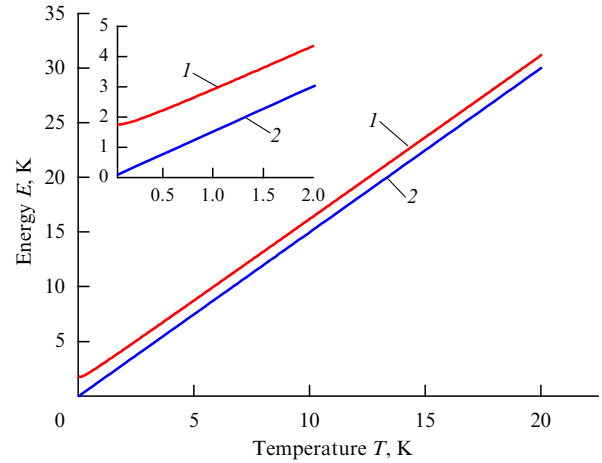


Figure 4. Dependence of the energy of the quantum (1) and classical (2) fluid system of hard spheres on the temperature.

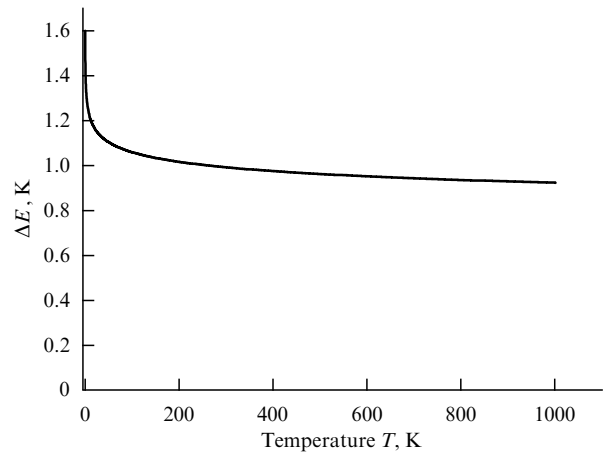


Figure 5. Dependence of $\Delta E = E_q - E_{cl}$ on the temperature. E_q is the energy of the quantum system of hard spheres; E_{cl} is the energy of the classical system of hard spheres.

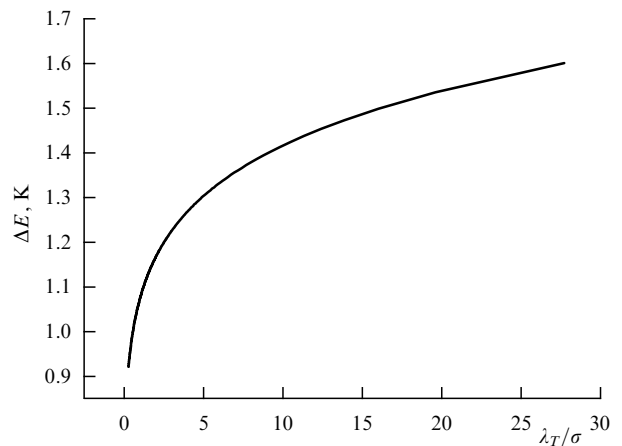


Figure 6. Dependence of $\Delta E = E_q - E_{cl}$ on the reduced thermal de Broglie wavelength λ_T/σ (σ is the diameter of the hard sphere).

dependence of the heat capacity of the system on the temperature has a ‘Debye’ form (Fig. 7), albeit with a very low Debye temperature, on the order of several kelvins. It is of interest to compare the obtained results with the behavior of

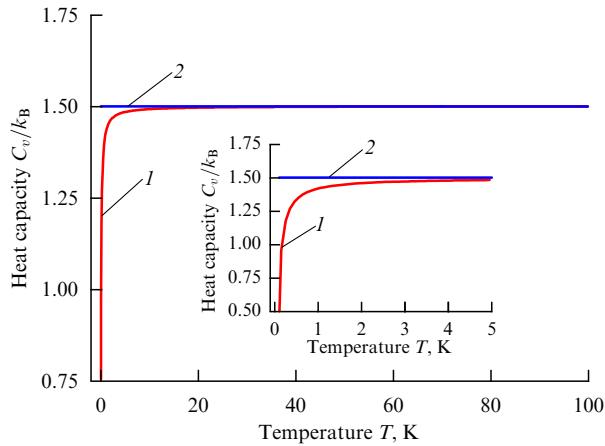


Figure 7. Heat capacity of quantum (1) and classical (2) fluid systems of hard spheres.

substances and models with a realistic interaction, where the heat capacity reaches $(3/2)k_B$ only in the asymptotic high-temperature limit [12, 13]. Note also that in the case of realistic quantum systems the presence of a high-temperature quantum contribution can be masked by the complex behavior of other components of the total energy, which is not observed in a system of hard spheres.

