

On the thermodynamics of simple systems

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Abstract. Thermodynamic properties of classical and quantum simple Boltzmann systems are discussed. It is pointed out that the standard formulas of a classical ideal gas actually describe a quantum Boltzmann gas. The heat capacity of classical and quantum Boltzmann systems is analyzed. The melting of classical systems and Boltzmann quantum hard spheres is considered.

Keywords: ideal gases, Sackur–Tetrode equation, heat capacity of hard and soft spheres, Boltzmann system of quantum hard spheres

1. Introduction

Gases, liquids, and solids surround us in everyday life. Obviously, the desire to understand and describe the properties of these bodies has been a natural challenge for humankind since ancient times. At present, we already know a great deal, and the base features of the material world are presented in numerous textbooks. Nevertheless, many important details of the behavior of even the simplest systems, i.e., gases, liquids, and solids possessing no magnetism, superfluidity, superconductivity, ferroelectricity, or other specific properties, require a special analysis. This is the very subject of the present paper.

2. Ideal gas

2.1 Classical ideal gas

The classical ideal gas is described by the free energy (1), this expression being considered purely classical. In fact, the

effects of phase space quantization and indistinguishability of particles are taken into account here, but the Maxwell–Boltzmann statistics are used to count the number of states. Hence, expression (1) actually describes an ideal quantum Boltzmann gas:

$$F = -kT \ln Q_N + NkT \left[\ln N - 1 - \frac{3}{2} \ln \left(\frac{mkT}{2\pi\hbar^2} \right) \right]. \quad (1)$$

Note that the logarithm argument expression $mkT/2\pi\hbar^2$ in Eqn (1) is nothing but the reciprocal square of the thermal de Broglie wavelength. Here, Q_N is the configuration integral, expressed as

$$Q_N = \int_V \cdots \int_V \exp \left[-\frac{U_N(q_1 \cdots q_N)}{kT} \right] dq_1 \cdots dq_N. \quad (2)$$

In the case of an ideal gas, $U_N=0$ and, therefore, $Q_N=V^N$.

From Eqn (1), we obtain for entropy $S = -(\partial F/\partial T)_V$ the following expression:

$$S = \frac{5}{2} Nk + Nk \ln V + \frac{3}{2} Nk \ln \left(\frac{mkT}{2\pi\hbar^2} \right). \quad (3)$$

From Eqn (3), it follows that the heat capacity of a classical ideal gas is

$$C_V = \frac{3}{2} Nk = 1.5R. \quad (4)$$

Equation (3), in fact, is the Sackur–Tetrode equation, formulated back in 1912, before the discovery of quantum mechanics (see Section 1.2). It is useful to rewrite Eqn (3) in the form

$$\frac{S}{kN} = \ln \left(\frac{V}{NA^3} \right) + \frac{5}{2}, \quad (5)$$

where A is the thermal de Broglie wavelength. Equation (5) is valid for $V/NA^3 > 1$; otherwise, the entropy becomes negative.

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Relation (5) means that, when the thermal wavelength becomes comparable to the mean interparticle distance, the Boltzmann statistics fail. Indeed, when the thermal wavelength exceeds the mean interparticle distance, the particles become indistinguishable. The corresponding combinatory distribution function, taking this circumstance into account [1, 2], has the form

$$W = \prod_i \frac{(m_i + n_i)!}{n_i! m_i!} \quad (6)$$

and finally leads to the Bose–Einstein distribution. Here, n_i are particles with energy ε_i , occupying the energy levels m_i .

However, when $m_i \gg n_i$, the distribution function can be written in the simplified form:

$$W = \prod_i \frac{(m_i)^{n_i}}{n_i!}. \quad (7)$$

This expression leads to the classical Maxwell–Boltzmann distribution. It is remarkable that the Boltzmann distribution corresponds to small occupation numbers, when it is in principle possible to identify particles, which makes them distinguishable. For completeness, we present the distribution function for a system in which every energy level can be occupied by only one particle, which corresponds to the Fermi distribution

$$W = \prod_i \frac{m_i!}{n_i! (m_i - n_i)!}. \quad (8)$$

In this case, the condition $m_i \gg n_i$ also leads to the classical distribution. To avoid misunderstanding, recall that Eqns (6)–(8) determine the distribution of n indistinguishable particles over m positions under certain limitations only. To get to the actual statistical expressions, it is necessary to perform a number of manipulations [1]. For us, it is important to emphasize that the classical Maxwell–Boltzmann statistics arise when particles are distinguishable.

