

On the question of the specific heat of liquids and dense gases at low temperatures

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It is shown that the behavior of the specific heat C_v of He^4 at temperatures that exceed the quantum-degeneracy temperature can be described on the basis of the classical model of particles with pairwise interaction by making simple assumptions about the binary correlation function.

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As experimental data show, the specific heat C_v of He^3 and He^4 , which exists in the liquid or dense-gas state, starts to decrease rapidly at temperatures of the order of 15–20 K, which are significantly higher than the corresponding quantum degeneracy temperatures.^{1,2}

The quasi crystalline or cellular models of the liquid state, whose systematic analysis gives a discrete energy spectrum and, consequently, decreases the specific heat at low temperatures, have been used to explain this effect.^{2,3}

Recently, Andreev⁴ attempted to describe the thermodynamic properties of liquid helium and hydrogen by means of the tunneling-state model, which was proposed in Refs. 5 and 6 to explain the low-temperature properties of glass and amorphous materials.

We shall show below that the behavior of the specific heat of liquid helium observed experimentally at temperatures exceeding the quantum degeneracy temperature can be obtained within the framework of the general model of a classical system of interacting particles without resorting to any additional concepts.

Let us write the energy of a classical system of particles in the form

$$E = \frac{3}{2} RT + \frac{N^2}{2V} \int_0^\infty \Phi(r) g(r) 4\pi r^2 dr, \quad (1)$$

where $\Phi(r)$ is the pairwise interparticle potential, $g(r)$ is the radial distribution function, V is the molar volume, N is Avogadro's number, and R is the gas constant.

We shall assume that at a moderate density of the system the $g(r)$ function can be approximately described by a step function of the form

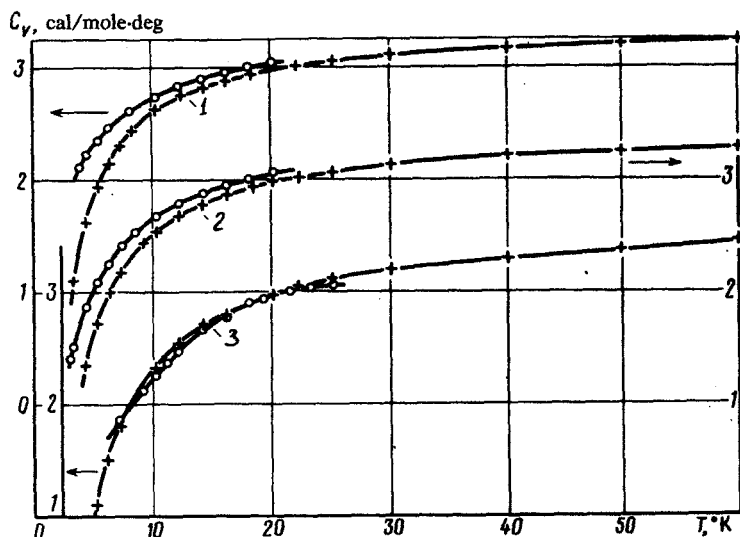


FIG. 1. Temperature dependence of the specific heat C_v of He^4 at constant density: \circ —experimental data,^{1,2} $+$ —calculation from Eq. (7), 1 — $V = 29.07 \text{ cm}^3/\text{mole}$, 2 — $V = 24.22 \text{ cm}^3/\text{mole}$, 3 — $V = 16.25 \text{ cm}^3/\text{mole}$.

$$g(r) = 0, \text{ for } r < \sigma,$$

(2)

$$g(r) = 1, \text{ for } r > \sigma.$$

Thus, Eq. (1) assumes the form

$$E = \frac{3}{2} RT + \frac{N^2}{2V} \int_{\sigma}^{\infty} \Phi(r) 4\pi r^2 dr. \quad (3)$$

We emphasize that in the case of a potential $\Phi(r)$ of general form the lower integration limit σ in (3) must be regarded as a decreasing function of the temperature. Consequently, at temperatures of the order of or lower than the depth ϵ of the potential well, the absolute value of the integral in (3) increases with temperature, since its sign is negative. The latter clearly gives a negative contribution to the specific heat and must cause its rapid decrease at low temperatures.

At high temperatures the absolute value of the potential energy, which is defined by the integral in (3), begins to decrease because of the increasing contribution of the repulsion interaction. At temperatures $T \gg \epsilon$ the potential energy changes sign and then slowly increases with a decreasing rate, thereby determining the asymptotic limit of the specific heat $C_v \rightarrow \frac{3}{2} R$ as $T \rightarrow \infty$. Let us illustrate the aforesaid by numerical estimates. We shall describe the interparticle interaction in liquid helium by the Lennard-Jones⁶⁻¹² potential:

$$\Phi(r) = 4\epsilon \left[\left(\frac{r_0}{r} \right)^{12} - \left(\frac{r_0}{r} \right)^6 \right]. \quad (4)$$

In the case of helium we assume that: $\epsilon = 10.22$ K and $r_0 = 2.556$ Å.⁷ After substituting (4) in (3) and integrating, we obtain

$$E = \frac{3}{2} RT + \frac{8\pi\epsilon N^2}{V} \left(\frac{1}{9} \frac{r_0^{12}}{\sigma^9} - \frac{1}{3} \frac{r_0^6}{\sigma^3} \right). \quad (5)$$

We determine σ from the condition:

$$\epsilon \left(\frac{r_0}{r} \right)^{12} = \frac{1}{2} kT, \text{ where } r = \sigma. \quad (6)$$

Here, for simplicity, we use only the repulsive branch of the potential.

Finally, we obtain for the specific heat:

$$C_v = \frac{3}{2} R + \frac{8\pi r_0^3 \epsilon N^2}{12V} \left[\frac{1}{(2\epsilon)^{3/4} T^{1/4}} - \frac{1}{(2\epsilon)^{1/4} T^{3/4}} \right]. \quad (7)$$

Figure 1 compares the results of calculations from Eq. (7) with the experimental data for He⁴ for three values of the density. As can be seen, the calculations and experiment agree quantitatively, although this may partially be the result of a mutual compensation of ignored effects.

There is no doubt, however, that the negative component of the specific heat, which causes a rapid decrease of the total specific heat at low temperatures and occurs as a result of the temperature dependence of the effective particle diameter, will also appear as a result of more exact calculations that take into account the quantum effects.

It must be emphasized that Eq. (7) has meaning only when the action radius of the attraction forces does not exceed the average particle separation in the system. Otherwise, when the action radius of the attraction forces is considerably greater than the average distance between particles, the attraction energy can be described in the average field approximation, which leads to the disappearance of the right-hand term inside the brackets of Eq. (7). The specific heat C_v of such a system decreases monotonically as $\sim 1/T^{1/4}$ at all temperatures.

Such a situation, as a comparison of calculations and experimental data shows, is apparently realized in the case of neon, argon, and other condensed noble gases.

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