4. Crystallization of a ‘Boltzmann’ system of quantum hard spheres [14]

In 1957, in the same issue of *J. Chem. Phys.* [15, 16], the results of two computer experiments were published that confirmed the ideas on the existence of a phase transition in the classical system of hard spheres. Subsequently, with the aid of the quantum Monte Carlo method, the phase transition was also discovered in the quantum system of hard spheres [3]. As it turned out, the system of hard spheres can crystallize and melt. The observations of the coordinates of particles left no doubt that the discovered phase transition is a process of melting–crystallization. According to the Landau analysis [17], this transition must be a first-order phase transition, although in the world literature it was sometimes assumed that, in view of the absence of interaction energy, this transition is a second-order phase transition [18]. Note that the system of solid particles is unstable at $P = 0$, since in the absence of an attracting interaction it is retained from flying off at $T > 0$ only due to an external pressure. The free energy of a classical system of solid particles does not contain a potential-energy contribution. The phase transformations in these systems occur as a result of the competition of entropy contributions, since the energy is independent of the aggregative state of the substance.

The equation of the line of a phase transition has the following form [19]:

$$P = \frac{c}{\sigma^3}, \quad (13)$$

where σ is the solid-sphere diameter. The numerical coefficient c was obtained in computer experiments [20]; this makes it possible to represent relationship (13) as follows:

$$P = \frac{11.7k_B T}{\sigma^3}. \quad (14)$$

The form of Eqn (14) means that in the system of solid particles the curves of phase equilibrium are straight lines, which come from the origin of coordinates $T = 0, P = 0$. In the phase transitions in systems of solid particles, the volumes of the coexisting phases V_s and V_L and the jumps of the volume ΔV and of the entropy ΔS are constants. In the quantum case, at $T = 0$ the free energy is $F = E_z$, where E_z is the zero-point energy. Correspondingly, in this case the phase transition (melting–crystallization) occurs as a result of the competition of zero-point energies.

Thus, the process of crystallization–melting in the classical case is purely an entropy effect ($\Delta E = 0, \Delta S \neq 0$), while in the limiting quantum case this transition is purely energy related ($\Delta S = 0, \Delta E \neq 0$). Note that the effective diameter of a quantum hard sphere in the quantum case is determined by the scattering cross section πS^2 , and in this case the effective diameter exceeds its classical value because of diffraction effects [3]. It is interesting that the densities of the coexisting phases at the melting point are in fact equal in the classical and quantum cases at $T = 0$, if we do manipulations by the effective diameter of the hard spheres [3]. The model of hard spheres was used in [1, 4, 21] in analyzing the melting of helium. In the case of small quantum effects, it is logical to turn to the perturbation theory. The standard approach, based on the Wigner–Kirkwood expansion [22] in powers of \hbar^2 , is inapplicable here, since it includes the derivatives of the potential with respect to the coordinates of particles. Instead of this, Yankovich [23] and subsequently Gibson [24] proposed an expansion in powers of the thermal de Broglie wavelength.

It was shown within the framework of the last approach that in the system of hard spheres the quantum effects in the first approximation lead to an increase in the effective diameter of particles by a value on the order of λ_T , which is natural, since the quantum particles try to be farther from each other in accordance with the uncertainty principle. Thus, according to [23], in the first approximation, to take into account quantum effects, the diameter of the hard sphere σ should be replaced by $\sigma + \lambda/2\sqrt{2}$. By substituting this quantity into (8), we obtain

$$P = \frac{11.7k_B T}{(\sigma + \lambda/2\sqrt{2})^3} \quad (15)$$

or

$$P = \frac{11.7k_B T}{\sigma^3(1 + 3\lambda/\sigma 2\sqrt{2})}. \quad (16)$$

Relationships (15) and (16) mean that the quantum effects in the first approximation do not displace the melting–crystallization line of the system of hard spheres from the origin of coordinates $T = 0, P = 0$. Thus, this correction does not take into account the effects connected with the tendency of the jump of the entropy of melting ΔS to zero at $T \rightarrow 0$ according to the Nernst theorem, whereas the jump of the volume always remains finite [1, 25]. In this case, the crystallization–melting phase transition at the zero temperature should occur at a finite pressure.

Let us look at what quantum calculations by the Monte Carlo method give in this respect [1, 25]. The appropriate data are given in Fig. 8. The calculations were carried out within the framework of the Boltzmann statistics with the use of the following numerical values: diameter of the particle

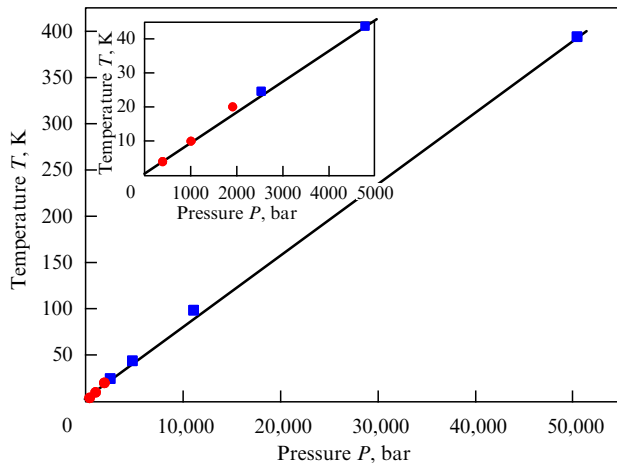


Figure 8. Dependence of the melting point of the Boltzmann system of quantum hard spheres on the pressure according to the data from [1] (solid circles) and [25] (squares). The inset shows the low-temperature part of the diagram. The results of [1, 25] are reduced by the author to the absolute values.