2.2 On the history of the Sackur and Tetrode equation

In 1912, Otto Sackur and Hugo Tetrode independently derived an equation for the absolute entropy of monoatomic ideal gas and published their discovery in *Annalen der Physik*, as pointed out in Refs [3, 4]. The main achievement of this discovery was discretization of the phase space into cells with the size $dp dq = h$, where p and q are conjugate variables, and h is the Planck constant. It is surprising that this was done long before the creation of quantum mechanics and became one more confirmation of the validity of Planck’s idea.

H Tetrode came from a rather rich Dutch family; he was only 17 when he wrote his paper for *Annalen*. Formally, he had no higher education and spent the year of 1912 at Leipzig University, where he apparently attended some lectures but did not pass ordinary exams. Tetrode corresponded with Dutch physicists of his time but had no lasting scientific contacts. Nor did he seek the patronage of those who could promote his scientific career. Once, Albert Einstein and Paul Ehrenfest decided to visit him at home, but the maid said he could not receive them. Hugo Tetrode died of tuberculosis in 1931.

O Sackur’s career as a scientist developed in the usual way. After receiving his doctorate from the University of Breslau (now the Polish city of Wrocław), he worked there with Rudolf Ladenburg, then in London with William Ramsey,

and finally in Germany with Walter Nernst, whose thermal theorem—with some help from Sackur’s and Tetrode’s work—finally led to the Third Law of Thermodynamics. O Sackur wrote well-accepted books on thermodynamics and in 1914 joined the prestigious Fritz Haber Institute in Berlin. Haber’s reputation at the time was very good due to his development of a method for synthesizing ammonia (he was later awarded the Nobel Prize for this work). His reputation began to suffer when he headed a project on using poisonous gases as a weapon in the First World War. Haber’s institute worked on this project, which involved Otto Sackur, James Frank, and others. At the end of 1914, O Sackur died in a laboratory explosion. Thus ended his career. But that was not all. Haber’s wife Clara Immerwahr was a close friend of Sackur’s. She was against her husband’s work with poisonous gases on moral grounds. When she learned of Sackur’s death, she considered it the result of working on an immoral project. Inconsolable, she committed suicide with her husband’s service pistol, thus completing a tragedy of Shakespearian proportions. Otto Sackur and Hugo Tetrode died too young, victims of disasters of their time, war and tuberculosis. Despite their different origins and careers, they, like Boltzmann, left their equation as an epitaph that unites them.

3. Simple systems with interaction

3.1 Hard and soft spheres

Let us now turn to the simplest system with interaction, which is the system of classical hard spheres interacting through a potential of the form (Fig. 1).

$$\Phi(r) = 0, \quad r > \sigma, \quad \Phi(r) = \infty, \quad r < \sigma. \quad (9)$$

Since the potential energy of the interaction in a system of hard spheres is always zero, it follows from Eqn (1) that the heat capacity of a system of hard spheres is equal to that of an ideal gas (4). At this point, the resemblance of these two systems is finished. In a system of hard spheres, along with the characteristic length L , the mean distance between particles,

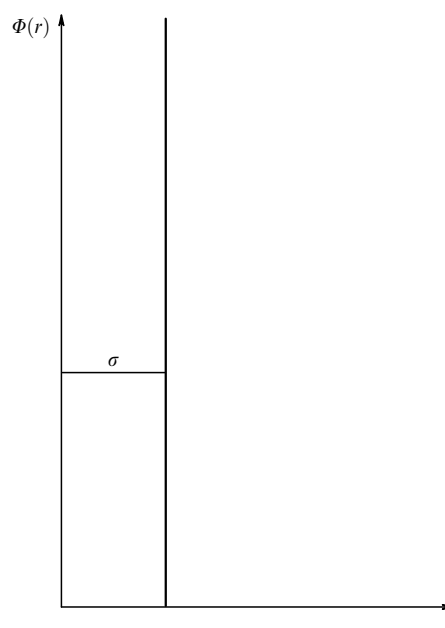


Figure 1. Potential of interaction of hard spheres.

