

The thermodynamics of melting of simple substances

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A review of the results of real and numerical experiments characterizing the thermodynamics of the melting of simple substances is given. With the examples of argon and sodium it is demonstrated that the qualitative trends in the behavior of the thermodynamic quantities along the melting curve are independent of the form of the interaction forces. The question of the form of the "characteristic" energy determining the melting or crystallization of a substance is analyzed. It is concluded that melting is the most general example of an order-disorder transition in coordinate space. The question of the nature of maxima in melting curves is discussed. The empirical relations of Lindemann and Simon are considered.

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1. INTRODUCTION

The ability of different substances to be in the gaseous, liquid and solid states is one of the most surprising and universal properties of matter. A reflection of this fundamental fact is the practically universal form of the phase diagrams of one-component systems, which contain three characteristic regions corresponding to the different states of aggregation of the substance (Fig. 1).

The beginning of scientific ideas on the phase diagram of a substance and on phase transitions must be placed at the end of the last century, when it was established that the boiling curve is not infinitely extended but terminates at a critical point, above which the transition between the gas and the liquid is continuous. Then van der Waals proposed the famous theory which explains qualitatively the nature of critical phenomena. Since then, the investigations of critical phenomena and of the second-order phase transitions discovered later have been transformed into a vigorously developing field of physical science. However, for a number of profound reasons, the powerful progress in the study of phase transitions has had almost no influence on the development of the theory of melting and crystallization of matter. At the present time no rigorous theory of melting exists. Moreover, there is not even a generally accepted philosophy that would reflect a qualitative understanding of the physical nature of melting. The reasons for this situation arise to a considerable extent from the fact that, until very recently, we did not have at our disposal sufficiently reliable experimental data characterizing the thermodynamics of the melting of simple substances. As a result, even such a fundamental question as the behavior of the melting curve of a substance at high pressures, which was discussed at the end of the 19th century, remains the subject of debate (see Fig. 1).

In this connection, we must regard the primary problem of theory and experiment in the field of the physics of melting to be the study of the behavior of the thermodynamic functions along the melting curve and the establishment of the shape of this curve. One of the

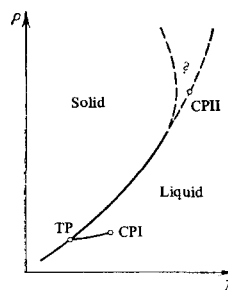
most important problems here is the rigorous analysis of the factors forbidding the realization of a melting as a second-order phase transition¹⁾.

There is clearly no necessity to prove the importance and relevance of the problem under consideration; the absence of a solution is a sufficient stimulus for research. However, it should be pointed out that, as has become clear in recent years, the ability to crystallize is not a prerogative of matter on the atomic or molecular scale only. It is not ruled out that in the interiors of certain astronomical objects crystallization of nucleons can occur. All this undoubtedly emphasizes the highly general character of the melting and crystallization problem.

In the last few years, thanks to new experiments and the development of numerical methods in statistical mechanics, results have appeared that make it possible to present a general picture of melting and crystallization, at least on the thermodynamic level. This review is devoted to analyzing these results. An account of earlier results and historical information can be found in the review^[1].

Before proceeding to describe specific material, we must warn the reader that in this article we study only those aspects of the thermodynamics of melting that can be explained by means of classical theory, and the extremely interesting question of "cold" melting^[2] is left out of consideration. This restriction arises from the author's view that the study of quantum effects

FIG. 1. Generalized phase diagram of a one-component system. [TP—triple point corresponding to liquid-gas-solid equilibrium; CPI—critical point on the liquid-gas equilibrium curve; CPII—hypothetical critical point on the crystal-liquid equilibrium curve (obviously, in Landau's terminology, we can only talk about a critical point of the second kind, at which the equilibrium curve of first-order phase transitions goes over into an equilibrium curve of second-order phase transitions)].



in melting should be preceded by elucidation of the fundamental questions in the physics of melting within the framework of classical statistical mechanics.

2. BRIEF SURVEY OF THE THEORETICAL SITUATION

It is usually assumed that statistical mechanics is able to describe all the features of the phase diagram of any system of particles if the forces acting between the particles are known. In fact, in view of the difficulties of taking all the interactions into account in any realistic system of particles, in the phase-transition problem a general approach based only on the principles of statistical mechanics has never been realized in anything like a systematic and rigorous manner. The modern approach in the theory of phase transitions consists in the development and study of plausible models, with subsequent comparison of the results with the experimental data. In precisely this way, substantial progress in the theory of second-order phase transitions and critical phenomena has been achieved^[3-5].

