

Toward the theory of melting

A. G. Khrapak

Institute of High Temperatures, Academy of Sciences of the USSR

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The asymptotic form of Simon's equation, $p \sim T^{8/5}$, is derived in a hole theory of liquids with holes of a quantum-mechanical nature (bubblons). This asymptotic form agrees well with experiments in inert gases.

The relationship between the pressure p and the temperature T on the melting curve of normal substances is described quite accurately by Simon's empirical equation (Ref. 1 and 2, for example)

$$p = AT^C + B. \quad (1)$$

Despite several attempts, it has not yet been found possible to explain this equation satisfactorily on the basis of either first principles or even other laws of melting, e.g., the semiempirical Lindeman equation.³ In the present letter we attempt to derive Simon's asymptotic equation on the basis of a quasicrystalline (or hole) model of melting^{1,4} in which the defects (or holes) are assumed to be some new collective excitations: "bubblons."⁵

It was shown in Ref. 5 that it is not possible to create a microscopic bubble in a

liquid without simultaneously exciting the wall of the bubble. The quantization of the spectrum of these vibrations and the obligatory presence of zero-point vibrations lead to the conclusion that there is a gap in the energy spectrum of bubbles and that it is not possible to create bubbles of arbitrarily small radius. Estimates for He^4 yielded a zero-point-vibration amplitude R_0 close to the radius of a unit cell. Estimates of the energy of the zero-point vibrations, E_0 , of a bubble at rest yielded a value of 19.4 K, which is close to 17 K, which is the gap of the "many-phonon" branch of the collective-excitation spectrum of liquid He^4 . The approximate agreement of the properties of bubbles in the ground state and the properties of vacancyons in quantum crystals⁶ has made it possible to speak of these entities as new collective excitations, bubblons, which exist along with phonons and rotons in a liquid.

The energy spectrum of bubblons was determined only for the case of zero pressure in Ref. 5. However, it is not difficult to generalize the results to the case of arbitrary p by incorporating in the bubble energy, along with the surface term $4\pi\sigma R^2$, a volume term $(4\pi/3)R^3 p$. Figure 1 shows results calculated on the ground-state energy of a bubblon at rest in an ideal incompressible liquid with a density ρ and a surface tension σ characteristic of liquid He^4 .

The qualitative behavior $E_0(p)$ can be analyzed without resorting to a quantization of the hydrodynamic equations of an incompressible liquid. It is sufficient to work from dimensional considerations. At $p = 0$, the energy of the zero-point vibrations of a

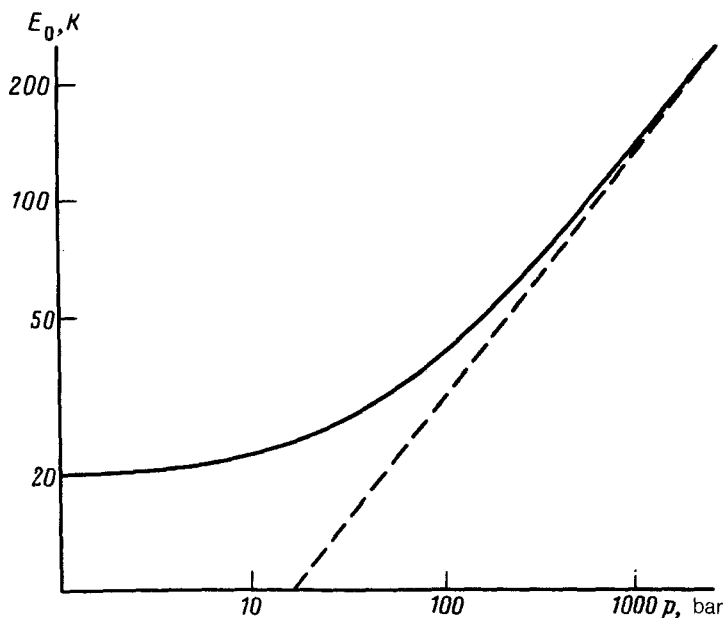


FIG. 1. Minimum bubblon formation energy E_0 versus the pressure p in liquid He^4 . Dashed Line— $E_0 \sim p^{5/8}$.