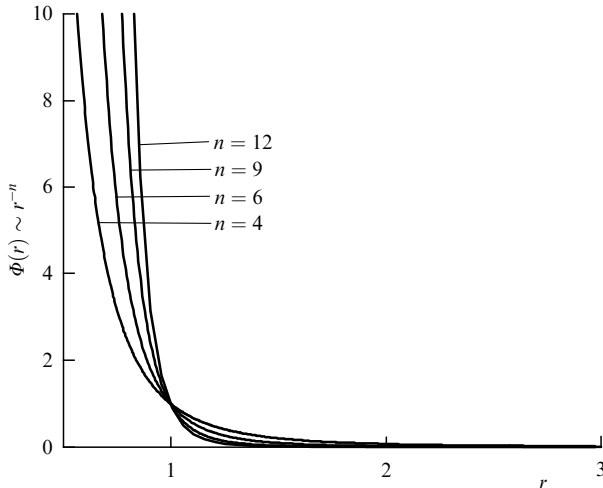


Figure 2. Potential of interaction of soft spheres $\Phi(r) \sim r^{-n}$.

one more characteristic length σ obviously appears, corresponding to the diameter of a hard sphere. It is clear that at $L/\sigma \approx 1$ each particle becomes a ‘prisoner’ of its neighbors, and the system crystallizes. However, the nature of the corresponding transition was not clear. Moreover, it was sometimes assumed that this transition would be a second-order phase transition [5]. In this regard, we emphasize L Landau’s conclusion about the fundamental difference between the symmetries of a liquid and a crystal, due to which crystallization cannot occur continuously and is always a first-order phase transition [6]. However, material evidence of crystallization–melting in a system of hard spheres as a first-order phase transition was obtained as a result of computer experiments [7–9]. Thermodynamic characteristics of melting–crystallization of hard spheres will be presented below together with the results for a system of particles interacting according to a power law (Fig. 2). As follows from O Klein’s theorem (cited from [10]), formulated back in 1919, the nonideal components of the thermodynamic quantities for a system of particles whose potential energy is an n th order homogeneous function of the particle coordinates do not depend separately on volume and temperature, and are functions of the combined variable $\rho(\varepsilon/kT)^{3/n}$, where ρ is the density of the system, and ε is the energy scale of the interparticle interaction. Melting as a phase transition of the first order is characterized by two values of this variable, from which follow the relationships for the densities of the liquid and solid phases (10), the melting curve equation (Fig. 3), and the jump in volume and entropy (11) [11, 12]:

$$\rho_l = c_l \left(\frac{kT}{\varepsilon} \right)^{3/n}, \quad \rho_s = c_s \left(\frac{kT}{\varepsilon} \right)^{3/n}, \quad (10)$$

where c_l and c_s are constants

$$P_m \sim \left(\frac{kT}{\varepsilon} \right)^{1+3/n}, \quad \frac{\Delta V}{V_s} = \text{const}, \quad \frac{\Delta S}{R} = \text{const}. \quad (11)$$

Note that, at $n \rightarrow \infty$, the relations that characterize the melting of hard spheres follow from Eqns (10) and (11):

$$P_m = cT, \quad V_l, V_s = \text{const}, \quad \frac{\Delta V}{V_s} = \text{const}, \quad \frac{\Delta S}{R} = \text{const}. \quad (12)$$

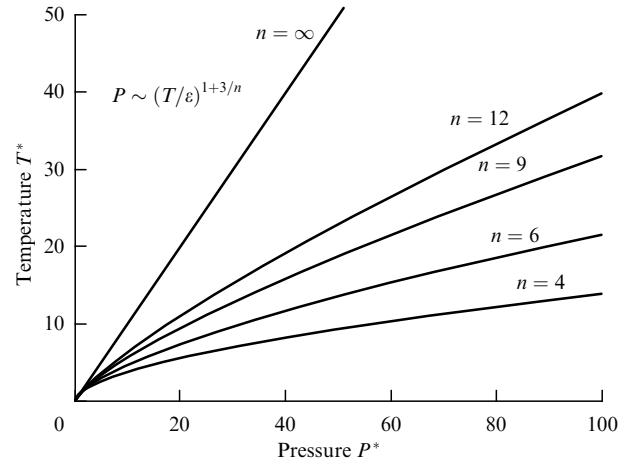


Figure 3. Melting temperature for systems of particles with purely repulsive interaction of the form $\Phi(r) \sim r^{-n}$ as a function of pressure. Corresponding numerical coefficients are determined from computer experiments (see Ref. [11]).

