

Thermodynamic model of a liquid

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In this model the thermal vibrations of atoms with respect to their positions of equilibrium are described in a modified Debye approximation which at high temperatures and low densities changes to the description of an ideal gas. The elastic (cold) component of the free energy differs from that of a solid by lower values of the density and heat vaporization at zero temperatures. A configurational component, which is peculiar to a liquid and which characterizes the degree of disorder in the liquid, is introduced. The thermodynamics of neon is studied, isotherms of the free energy and pressure are constructed, and solid–liquid, solid–gas, and liquid–gas phase transitions are described.
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We write the free energy per unit mass for the liquid phase in the form

$$F = F_T(v, T) + F_c + U(v), \quad (1)$$

where U is the elastic (cold) component of the energy at $T=0$, and F_T is the thermal component of the energy. We write F_T in the generalized Debye approximation¹

$$F_T = \frac{RT}{\mu} \left[3 \ln(1 - e^{-\Theta/T}) - D\left(\frac{\Theta}{T}\right) \right], \quad (2)$$

where R is the universal gas constant, μ is the atomic weight, T is the temperature, and

$$\Theta = \Theta_D(1 + L) \quad (3)$$

is the effective Debye temperature. We assume that the solid and liquid phases are described by the same volume dependence of the Debye temperature $\Theta_D(v)$. The change in the Debye temperature from a solid to a liquid corresponds to a change of Θ_D from $\Theta_D(v_s)$ to $\Theta_D(v_l)$. The Debye temperatures of the solid and liquid phases are related as follows:

$$\Theta_D(v) = \Theta_{0s} \exp\left(-\int_{v_{0s}}^v \Gamma d \ln v\right) = \Theta_{0l} \exp\left(-\int_{v_{0l}}^v \Gamma d \ln v\right), \quad (4)$$

where $\Theta_{0l} = \Theta_{0s} \exp(-\int_{v_{0s}}^{v_{0l}} \Gamma d \ln v)$ is the Debye temperature of the liquid at $T=0$, v_{0s} and v_{0l} are the specific volumes of the solid and liquid at $T=0$, and Γ is the Grüneisen coefficient. Next,

$$L = \frac{\hbar T^{1/2}}{(2\pi mk)^{1/2} (g_a m v)^{1/3} \Theta_D} \quad (5)$$

is the generalized Lindemann parameter. In Eq. (4) g_a is the partition function of a gas atom with a mass m , v is the specific volume of the gas, and

$$D(x) = \frac{3}{x^3} \int_0^x \frac{y^3 dy}{e^y - 1}$$

is the Debye function.

It is easy to show that in the limit $L \rightarrow \infty$ the free energy (1) passes into the corresponding expression for an ideal gas.

In Eq. (1) the quantity F_c is the configurational component of the free energy which distinguishes the liquid state from the solid state. We now formally extrapolate the thermodynamic functions of the liquid to zero temperatures, under the assumption that there is still some disorder of the liquid. Like amorphous solids,² the configuration entropy $S_c = -\partial F_c / \partial T$ must then remain finite at $T=0$. On passing to an ideal gas $F_c \rightarrow 0$. It is well known that the entropy jump between the solid and liquid phases on the melting curves remains right up to the highest temperatures.³ The density in this case changes very little. We write the simple expression satisfying all of these conditions in the form

$$F_c = -(RT/\mu)sv_{0l}/v. \quad (6)$$

Correspondingly

$$S_c = (R/\mu)sv_{0l}/v, \quad (7)$$

where the dimensionless quantity s is of order unity — the residual entropy.

The cold curves for a liquid are similar to the cold curves for a solid, but they are characterized by a somewhat lower value of q_{0l} and higher value of v_{0l} . The density of the liquid, extrapolated to zero temperatures, is somewhat lower than the corresponding density of a solid.^{1,4} The heat of vaporization is proportional to the number of bonds (coordination number) that must be broken in order to remove an atom from the condensed state and form a vacancy. In the crystalline state this number is, as a rule, larger than in a liquid. In systems with a short-range potential⁵ the heat of vaporization from the solid state at $T=0$ is $q \cong 6D$, where for the crystal state the number 6 is the number of atoms per vacancy and D is the depth of the potential. For a liquid at temperatures of the order of the melting temperature this number is equal to 5.6.

