

Quantum crystal equation of state

© S.Sh. Rekhviashvili, M.M. Bukurova, A.A. Sokurov

Institute of Applied Mathematics and Automatization, Kabardino-Balkar Scientific Center, Russian Academy of Sciences, Nalchik, Russia

E-mail: rsergo@mail.ru

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A new and simple equation of state of a monatomic quantum crystal is constructed using the continuum approximation for interacting atoms and the Mie–Grüneisen theory. The equation makes it possible to describe the phase diagram both in the region of compressive pressures and in the vicinity of the critical point. Expressions for critical volume, pressure and temperature are found analytically. Comparison of numerical calculations with experimental data for helium shows satisfactory agreement.

Keywords: quantum crystal, continuum approximation, Mie–Grüneisen model, Debye model, equation of state, critical parameters.

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It is known that a quantum liquid crystallizes under a certain pressure. A so-called quantum crystal forms as a result. The amplitude of oscillations of atoms in a crystal of this kind is comparable to the lattice period or is even greater. For example, liquid isotopes of helium and their solutions crystallize under a pressure of 2.5–10 MPa, and this process is accompanied by just a slight density variation ($\sim 5\%$) [1]. The produced crystals retain unique quantum properties.

Equations of state of solid helium were constructed and analyzed in [2–14], and its heat capacity was measured and calculated theoretically. The molar volume, the Debye temperature, and the Grüneisen parameter were determined as functions of temperature and pressure. Both low- and high-pressure conditions were considered. However, the critical parameters of helium, which define the temperature, volume, and pressure at the critical point (i.e., the state in which liquid and gas phases are indistinguishable), have not been determined based on the equations of state in the indicated studies. This is the reason why the conditions of stability of thermodynamic phases of helium have not been formulated. The present study is aimed at filling these gaps.

Let us consider a defect-free monatomic quantum crystal. Since the amplitude of atom oscillations in this crystal at low temperatures is comparable to the interatomic distance, the probability function of finding an atom within a specified small crystal volume broadens. Therefore, its density may be assumed, as a first approximation, to be independent of coordinates. In view of this, we use the continuum approximation for atoms. The potential energy of one mole of matter in this approximation is

$$U = \frac{N_A n_V}{2} \int_V \phi(|\mathbf{r}|) dV, \quad (1)$$

where $\phi(|\mathbf{r}|)$ is the atomic pairwise interaction potential, $|\mathbf{r}|$ is the interatomic distance, N_A is the Avogadro

number, and n_V is the volume concentration of atoms. The integral in formula (1) multiplied by the concentration of atoms yields the energy of interaction of one atom in a volume with its entire environment, which is an infinite continuum. The multiplier of 1/2 implies that any two interacting points (atoms) from this continuum should be factored into calculations only once. Let us assume that each crystal atom occupies a sphere with radius R that corresponds to the equilibrium state of matter. The concentration of atoms is then equal to $n_V = 3/(4\pi R^3)$. With this expression taken into account, formula (1) assumes the following form in spherical coordinates:

$$\begin{aligned} U &= \frac{3N_A}{8\pi R^3} \int_0^{2\pi} \int_0^\pi \int_R^{+\infty} \phi(r, \theta, \varphi) r^2 \sin \theta dr d\theta d\varphi \\ &= \frac{3N_A}{2R^3} \int_R^{+\infty} \phi(r) r^2 dr. \end{aligned} \quad (2)$$

We use the Lennard–Jones form of the pairwise potential:

$$\phi(r) = D \left[\left(\frac{r_0}{r} \right)^{12} - 2 \left(\frac{r_0}{r} \right)^6 \right], \quad (3)$$

where D is the potential well depth and r_0 is the equilibrium distance between two atoms. Having inserted (3) into (2) and integrated the result, we obtain

$$U = U_0 \left[\left(\frac{V_0}{V} \right)^4 - 2 \left(\frac{V_0}{V} \right)^2 \right], \quad (4)$$

where V is the volume of one mole of a phase, $V_0 = 4\pi R_0^3 N_A / 3$ is the equilibrium molar volume corresponding to the potential energy minimum in the lack of

thermal oscillations of atoms ($U(V_0) = -U_0 = -3DN_A/2$), and $R_0 = r_0/\sqrt[6]{3}$. Expression (4) is used to determine the volume modulus of elasticity without thermal oscillations of atoms

$$B_0 = \left(V \frac{d^2U}{dV^2} \right)_{V_0} = \frac{8U_0}{V_0}. \quad (5)$$

The volume modulus of elasticity calculated in accordance with (5) has a limit value that is essentially inaccessible in a quantum crystal.