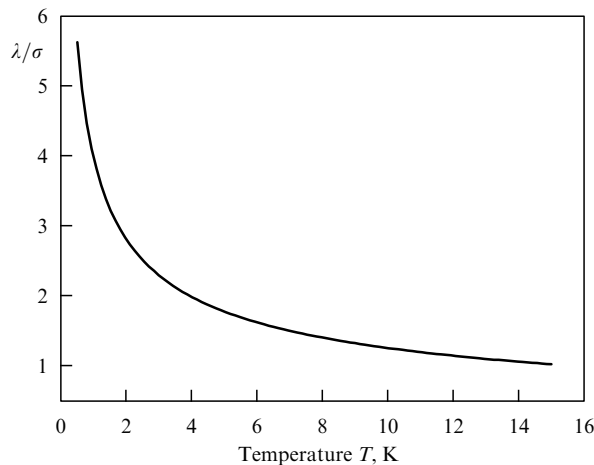


Figure 9. Temperature dependence of the thermal de Broglie wavelength reduced to the diameter of a hard sphere.

$\sigma = 2.2 \text{ \AA}$; its mass $m = 4$, which corresponds to the helium atom. As can be seen from Fig. 8, the two systems of data agree well between themselves and can be represented by a straight line that passes through the origin of coordinates. In this case, no effects connected with the degeneracy of the entropy jump are observed either. Apparently, the thermal length of the wave $\lambda_T \approx 2\sigma$ at $T = 4 \text{ K}$ (the lowest temperature of the Monte Carlo simulation) is still insufficiently large (Fig. 9) to make the different liquid configurations indistinguishable. A difficult question here arises immediately: how to make the quantum equilibrium line agree with the classical line passing through the origin of coordinates? These lines cannot diverge, since then the classical asymptotic at $T \rightarrow \infty$ will be unattainable. If these lines diverge near $T = 0$, then they must be merged at large temperatures within the classical limit, i.e., the quantum line would not be straight. No signs of this are evident in Fig. 8, even at temperatures of approximately 400 K.

In other words, it should be assumed that, if quantum statistics are disregarded, the quantum-wave effects make almost identical contributions to the thermodynamics of the

liquid and crystalline phases of the system of hard spheres, which, in fact, does determine the coincidence of the classical and quantum lines of the crystal–liquid equilibrium at $T > 4 \text{ K}$.

A completely different situation appears if we take into account attracting forces. In this case, the attracting interaction at the quantum expansion of the system determines the advantage of the disordered (liquid) phase at low pressures. Specifically, it is just this situation that occurs in the melting of ^3He and ^4He [21]. In this connection, recall that S Domb and J Dagdale [26] wrote that, upon heating helium at a constant molar volume equal to 14 cm^3 from absolute zero, it was found that the value of the zero-point energy equal to 127 cal was insufficient to melt solid helium, while the additional 3.18 cal of thermal energy caused melting.

On the other hand, in the so-called cold melting of a Coulomb substance that was forecast in [27], even if takes place, its mechanism is connected with the relatively low value of the kinetic (zero-point) energy of the liquid because of the freedom acquired by point-like particles upon transitioning into the liquid state upon compression of the substance, as was shown for the first time by Wigner [29] and was demonstrated in [28] for the case of a quantum system of point charges against a uniform background (quantum single-component plasma).

Thus, the manifestation of quantum effects in the above-described cases has a fundamentally different nature. In the condensed ‘Boltzmann’ system of hard spheres, the quantum phenomena (directly determined by the uncertainty principle) lead to a total increase in the energy of the system in its volume because of the strong localization of particles. In the case of simple Coulomb systems, the quantum effects act selectively, creating under specific conditions an advantage to the liquid phase of the substance, to whose particles the entire volume of the system becomes accessible.

5. Conclusions

The quantum contribution to the energy of the ‘Boltzmann’ gas of hard spheres proves to be practically additive up to the highest temperatures at which the thermal de Broglie wavelength is only a small fraction of the diameter of the hard sphere. Correspondingly, the heat capacity of the system hardly differs from the classical value $(3/2)k_B$ everywhere except for the region of lowest temperatures, where the temperature dependence of the heat capacity of the system takes a ‘Debye’ form, but with a very low Debye temperature, on the order of several kelvins.

The quantum line of the crystal–liquid equilibrium of a ‘Boltzmann’ system of hard spheres almost completely coincides with the classical line, with the exception of the region of very low temperatures. This means that the quantum-wave effects make identical contributions to the thermodynamics of the liquid and crystalline phases of the system of hard spheres. Apparently, this conclusion can also be valid in the case of a more realistic system of particles with short-range interactions.

Finally, note that in the case of realistic quantum systems the presence of a high-temperature quantum contribution can be masked by the complex behavior of other components of the total energy, whereas in the system of hard spheres the quantum contribution appears in a ‘naked’ form.

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