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The Stability of Homogeneous Phase. III
THEORY OF THE CRYSTALLIZATION CURVE

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A theoretical justification of an empirical law by Simon for pressure along the melting curve of ordinary materials is given. Theory is compared with experimental results.

1. INTRODUCTION

THE most significant and physically interesting problem of the theory of the stability of the liquid state is the study of the loss of stability of a liquid due to its crystallization. This is the problem of the "theory of crystallization" or the "theory of melting". For simple systems like argon the empirical relation of Simon gives the equation of the melting curve in the *p*- *T* plane as follows[1]:

$$p_{\text{melt}}(T) = -A + BT^m, \tag{1}$$

which is correct with sufficient accuracy in a very broad range of temperatures and pressures. Here *A*, *B*, and *m* are constants. For argon, for example,

$$A = 3000 \text{ kg/cm}^2; \tag{2}$$

$$B = 2.73 \text{ kg/cm}^2 \text{ (degree)}^m; \; m = 1.288.$$

The recent experimental results verified the correctness of Simon's relation[2,3].

The major task of the "theory of crystallization" should be the theoretical derivation of Eq. (1). Domb[4] has given a physical interpretation of Eq. (1) in terms of the known melting theory[5,6], which considers melting as an order-disorder transition of binary alloy of atoms and vacant cells. Since the physical foundations of this latter theory are doubtful, Eq. (1) still remains theoretically unexplained.

In the present work it will be shown that the problem of the theoretical derivation of the empirical relation (1) can be solved using the theory of the limit of stability of a homogeneous phase, developed in references 7,8.

2. THE LIMIT OF STABILITY OF HOMOGENEOUS PHASE FOR THE INVERSE POWER LAW MODEL

We consider a system of particles with intermolecular potential of the form

$$\Phi(r) = 4\varepsilon (a_0/r)^n \tag{3}$$

("inverse law model"). Here ϵ is a constant with the dimensions of energy, a_0 is a constant of the dimension of length, and *n* is some number which we shall consider large. We shall introduce dimensionless length using as a unit of length the quantity $a = a_0 (4\epsilon/kT)^{1/n}$ so that

$$r \to \rho = \frac{r}{a_0}\left(\frac{kT}{4\varepsilon}\right)^{1/n} \tag{4}$$

Then

$$e^{-\Phi(r)/kT} = e^{-1/\rho^n}, \tag{5}$$

and the parameter λ of the general theory [7,8] is equal to

$$\lambda = \frac{2\pi a^3}{v} = \frac{2\pi a_0^3}{v}\left(\frac{4\varepsilon}{kT}\right)^{3/n} \tag{6}$$

Furthermore, the solution $K(\zeta)$ of the integral equation which determines the behavior of the radial function as $g(\rho)$ approaches infinity, turns out to be (cf. reference 7)

$$K(\zeta) = {}^1/_2 \int_{|\zeta|}^{\infty} (e^{-1/\rho^n})' \, u(\tau)(\zeta^2 - \tau^2)\, d\tau. \tag{7}$$

If the number *n* is sufficiently large, then the function $(e^{-1/\rho^n})'$ has a sharp maximum in the neighborhood of the point $\rho = 1$ and vanishes very

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[7] I. Z. Fisher, J. Exper. Theoret. Phys. USSR **28**, 171 (1955); Soviet Phys. 1, 154 (1955)

[8] I. Z. Fisher, J. Exper. Theoret. Phys. USSR **28**, 437 (1955); Soviet Phys. 1, 273 (1955)

rapidly for all other ρ. Furthermore, the integral of this function from $\rho = 0$ to $\rho = \infty$ is equal to unity and the following relation holds

$$(e^{-1/\rho^n})' \to \delta(\rho - 1), \quad \text{if} \quad n \to \infty. \tag{8}$$

If n is finite, but sufficiently large, then in the first approximation we can substitute a δ-function instead of $(e^{-1/\rho^n})'$ in Eq. (7). Finally we obtain

$$K(\zeta) \approx {}^1\!/_2\, u(1)(\zeta^2 - 1), \quad \text{if} \quad \zeta < 1, \tag{9}$$

$$K(\zeta) \approx 0, \quad \text{if} \quad \zeta > 1.$$

In this approximation the solution $K(\zeta)$ is identical with the solution $K(z)$ of the problem of hard non-interacting spheres which was considered in detail in reference 8. We can write then

$$(2\lambda u(1))_{\lim} = 34.81; \ (u(1))_{\lim} = 2{,}90 \tag{10}$$

(cf. reference 8). Using Eq. (6) we find then that

$$v_{\lim}(T) \approx \frac{\pi a_0^3}{3}\left(\frac{4\varepsilon}{kT}\right)^{3/n}. \tag{11}$$