cavity in an ideal incompressible liquid can be a function of only three parameters: ρ , σ , and \hbar . From these parameters, one can construct only a single combination with dimensions of an energy:

$$E_0(0) \sim \hbar^{4/7} \sigma^{5/7} \rho^{-2/7} . \quad (2)$$

This expression naturally agrees with that derived in Ref. 5, within a factor on the order of unity. In the large- p limit we can ignore surface forces and set $\sigma = 0$. In this case we can also construct the following combination with the dimensions of an energy from the parameters ρ , p , and \hbar :

$$E_0(p) \sim \hbar^{3/4} \rho^{-3/8} p^{5/8} . \quad (3)$$

This dependence in the limit $p \rightarrow \infty$ gives a good approximation of the results of a hydrodynamic calculation, which are shown in Fig. 1. The transition from one regime to the other occurs in the region in which the dimensionless parameter

$$K = \hbar^2 p^7 \sigma^{-8} \rho^{-1} \quad (4)$$

becomes equal to unity. In He^4 at $T=0$ we have $K = 1$ at a pressure close to the crystallization pressure.

We turn now to the melting process. In a large number of simple substances, inert gases in particular, the relative change in volume upon melting is a constant at high pressures. In the hole theory of liquids, this fact is evidence of a constant bubble concentration N_b on the melting curve. Since we have $N_b \sim T^\alpha \exp(-E_0(p)/T)$, however, with $E_0/T \gg 1$, it follows that we have $E_0(p) \sim T$ on the melting curve. Using (3), we find that at high pressures the relationship between the pressure and the temperature on the melting curve is

$$p \sim T^{8/5} , \quad (5)$$

in agreement with Simon's asymptotic equation with $C = 1.6$. This value agrees well with the experimental values of C shown in Table I, which were found through a least-squares fit of experimental results over the entire range of the parameters, up to the triple point (the λ point in the case of He^4).⁷

In Fig. 2. we can clearly see a scaling for the dependence of the quantity $\partial \ln p / \partial \ln T$ on the reduced temperature $\tilde{T} = T/T_t$, where T_t is the temperature of the triple point (in the case of He^4 , $T_t = 0.774$ K is an adjustable parameter). According to Simon's equation, (1), this quantity should approach C at large p . According to our model, the value would be $C = 1.6$ for all normal substances. From Fig. 2 we see that, at least for inert gases, this fact agrees well with experiment and can be utilized to

TABLE I.

He^4	Ne	Ar	Kr	Xe
1.555	1.517	1.523	1.547	1.593

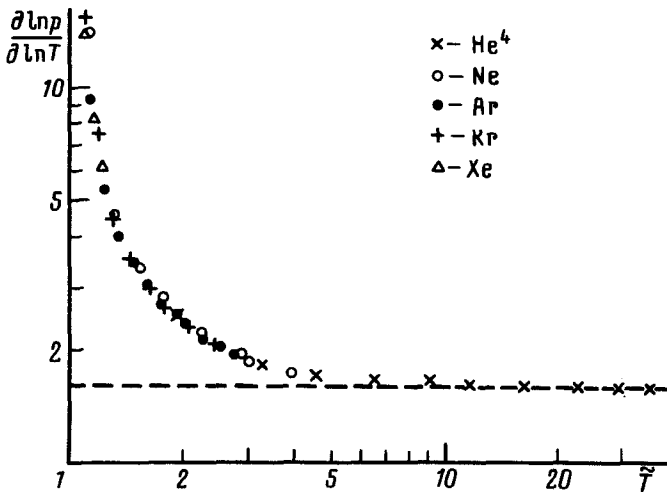


FIG. 2. The quantity $\partial \ln p / \partial \ln T$ versus the reduced temperature T on the melting curve.⁷ Dashed line— $\partial \ln p / \partial \ln T = C = 1.6$.

extrapolate the parameters of the melting curve to extremely high pressures and temperatures.

The model proposed here does not apply to anomalous substances, which exhibit abrupt structural changes during melting. The range of applicability is also limited to the class of substances for which the relative change in volume upon melting is constant along the entire melting curve. A theoretical derivation of this result, which renders the model semiempirical, is the goal of further study.

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