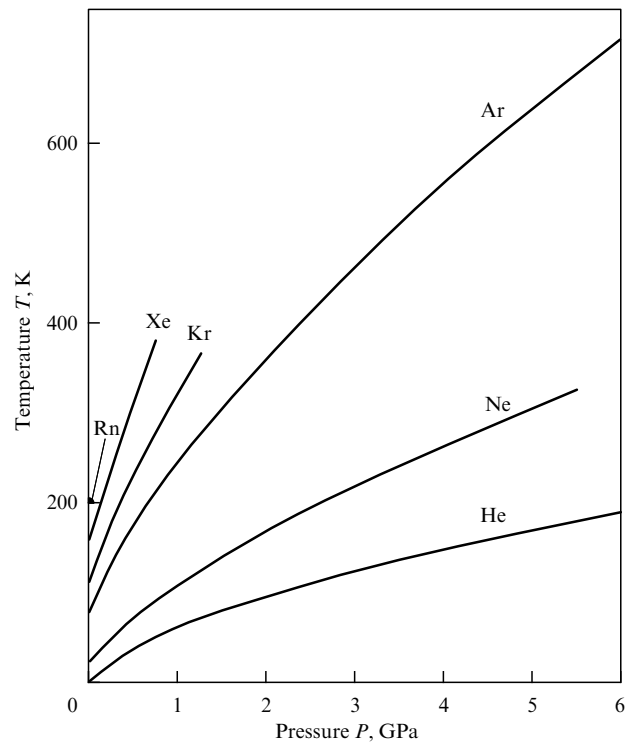


Figure 4. Melting temperature of condensed noble gases as a function of pressure.

Here, it should be recalled that the interaction potential in a realistic system always contains an attractive part, due to which the melting temperature of classical substances at atmospheric pressure is always greater than zero (Fig. 4).

3.2 Heat capacity

Above, we have found that the heat capacity of a system of hard spheres is a constant equal to $C_V = 1.5R$. However, in a simple case of soft spheres, it is no longer so. Indeed, addressing the Klein theorem again, for a system of particles interacting by means of a power-law potential, we can express the system heat capacity as $C_V = 1.5R + f(\rho(\varepsilon/kT)^{3/n})$. It is interesting to compare this result with experimental data; for example, let us see

whether this approach works in the case of argon. For this purpose, let us use the results of Ref. [13].

Here, the radial distribution function $g(r)$ at moderate density is approximated by the step function:

$$\begin{aligned} g(r) &= 0, & r < \sigma, \\ g(r) &= 1, & r > \sigma. \end{aligned} \quad (13)$$

This approximation should work well enough at high temperatures.

For further analysis, the potential $\Phi(r)$ was used,

$$\Phi(r) = 4\varepsilon \left[\left(\frac{r_0}{r} \right)^{12} \right]. \quad (14)$$

It is assumed that the evolution of function $g(r)$ with temperature is determined by the temperature dependence of the collision diameter $\sigma(T)$. Let us define the temperature dependence of σ using the relation

$$4\varepsilon \left(\frac{r_0}{r} \right)^{12} = kT, \quad (15)$$

where $r = \sigma$.

Finally, for the heat capacity C_V , we have

$$\frac{C_V}{R} = \frac{3}{2} + \frac{\pi r_0^3}{6V} N \left[\left(\frac{4\varepsilon}{kT} \right)^{1/4} \right]. \quad (16)$$

As is seen from Eqn (16), the heat capacity C_V at a constant density of the system of particles interacting via the potential of the form $\Phi(r) \sim 1/r^{12}$ decreases at high temperatures according to the law $\sim T^{-1/4}$, approaching the value of the heat capacity of hard spheres $C_V = (3/2)R$. Using the potential parameters known for Ar, the values of the Ar molar volume at the triple point ($\varepsilon/k = 119.3$, $r_0 = 3.405 \text{ \AA}$, $V_{T.P.} = 28.33 \text{ cm}^3 \text{ mol}^{-1}$) [14], and Eqn (16), appropriate calculations have been performed, illustrated in Fig. 5. It is remarkable that the reference data for C_V of Ar [15] are very close to the calculated curve (see Fig. 5), which means that using only the repulsive part of the interaction potential is quite satisfactory to reproduce the experimental result for argon. This is not surprising, since a system of soft spheres against a homogeneous attraction background works well for noble gases. Note that the homogeneous attractive background does not affect the heat capacity.

As is seen from Fig. 5, the asymptotic value $(3/2)R$ is practically unachievable. A significant part of the heat capacity curve is near the value $1.7R$, thus passing the ‘magic value’ $2R$ at approximately 300 K. We recall that earlier in Ref. [16] it was proposed that the decrease in heat capacity of a liquid with an increase in temperature is related to the disappearance of transverse elastic modes, due to which the heat capacity of the liquid tends to the value $2R$. In our case, at 10^5 K (the critical point for Ar is $\approx 150 \text{ K}$), the heat capacity is still close to $1.6R$. However, this value is not a result of losing vibrational modes but arises in our model due to a temperature change in the collision diameter σ .