It would seem that this is also the natural way to develop a theory of melting. However, we must emphasize here that to construct a model of a phase transition, knowledge of the "characteristic" interaction or "characteristic" energy responsible for the phase transition is essential. The role of the "characteristic" energy can be played by the interaction energy of the spins in magnetic phase transitions, the pair-interaction energy of the particles in the case of boiling and critical phenomena in simple liquids, the electron-electron interaction energy leading to the formation of Cooper pairs in the superconductor-normal-metal transition, etc. It has now become clear that in the case of second-order phase transitions and critical phenomena the form of the interaction determining the "characteristic" energy has a direct effect only on the transition temperature ($kT_C \approx \epsilon_0$; T_C is the transition temperature and ϵ_0 is the "characteristic" energy), while the behavior of the thermodynamic quantities near the transition point is essentially independent of the actual interaction law. Thus, here the general qualitative properties of the interaction are pushed into prominence.

In a first-order phase transition (and, in particular, in the case of melting) there is no simple relation between the potential energy and the transition temperature, and the transition point is determined by the equality of the thermodynamic potentials. Nevertheless, there is no doubt that melting as a universal physical phenomenon arises from properties of the inter-particle interaction that are just as universal. However, the character of this interaction is not clear a priori.

In recent years, proofs have been obtained of the existence of a phase transition of the crystal-liquid type in a system of hard spheres and in a system of particles repelling each other according to the law $\Phi(r) \sim 1/r^n$. By means of these results, it is possible to interpret the melting of the inert gases and it turns out that the van der Waals attraction can be treated in the framework of mean-field theory (see below). Therefore, it is not surprising that the assertion of the dominant role of the short-range repulsion in the crystallization of matter is extremely popular at the present time^[6].

It should be remarked that the physical meaning of this assertion is not completely clear even in the case

of the inert gases. Moreover, it is obvious that the above conclusion cannot be extended directly to, e.g., the alkali metals, in which short-range repulsion certainly plays a small role^[7].

In view of this, the thought naturally arises that the important thing for melting is not the concrete inter-particle interaction law determining the form of the "characteristic" energy, but a special property of the potential energy, namely, its sensitivity to the way in which the particles are distributed in space. This conclusion follows directly from the fact that the long-range order disappears in the crystal-liquid transition.

Thus, it appears reasonable to regard the crystal-liquid transition as an order-disorder transition. This concept is not new (we recall the theory of Lennard-Jones and Devonshire^[8]), but its application in the framework of lattice models is not fruitful^[2]. The reason for this obviously lies in the impossibility of an adequate description of the configuration space of a dense system in the framework of lattice models with a large mesh, i.e., with a large ratio of the lattice constant to the range of interaction of the particles. It might be thought that a three-dimensional lattice model with a sufficiently fine mesh will give a satisfactory description of melting, but the analytic study of such a model is no less complicated than for the continuum model.

Thus, in constructing a realistic model of the crystal-liquid phase transition we are bound by the necessity of considering a continuous coordinate space^[3]. Otherwise, even with the "correct" Hamiltonian the model selected can have no relation to reality.

Nevertheless, it turns out that the possibility exists of obtaining a number of rigorous relations characterizing melting in systems of particles interacting through an inverse power law, outside the framework of any models of space, using only properties of the partition function. For this purpose, we shall make use of Klein's theorem^[3,12], which states that, for a system whose potential energy is a homogeneous function of order n of the particle coordinates, the nonideal part of the partition function does not depend separately on the volume and temperature but is a function of the combined variable $\rho^{n/3}/kT$, where ρ is the dimensionless density and T is the temperature. The physical justification for applying this theorem in a given specific case lies in the happy circumstance that in a number of the simplest systems (inert gases, alkali metals) the "characteristic" energy can be expressed in the form of a power function of the particle coordinates.

Thus, we shall assume that the potential energy of the system has the form

$$U = \sum_{i < j} \Phi(r_{ij}), \quad (1)$$

where

$$\Phi(r) = \epsilon \left(\frac{\sigma}{r} \right)^n; \quad (2)$$

ϵ and σ are constants with the dimensions of energy and length, and r is the distance between the particles.