The entropy and pressure for a liquid, which follow from Ref. 1, are

$$S = \frac{R}{\mu} \left\{ 4D \left(\frac{\Theta}{T} \right) \left[1 - \frac{3L}{8(1+L)} \right] + s \frac{v_{0l}}{v} - 3 \ln(1 - e^{-\Theta/T}) \right\}, \quad (8)$$

$$p = \frac{RT}{\mu v} \left[3D \frac{\Gamma + L/3}{1+L} - \frac{sv_{0l}}{v} \right] + \Pi(v), \quad (9)$$

where

$$\Pi(v) = -dU(v)/dv \quad (10)$$

is the elastic (cold) component of the pressure.

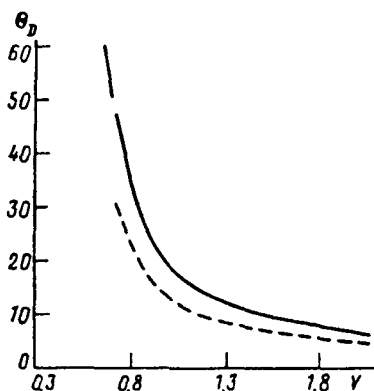


FIG. 1. Solid lines — Debye temperature Θ_D (in K) versus v (in cm^3/g) as determined from the reference data with $s=0.87$. The dashed curve represents the analogous calculation with $s=0$.

The free energy of the solid phase does not contain the component F_c and the elastic component is characterized the quantities q_{0s} and v_{0s} .

We shall find the volume dependence of the Debye temperature for neon from the condition that the entropy and pressure calculated from Eqs. (8) and (9) on the lines of coexistence of the phases correspond to the tabulated data.⁶ Figure 1 gives the Debye temperature Θ_D , in K, as a function of the volume v in the units cm^3/g ; (the same units are also used below). The dashed curve represents the calculations with $s=0$. In this case the transition from a solid to a liquid is accompanied by a sharp jump in the Debye temperature. This jump is difficult to explain from the physical standpoint. Indeed, the loss of long-range order in the crystal cannot influence so radically the frequency of the vibrations of the atoms near the positions of equilibrium (Ref. 7, p. 201). The positions of equilibrium depend on the nearest-neighbor environment of the atom, which also changes at the transition to a liquid but not so radically. The solid lines in Fig. 1 represent the results with $s=0.87$. As one can see, the small jump in the Debye temperature corresponds in this case to the volume jump at the solid-liquid transition. The value found for s is consistent with the lattice models,⁸ according to which in a crystal $s=0$ and in an ideal gas $s=1$. An intermediate value is realized in a liquid.

In Fig. 2 the solid lines, on which the dots are the computed points, are the curves of the elastic (cold) pressure in atm. For the solid (S) phase the curve intersects the volume axis at the point $v_{0s}=0.664 \text{ cm}^3/\text{g}$, which corresponds to the density of solid neon at $T=0$. The cold curve of the liquid (L) intersects the volume axis at the point $v_{0l}=0.74 \text{ cm}^3/\text{g}$. The thin solid lines represent an approximation of the cold curves. The cold components of the energy $U' = \mu U_1 / RT_c$ (T_c is the critical temperature), which have minima at the points v_{0s} and v_{0l} , and which are $q_{0s}=93.3$ and $q_{0l}=84.4 \text{ J/g}$, respectively, are constructed in Fig. 3. At $T=0$ the minimum of the solid-state curve is deeper — the crystalline state is thermodynamically more advantageous.

Isotherms of the pressure (in atm) and the free energy $F' = \mu F / RT$ of the solid (solid lines) and liquid (solid lines with the computed points) phases for $T=0, T_T$ — the

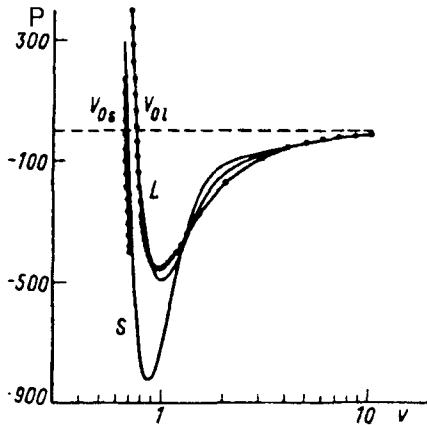


FIG. 2. Solid lines with computed points — cold pressure p (in atm) for the solid and liquid phases as a function of v , as found from the reference data ($s=0.87$). Thin solid lines — Approximation.

triple-point temperature, and T_c are shown in Figs. 4 and 5. In Fig. 6 the energy isotherm for T_T is constructed in a wider range of volumes. The pressure isotherms (Fig. 4) at temperatures $T < T_c$ have a van der Waals form. The maxima and minima in the solid-state curve are sharper than in the liquid-gas curve. At the critical point the liquid-gas isotherm has only an inflection point and the solid-state isotherm is still nonmonotonic.