3.3 On the heat capacity of a quantum system of hard spheres

As already mentioned, a system of classical hard spheres is the simplest nontrivial system with interaction of the form (9).

In contrast to the classical system of hard spheres, in the quantum case, due to the uncertainty principle, interparticle

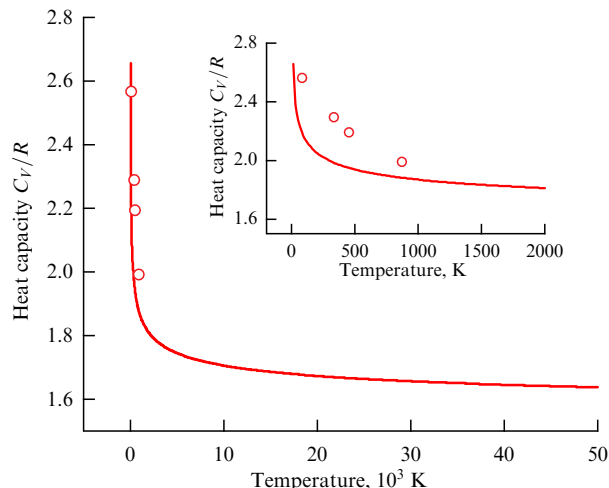


Figure 5. Heat capacity C_V of virtual Ar at constant volume, equal to its value at the triple point. Circles represent C_V of Ar at 83.8, 330, 450, and 1990 K [15].

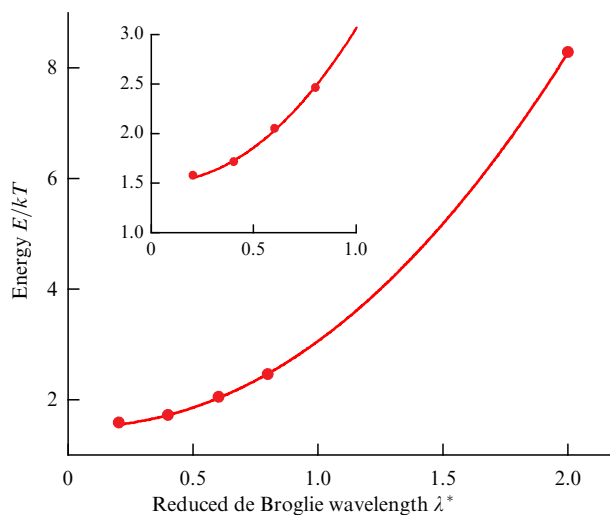


Figure 6. Dependence of dimensionless energy E/kT of a liquid of quantum hard spheres on reduced de Broglie wavelength $\lambda^* = h/(2\pi mkT\sigma^2)^{1/2}$; circles are the result of calculations [28], line is the approximation.

repulsion occurs, giving rise to a ‘returning’ force with respect to long-wave acoustic deformations [17].

The quantum model of hard spheres was used in the analysis of behavior of quantum systems with short-range interaction, in particular, helium [18, 19]. This section is based on an analysis [28] of the results of calculations carried out using the quantum Monte Carlo method [20].

The author of [20] presented the values of dimensionless energy E/kT of the liquid state of the system depending on the specific density $\rho^* = \rho\sigma^3$ (diameter of σ -sphere) along the directions with constant λ^* ($\lambda^* = h/(2\pi mkT\sigma^2)^{1/2}$ being the ratio of the thermal de Broglie wavelength to the diameter of a hard sphere). For the present analysis, the results of calculating the energy were chosen for the density $\rho^* = 0.3$, covering the maximum range of reduced de Broglie wavelengths λ^* . The corresponding data are shown in Fig. 6. As is seen from Fig. 6, the results of calculations explicitly extrapolate to the classical values $E/kT = 1.5$ at $\lambda^* \rightarrow 0$, which confirms their validity. Note that the total energy of quantum hard spheres includes

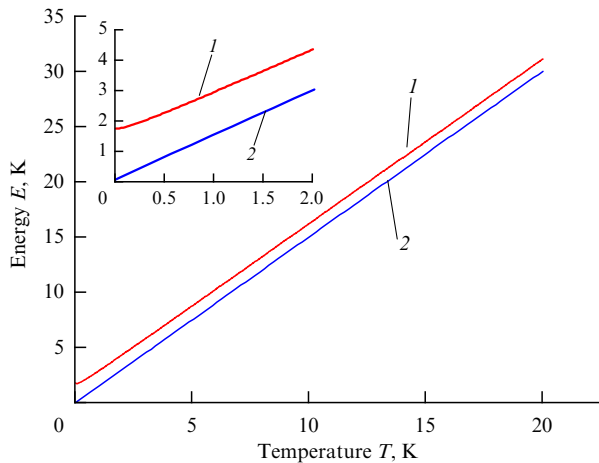


Figure 7. Temperature dependence of energy of quantum (1) and classical (2) systems of hard spheres.