Both a finite temperature and zero-point oscillations of atoms need to be taken into account in a quantum crystal. By definition, pressure $p = -(\partial \langle F \rangle / \partial V)_T$, where $\langle F \rangle$ is the mean free energy. The following equation of state of a quantum crystal is obtained in the Mie–Grüneisen approximation [5,12,15] with (4), (5) and the results from [16] taken into account:

$$p = \frac{B_0}{2} \left[\left(\frac{V_0}{V} \right)^5 - \left(\frac{V_0}{V} \right)^3 \right] + \frac{9\gamma R\theta}{8V} f\left(\frac{\theta}{T}\right), \quad (6)$$

where

$$f(x) = 1 + \frac{8}{3} \int_0^1 \frac{\sqrt[3]{y} dy}{\exp(x\sqrt[3]{y}) - 1},$$

$$\gamma = -\frac{\partial \ln \theta}{\partial \ln V},$$

γ is the Grüneisen parameter, θ is the Debye temperature, and R is the gas constant. Specifically, at $\gamma = \text{const}$, (6) yields equation

$$p = a(z^5 - z^3) + bz^{1+\gamma} f(cz^\gamma), \quad (7)$$

where $z = V_0/V$, $a = B_0/2$, $b = 9\gamma R\theta_0/(8V_0)$, $c = \theta_0/T$, and θ_0 is the Debye temperature at $V = V_0$. Figure 1 presents the results of an example calculation performed using (7) at $T = 0$ ($c \rightarrow \infty$) and $f = 1$ for solid helium. Optimized values of the model parameters are $B_0 = 52.81$ MPa, $\gamma = 3$, $\theta_0 = 26$ K, and $V_0 = 14.68$ cm³/mol. Literature values of the Grüneisen parameter and the Debye temperature are similar [4,6,17]: $\gamma = 2-3$, $\theta_0 = 25-33$ K. At $p = 2.5$ MPa and $T = 0$, helium assumes a solid state [18,19]. The calculated and experimental values of the molar volume at this point also agree in the order of magnitude: 24.8 and 21.1 cm³/mol. Note that the errors of measurement of pressure and molar volume of helium at low temperatures are fairly small (below 1% [4,6]).

Using (6), one may write analytical expressions for critical parameters. It is important to bear in mind that phonons in a crystalline solid cannot be identified with quasi-phonons in a quantum liquid. In contrast to oscillations in crystalline solids, oscillations of atoms in any liquid are strongly damped. However, if one admits asymptotics at $\theta \rightarrow 0$, function $f(x)$ and Debye temperature θ are excluded from (6) due to the presence of the $\lim_{x \rightarrow 0} xf(x) = 8/3$ limit (Fig. 2). Thus, this equation technically loses its „phonon

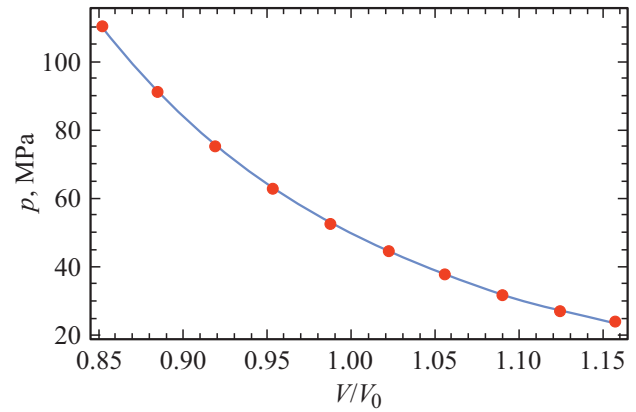


Figure 1. Isotherm of helium in the region of compressive pressures. The solid curve is the result of calculation in accordance with (7) at $f = 1$, while dots are experimental data from [4].

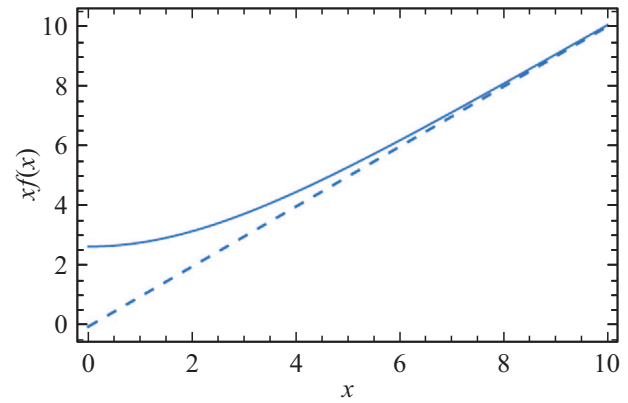


Figure 2. Function characterizing the temperature dependence of pressure in equation of state (6).

form“ and becomes applicable, with certain reservations, to monatomic matter in the critical region. The proposed transition from a solid to a liquid in the equation of state has a rather simple physical foundation. It is well-known that the molar heat capacity of simple liquids is close to $3R$. This value follows exactly from the Debye theory of specific heats at $\theta \rightarrow 0$. It can also be said that the Debye temperature of a liquid is negligible compared to the one for a solid.