The tangent with a negative slope with respect to the free-energy curves (Fig. 5 and 6) determines the condition of phase equilibrium. It follows from the topology of the curves in Fig. 5 that at temperatures $T < T_T$ only points of the solid and gas phases can be associated with such a tangent. As the temperature increases, the minimum in the liquid-

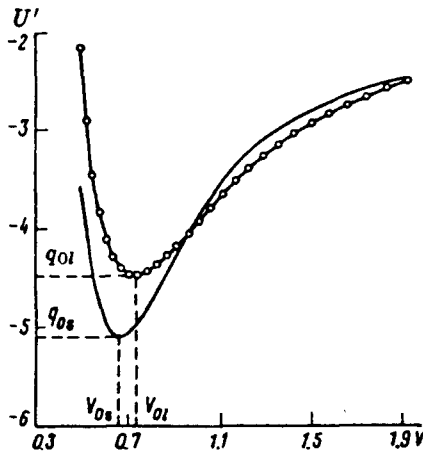


FIG. 3. Cold components of the free energy for a solid phase (solid line) and liquid phase (line with dots) as a function of v .

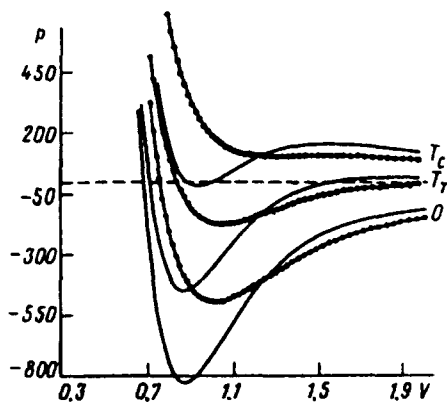


FIG. 4. Pressure isotherms for the solid phase (solid lines) and liquid phase (solid lines with dots) for different temperatures. Dashed line — $p=0$.

gas curve becomes deeper and at $T=T_T$ the points of the solid-liquid phase and the gas phase can be connected by a tangent (the tangent for this case is represented by the dashed lines in Figs. 5 and 6). At $T>T_T$ two different tangents connect the points of the liquid phase and the gas phase, as well as those of the solid phase and the liquid phase. At $T=T_c$ the liquid-gas curve becomes monotonic — points of tangency of the liquid and gas phases merge, and the tangent to the solid and liquid phases remains. It remains the same as the temperature increases further, thus describing the high-temperature melting of the material.

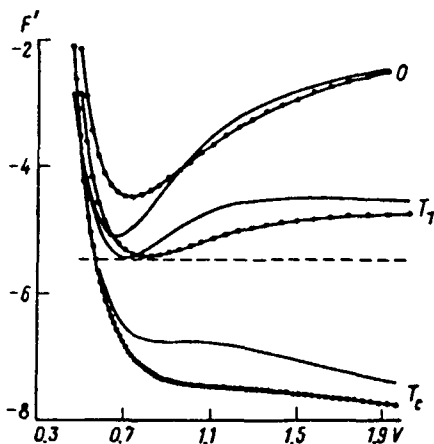


FIG. 5. Free-energy isotherms for the solid phase (solid lines) and liquid phase (solid lines with dots) for different temperatures. Dashed line — tangent determining the equilibrium pressures and volumes of the phases.

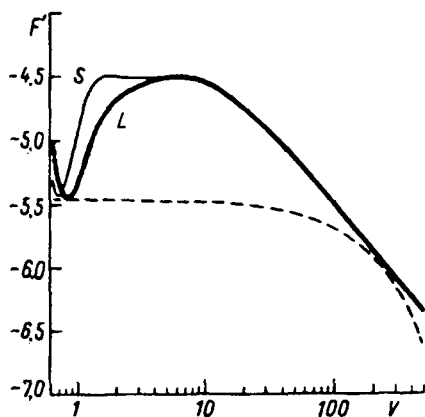


FIG. 6. Free-energy isotherm at $T = T_T$. Dashed curve — tangent to the solid, liquid, and gas phases.

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