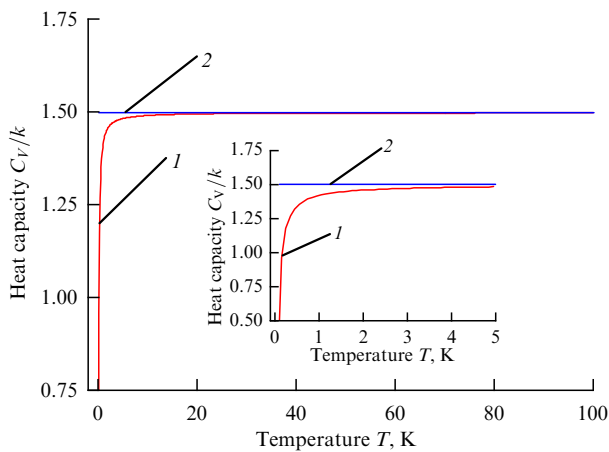


Figure 8. Heat capacity of quantum (1) and classical (2) systems of hard spheres.

only the kinetic energy of translational motion of particles and the zero-point energy related to the uncertainty principle.

The data obtained lead to rather unexpected conclusions. The zero-point energy decreases with temperature so slowly that it turns out to be an almost constant addition to the classical value (Fig. 7). The behavior of the quantum contribution to the energy of the system of hard spheres (see Fig. 7) confirms the conclusion of Ref. [21] that, despite naive expectations, quantum effects turn out to be very important, even when the thermal de Broglie wavelength amounts to only a small part of the hard sphere diameter. Due to these specifics of the quantum contribution, the heat capacity of the system slightly differs from the classical value $(3/2)k$ everywhere except a narrow region of low temperatures, where the system heat capacity decreases to zero (Fig. 8).

3.4 On the melting of a Boltzmann system of quantum hard spheres

At high enough temperatures or in systems with strong repulsive interaction, when the exchange of particles is practically impossible, the effects of Bose and Fermi statistics can be ignored. However, the system can still be quantum. The fact is that the effects of quantum statistics exponentially decrease with the temperature growth, whereas the ‘diffraction’ effects, associated with the wave nature of particles,

decrease only as a degree of reciprocal temperature at $T \rightarrow \infty$. Thus, in a quantum system of hard spheres, there is a significant range of temperatures where the effects of quantum statistics play only an insignificant role [17]. Below, we will use as our basis recent paper [24]. First, a few words about the crystallization of classical systems of hard spheres.

As was established in pioneering numerical calculations [7, 8], a classical system of hard spheres can crystallize and melt via a first-order phase transition. It is not difficult to show that the classical melting curve for hard spheres has the form $P = kT/C$, where P and T are the pressure and temperature, and C is a constant with the dimension of volume [12]. Obviously, the only constant with the dimension of volume in a system of hard spheres is the volume of hard spheres. Then, for the melting of a classical system of hard spheres, it is possible to write an expression with a dimensionless constant, adopted from detailed study [22]:

$$P = \frac{11.7 kT}{\sigma^3}, \quad (17)$$

where σ is the diameter of a hard sphere. From here, obviously, the melting line (17) is a straight line, going from the origin of coordinates $P = 0, T = 0$.