Thus, it follows from (6) that

$$p = \frac{B_0}{2} \left[\left(\frac{V_0}{V} \right)^5 - \left(\frac{V_0}{V} \right)^3 \right] + \frac{3\gamma RT}{V}. \quad (8)$$

As usual, the critical point is characterized by conditions

$$\left(\frac{dp}{dV} \right)_T = 0, \quad \left(\frac{d^2p}{dV^2} \right)_T = 0. \quad (9)$$

Solving (8) and (9) together, we obtain

$$V_c = \frac{\sqrt{30}}{3} V_0, \quad p_c = \frac{3\sqrt{30}}{250} B_0 = \frac{8\gamma RT_c}{5V_c}. \quad (10)$$

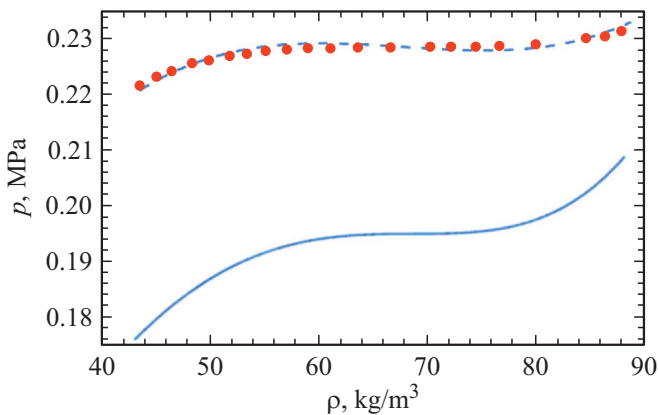


Figure 3. Isotherm of helium in the neighborhood of the critical point. Solid and dashed curves are the results of calculations in accordance with (8), while dots are experimental data from [20].

The stability condition for a thermodynamic phase is $(\partial p/\partial V)_T < 0$. With this condition taken into account, we derive $V > V_c$ and $V < V_c$ from (8) and (10) to the right and to the left of the critical point. This is exactly how it should be.

Formulae (8), (10) provide an opportunity to characterize with a certain accuracy the phase diagram of matter in the neighborhood of the critical point with the pairwise interatomic interaction parameters taken into account. Let us again consider helium as an example. Its parameters are well-known: $D/k_B = T_m = 0.95$ K (T_m is the melting point of helium under the lowest possible pressure of 2.5 MPa), $r_0 = 2r_A = 280$ pm ($r_A = 140$ pm is the van der Waals radius of a helium atom). The following critical pressure and density values may then be calculated using (10): $p_c = 0.195$ MPa and $\rho_c = 68.572$ kg/m³. The obtained values are comparable with experimental data reported in a number of studies [18,19]: $p_c = 0.227$ MPa and $\rho_c = 69$ kg/m³. If we use the experimental value of $T_c = 5.2$ K for the critical temperature of helium, the Grüneisen parameter is $\gamma = 0.164$. The smallness of γ is attributable in the present case to a finite growth of isochoric heat capacity at the critical point.

The results of calculations performed in accordance with (8) are compared with the experimental data [20] in Fig. 3. The solid curve corresponds to the theoretical calculation with the critical parameters indicated above, and the dashed curve is the polynomial $p = A\rho^5 - B\rho^3 + C\rho$ approximation, where coefficients A , B , and C were determined using the least squares method; $\rho = M/V$ is the density of helium; and M is molar mass. The mean percentage error of theoretical calculation and approximation of pressure within the entire presented density interval is 15 and 0.25%, respectively. This accuracy is acceptable for such a simple physical model.

To conclude, let us summarize the key findings:

(1) A new practically convenient equation of state (6) of a quantum crystal was constructed.

(2) Formulae (10) for critical parameters of matter were derived.

(3) Numerical calculations of the isotherm of helium in the region of compressive pressures and in the vicinity of the critical point were performed. The obtained results were in reasonable agreement with experimental data.

In our view, it is also noteworthy that function (8) in coordinates p – ρ characterizes a fold-type catastrophe in the mathematical catastrophe theory (see, e.g., [21]).

Conflict of interest

The authors declare that they have no conflict of interest.

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