Furthermore, we have from the general theory the following relation for pressure

$$\frac{pv}{kT} = 1 + \frac{\lambda}{3}\int_0^\infty (e^{-1/\rho^n})'\, u(\rho)\rho^3 d\rho \tag{12}$$
$$\approx 1 + \frac{\lambda}{3}u(1),$$

so that according to Eq. (10), $(pv/kT)_{\lim} = 6.80$ and, using Eq. (11), we obtain

$$p_{\lim}(T) \approx \frac{20.4}{\pi a_0^3}\frac{(kT)^{1+3/n}}{(4\varepsilon)^{3/n}}. \tag{13}$$

The Eqs. (11) and (13) describe in an exhaustive manner the limit of stability of homogeneous phase for the inverse law model for large values of n. As $n \to \infty$, the derived equations become exact expressions for the problem of hard spheres, as should be expected. The result allows an elementary physical interpretation[9]. The particles, according to Eq. (3), possess a property of natural compressibility and their effective diameter, i.e., the smallest separation to which two particles can come, depends on the energy of the colliding particles. It is evident that we can write for the effective diameter

$$\Phi(a_{\text{eff}}) \sim kT, \tag{14}$$

so that Eq. (3) yields

$$a_{\text{eff}} \sim a_0(4\varepsilon/kT)^{1/n}; \ (v_0)_{\text{eff}} \sim v_0(4\varepsilon/kT)^{3n}. \tag{15}$$

Since for spheres of constant natural volume v_0 we have, according to Eq. (8) $v_{\lim} = 2v_0$, so that we obtain from Eq. (15)

$$v_{\lim}(T) \sim 2(v_0)_{\text{eff}} \sim 2v_0(4\varepsilon/kT)^{3n}, \tag{16}$$

which is the previous result. An elementary proof of the relation (13) follows from this expression and the equation of melting curve of a system of hard spheres[8] $p_{\text{melt}} = (3.4/v_0)kT$.

3. TRANSITION TO REAL SYSTEMS AND COMPARISON WITH EXPERIMENTAL DATA

The model discussed so far differs from real systems mainly because it neglects intermolecular forces of attraction. These forces can be included by considering, instead of the potential (3), the potential usually employed.

$$\Phi(r) = 4\varepsilon\{(a_0/r)^n - (a_0/r)^6\}, \tag{17}$$

where the term r^{-6} has been added to the potential (3). However, a rigorous solution of the problem for such potential encounters serious mathematical difficulties. The problem can be solved approximately if we take into account in the main term of Eq. (17) only repulsive forces, and then introduce a correction for forces of attraction. This is entirely correct at high temperatures when the crystallization (and even more, the absolute loss of stability of the liquid) takes place at very high pressures, so that the density of the particles is very large. Under such conditions the repulsive force of particles strongly compressed by the external pressure are the most important, and the forces of attraction play only a secondary role.

In this case the main member determining the pressure at the limit of stability of liquid appears to be Eq. (13). To this pressure it is necessary to add a correction which accounts for the attractive forces between particles. Such correction is, evidently, the "internal pressure" of a liquid which is opposite in sign, so that

$$p_{\lim}(T) \approx -|p^{(\text{int})}| + \frac{20.4}{\pi a_0^3}\frac{(kT)^{1+3/n}}{(4\varepsilon)^{3/n}}. \tag{18}$$

The internal pressure turns out to be only slightly dependent on temperature at the very high densities which are present during crystallization and at the limit of stability of the liquid. As a first approximation we can consider this internal pressure to be a constant quantity, and then dimensional

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[9] I. Fisher Usp. Fiz. Nauk **51**, 71 (1953)

considerations lead to $p_{\text{int.}} \sim (\epsilon/a_0^3)$. In such a way we finally obtain

$$p_{\text{lim}}(T) \approx -\gamma \frac{\varepsilon}{a_0^3} + \frac{20.4}{\pi a_0^3} \frac{(kT)^{1+3/n}}{(4\varepsilon)^{3/n}}, \tag{19}$$

where γ is some dimensionless coefficient of the order of unity.

A direct comparison of the theory with experimental results is not possible because of the lack of quantitative data on the behavior of the curve of the limiting stability of supercooled liquids. However, it is possible to assume that the difference in behavior of this curve from the curve of equilibrium phase transition from liquid to crystal is not important for liquids similar to argon. Then a possibility appears to interpret the relations (11) and (19) as referring to the crystallization curve, and compare them with the experimental data. It is well known that the potential (17) corresponds to the experimental results for compressed gases most accurately when $n \sim 10 - 12$. The investigation of the second virial coefficient results in the following values for a_0 and ϵ for argon [10]:

$$a_0 = 3.50 \cdot 10^{-8}\ \text{cm};\ \varepsilon = 13.9 \cdot 10^{-15}\ \text{erg}, \quad \text{if} \quad n = 10, \tag{20}$$

$$a_0 = 3.41 \cdot 10^{-8}\ \text{cm};\ \varepsilon = 16.5 \cdot 10^{-15}\ \text{erg}, \quad \text{if} \quad n = 12$$

We shall use these data to verify the theory, assuming that Eq. (11) and (19) apply to the melting curve.