Let us now see how quantum effects affect the melting of hard spheres. It is to be noted that in a system of dense hard spheres particles are imprisoned in a kind of cage arising due to their impermeability. Thus, the particles become distinguishable and, therefore, obey the Boltzmann statistics. The only quantum property of the system of hard spheres is the wave nature of particles. It has been shown that in a system of hard spheres it is possible to allow for quantum effects in the first approximation using the effective diameter of particles, increased approximately by the thermal de Broglie wavelength $\lambda_T = h/(2\pi mT)^{1/2}$ [17, 23, 25]. This could be expected, since, in correspondence with the uncertainty principle, quantum particles tend to repulse each other. The effective diameter of a quantum hard sphere becomes equal to $\sigma + \lambda_T/2\sqrt{2}$. Then, Eqn (17) can be rewritten in the form

$$P = \frac{11.7 kT}{(\sigma + \lambda_T/2\sqrt{2})^3} \quad (18)$$

or

$$P = \frac{11.7 kT}{\sigma^3(1 + 3\lambda/\sigma 2\sqrt{2})}. \quad (19)$$

As is seen from Eqn (19), quantum effects do not shift the quantum melting line from the origin of coordinates $P = 0, T = 0$, but its slope must differ from the classical one for one and the same hard sphere diameter at any final temperature. From Eqns (17) and (19), it follows that, for the melting lines, the following inequality should be valid:

$$\left(\frac{dP}{dT}\right)_{\text{classical}} > \left(\frac{dP}{dT}\right)_{\text{quantum}} \quad (20)$$

or

$$\left(\frac{dT}{dP}\right)_{\text{classical}} < \left(\frac{dT}{dP}\right)_{\text{quantum}}. \quad (21)$$

On the other hand, the quantum correction to the melting line of hard spheres should decrease to zero under an increase in temperature as $T^{-1/2}$ (see Eqn (19)), which means that the quantum melting line should be a curve rather than a straight line, as in the case of classical melting. Moreover, the classical

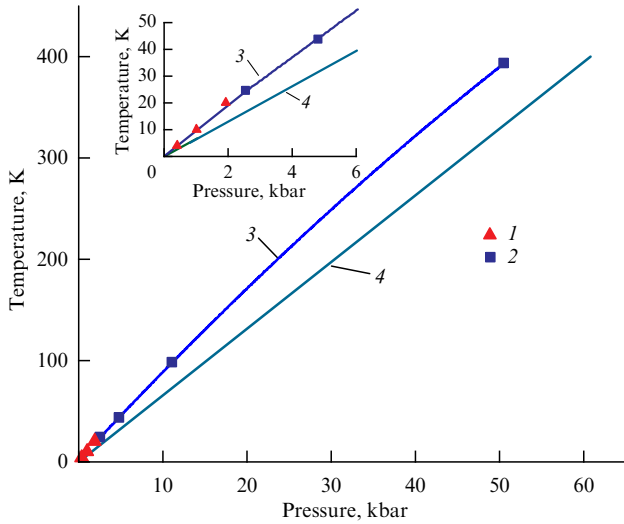


Figure 9. Melting temperatures of quantum and classical systems of hard spheres. 1 — Ref. [17], 2 — Ref. [26], 3 — power-law approximation of data from Ref. [17], 4 — classical melting line. Absolute values of temperature and pressure are obtained from reduced data in Refs [17, 26].

limit in a quantum system of hard spheres can be reached only at $T \rightarrow \infty$.

Now, let us proceed to the quantum Monte Carlo data describing the melting of a Boltzmann system of hard spheres [17, 26]. Calculations by the quantum Monte Carlo method [17, 26] were carried out within the framework of the Boltzmann statistics for the particle diameter $\sigma = 2.2 \text{ \AA}$ and mass $m = 4$. The corresponding data, together with the classical melting line of hard spheres, are shown in Fig. 9. The calculations of a classical melting line were consistently carried out for the case $\sigma = 2.2 \text{ \AA}$. Note that the slopes of melting lines in Fig. 9 agree with the prediction (20), (21).

The Monte Carlo data for the melting line of a system of quantum hard spheres and the classical melting line (see Fig. 9) are described well by the expressions

$$T_{\text{quantum}} = 1.812 \times 10^{-2} P^{0.92202}, \quad (22)$$

$$T_{\text{classical}} = 6.57 \times 10^{-3} P. \quad (23)$$

As follows from (22) and (23), both melting lines in Fig. 9 can intersect only at the origin of coordinates $T = 0, P = 0$, which means that the classical limit is unattainable at any finite temperature. To conclude, it is worth noting that by inverting expression (22) one can obtain a melting line with a similar shape to the melting line of soft spheres [12, 22]:

$$P \sim T^{1+3/n}, \quad (24)$$

where $n \approx 35$. Therefore, the effective quantum repulsion that turned out to be very steep can be described by the relation $\Phi(r) \sim 1/r^{35}$ (compare it with the Van der Waals repulsion, where $n \approx 12$). Thus, the quantum melting line always differs from the classical one, except for the cases $T = 0, P = 0$, when both lines intersect. Quantum corrections to the melting line of a system of hard spheres fade as $T^{-1/2}$ with an increase in temperature. The quantum melting line is curved, in contrast to the classical case. The classical limit in a quantum system of hard spheres cannot be reached at any finite temperature.¹

¹ Thus, the earlier analysis of Refs [27, 28] turned out to be not quite correct as to melting in a system of quantum hard spheres.

4. Appendix

Let us derive the equation of state for an ideal classical and ideal quantum gas of Boltzmann ‘spinless’ particles from the dimension relations.

4.1 Equation of state of a classical ideal gas

From Eqn (1), we obtain the equation of state in a standard form:

$$\left(\frac{\partial F}{\partial V} \right)_T = -P = -kT \frac{\partial \ln V^N}{\partial V} = -\frac{NkT}{V}, \quad (25)$$

$$PV = NkT = RT. \quad (26)$$

However, a simpler approach is possible. Considering that in an ideal gas system there is only one characteristic length $L = (V/N)^{1/3}$, the average distance between particles, and only one quantity with the dimension of energy, the temperature T , we use the dimensionality consideration (pressure = energy/volume) to obtain the equation of state in the form $P = kT/L^3$, or $PV = RT$.

Let us now derive the equation of state for a classical ideal gas using the regular analysis of dimensionalities [29, 30]. We assume that the pressure in the system is determined by the function $P = f(L, M, \Theta, k)$, where L is the characteristic length, M is the mass, Θ is the temperature, and k is the Boltzmann constant. Let us write down the dimensionality equation:

$$\begin{aligned} L^{-1} M T^{-2} &= L^a M^b \Theta^c k^d = L^a M^b \Theta^c (L^2 M T^{-2} \Theta^{-1})^d \\ &= L^{a+2d} M^{b+d} \Theta^{c-d} T^{-2d}. \end{aligned} \quad (27)$$

Comparing the exponents on the left and right sides of equation (27), we obtain $a = -3, b = 0, c = 1, d = 1$. As a result, for the pressure, we have $P = k\Theta/L^3$ or, assuming that L^3 is the volume per particle and introducing the factor n , the Avogadro number, we finally obtain $P = R\Theta/V$.

4.2 Equation of state of a Boltzmann quantum gas

Let us repeat the exercise for the case of an ideal quantum gas of Boltzmann ‘spinless’ particles in the limit of low temperatures. We write the corresponding function in the form $P = f(h, L, M)$, where h is the Planck constant. The dimensionality equation in this case will be

$$\begin{aligned} L^{-1} M T^{-2} &= h^a L^b M^c = L^b M^c (L^2 M T^{-1})^a \\ &= L^{2a+b} M^{a+c} T^{-a}. \end{aligned} \quad (28)$$

By comparing the left- and right-hand sides of Eqn (28), we get $a = 2, b = -5, c = -1$, which makes it possible to express the pressure in the system as

$$P = \frac{h^2}{L^5 M} = \frac{h^2}{M V^{5/3}}. \quad (29)$$

It is remarkable that, in Eqn (29), a dependence of mass has appeared, which had to be expected in the quantum case. Note that, from the uncertainty principle $\Delta x \Delta p \geq \hbar/2$, it follows that

$$E \sim \frac{\hbar^2}{M V^{2/3}} \quad \text{and} \quad P \sim \frac{\hbar^2}{M V^{5/3}}.$$

5. Conclusion

To conclude, I would like to emphasize the following important results of the analysis carried out.

(1) The heat capacity of a classical real gas tends to the value of $(3/2)k$ at $T \rightarrow \infty$. A decrease in the heat capacity of a liquid with an increase in temperature is not due to the disappearance of transverse elastic modes, as was assumed in Ref. [16].

(2) The zero-point energy of a quantum system of hard spheres decreases with an increase in temperature so slowly that it turns out to be an almost constant addition to the classical value. Due to this feature of the quantum contribution, the heat capacity of a system of quantum hard spheres differs only a little from the classical value $(3/2)k$ everywhere, except in a narrow region of low temperatures, where the heat capacity of the system falls to zero (see Fig. 8).

(3) The melting line of a system of quantum hard spheres always differs from the classical one, except the case $T = 0$, $P = 0$, when both lines intersect. Quantum corrections to the melting line of a system of hard spheres vanish with an increase in temperature as $T^{-1/2}$. The quantum melting line is a curved line, in contrast to the classical case. The classical limit in a quantum system of hard spheres cannot be attained at any finite temperature.

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