The data for pressure: It is immediately evident that the temperature dependence of p_{melt} of the theoretical expression (19) is the same as for the experimental law (1). The constant m in Eq. (1) is

$$m = 1 + \frac{3}{n} = \begin{cases} 1.30, & \text{if} \quad n = 10, \\ 1.25, & \text{if} \quad n = 12, \end{cases} \tag{21}$$

which agrees very well with the experimental data (2). For the coefficients A and B in Eq. (1) we have

$$A = \frac{\gamma\varepsilon}{a_0^3}; \quad B = \frac{20.4 \cdot k^{1+3/n}}{\pi a_0^3 (4\varepsilon)^{3/n}} \tag{22}$$

The substitution of the values (20) results in evaluation of the quantity $\gamma \sim 7 - 9$ which is quite satisfactory. Finally the numerical evaluation of B results in

$$B = \begin{cases} 3.47\ \text{kg/cm}^2\ (\text{degree})^{1.30}, & \text{if} \quad n = 10, \\ 4.54\ \text{kg/cm}^2\ (\text{degree})^{1.25}, & \text{if} \quad n = 12. \end{cases} \tag{23}$$

The agreement with the experimental data (2) within an order of magnitude is good, but the theoretical values are somewhat too high. This can be partially explained by the fact that Eq. (19), strictly speaking, applies only to the limiting pressure of the supercooled liquid which should be somewhat larger than the pressure of the equilibrium crystallization.

THE DATA FOR VOLUME: A comparison of the theoretical result (11) with the experimental data for volume of liquid undergoing equilibrium crystallization is given in Table 1. The second column of the table is computed from the data of reference 11. The third and fourth columns are computed from Eq. (11), using Eq. (20).

In this manner we find that the theory describes well the general behavior of the change of the limiting volume of the liquid and leads to values of the correct order of magnitude for the limiting volume of the liquid. Numerically the volume computed from the theoretical expressions is somewhat too large.

TABLE 1

T°K	$(v_{\text{liq}})_{\text{melt}}$ x 10^{23} cm³ Experimental	$(v_{\text{liq}})_{\text{lim}}$ x 10^{23} cm³ Theoretical	
		$n = 10$	$n = 12$
83.9	4.63	7.20	6.41
126.3	4.33	6.39	5.82
162.0	4.20	5.94	5.49
193.1	4.14	5.53	5.24

THE DATA FOR (pv): The experimental data for the melting curve result in a linear temperature dependence of the quantity $[(p + A)\, v\,]_{\text{melt}}$, where A is the internal pressure from Eq. (1):

$$[(p + A)\, v]_{\text{melt}} = CT. \tag{24}$$

This relation is easily derived from the numerical data of reference (11). The theory results in the same conclusion. From Eqs. (11) and (19) we find that theoretically the following relationship holds:

$$\left[\left(p + \gamma \frac{\varepsilon}{a_0^3}\right) v\right]_{\text{lim}} = 6.8\, kT. \tag{25}$$

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[10] P. Fowler and E. Guggenheim, *Statistical Thermodynamics*

[11] O. Rice, J. Chem. Phys. 7, 136 (1939)

A comparison of the coefficients of T on the right hand side of Eqs. (23) and (24) shows that they are of the same order of magnitude. This fact should be evident from the data for p and v already discussed.

4. DISCUSSION OF RESULTS

The results of comparison of the theory with the experimental data show that the inverse law model can be used as a first approximation to describe the properties of the melting curve or real liquids. It was already pointed out at the beginning of Part 3 that the inverse law model is not appropiate at low temperatures and should become more accurate with higher temperatures. This expectation is verified by the data in Table 1. The remaining disagreement in numerical values of the volume v_{melt} and v_{lim} can be partly explained in the following manner. A correction of the same origin as the correction for internal pressure in $p_{\text{lim}}(T)$ should have been introduced in $v_{\text{lim}}(T)$. It is physically evident that this correction would diminish the numerical values of $v_{\text{lim}}(T)$ and so improve the agreement with experimental results.

Another source of inaccuracy in the numerical evaluations of the theoretical results enters in a_0 and ϵ which is derived by us from the data for only moderately compressed gases. Generally speaking, using such data for liquids is not correct since the collective interaction of particles causes the interaction potential of two particles in the liquid to be different from that of an isolated pair of particles.

It can be concluded that the general theory of the limit of stability of a homogeneous phase developed in references 7,8 describes correctly the basic behavior of the melting curve (crystallization curve) of real systems.

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