We introduce the dimensionless density $\rho = N\sigma^3/V$ and the dimensionless length $s = r(N/V)^{1/3}$ (here V is the volume of the system). Then for the partition function we have

$$Z = \frac{1^N}{N! \lambda^{3N}} \int_{s_i} \dots \int_{s_N} \exp \left(- \frac{\rho^{n/3} \epsilon \sum_{i < j} s_{ij}^n}{kT} \right) ds_1 \dots ds_N, \quad (3)$$

where

$$\lambda = \frac{\hbar}{(2\pi mkT)^{1/2}}$$

From (3) follows the equation of state

$$\frac{PV}{RT} = 1 + \varphi \left(\rho \left(\frac{\epsilon}{kT} \right)^{3/n} \right). \quad (4)$$

If a first-order phase transition occurs in a system describable by the equation of state (4), the beginning and end of the phase transition are characterized by two universal values of the variable $\rho (\epsilon/kT)^{3/n}$. We shall assume that a crystal-liquid phase transition takes place in a system of particles interacting through the law (2). Then the densities of the liquid and solid phases are

$$\rho_l = c_l \left(\frac{kT}{\epsilon} \right)^{3/n}, \quad \rho_s = c_s \left(\frac{kT}{\epsilon} \right)^{3/n}, \quad (5)$$

where c_l and c_s are constants. From (4) and (5), we have for the equation of the melting curve, the relative volume discontinuity and the entropy discontinuity:

$$p \sim \left(\frac{kT}{\epsilon} \right)^{1+(3/n)}, \quad (6)$$

$$\frac{\Delta V}{V_s} = \text{const}, \quad (7)$$

$$\frac{\Delta S}{R} = \text{const}. \quad (8)$$

We note that as $n \rightarrow \infty$ the relations characterizing the phase transition in a system of hard spheres follow from (5) and (6):

$$\rho_l = c'_l, \quad \rho_s = c'_s, \quad (9)$$

$$p \sim T, \quad (10)$$

where c'_l and c'_s are constants. It is easily seen that relations (7) and (8) remain valid for a system of hard spheres.

The validity of the relations (7)–(10) for the phase transition in a system of hard spheres is easily proved on the basis of thermodynamic arguments.

The free energy of a classical system of hard spheres equals $F = (\frac{3}{2})kT - TS$. Consequently, the equation of state of a system of hard spheres is

$$p = T \left(\frac{\partial S}{\partial V} \right)_T. \quad (11)$$

From (11) and the Maxwell relation $(\partial S/\partial V)_T = (\partial p/\partial T)_V$ it follows that

$$p = T \left(\frac{\partial p}{\partial T} \right)_V. \quad (12)$$

Integrating (12), we obtain the equation of state in the form

$$\frac{p}{kT} = f(V). \quad (13)$$

On the other hand, from the equality of the chemical potentials in the phase transition we have

$$p\Delta V = T\Delta S. \quad (14)$$

Then, using (14) and the Clausius-Clapeyron equation $dP/dT = \Delta S/\Delta V$, we obtain the equation of the melting curve

$$\frac{dP}{dT} = \frac{P}{T},$$

or

$$P = cT. \quad (15)$$

It is easy to see that the relations (7)–(10) follow from (13) and (15).

Klein's theorem also finds application in the treatment of the properties of a system of point charged particles in a background of a uniform compensating field (the model of the classical one-component plasma).

In fact, the potential energy of this system can be written in the form

$$U = \frac{Z^2 e^2}{r_a} \eta(s_1, \dots, s_N), \quad (16)$$

where r_a is the radius of the sphere containing one particle, determined from the condition $4\pi r_a^3/3 = V/N$, and $s = r(N/V)^{1/3}$ is a dimensionless length.

The function $\eta(s_1, \dots, s_N)$ in (16) characterizes the arrangement of the ions and is a constant for any fixed configuration. In the case of a static crystal lattice, the quantity defined by $\eta(s_1, \dots, s_N)$ is called the Madelung constant.

The partition function of a system of point charges in a uniform compensating background has the form

$$Z = \frac{V^N}{N! \lambda^{3N}} \int_{s_1} \dots \int_{s_N} \exp[-\Gamma \eta(s_1, \dots, s_N)] ds_1 \dots ds_N, \quad (17)$$

where

$$\Gamma = \frac{Z^2 e^2}{r_a kT} = \frac{Z^2 e^2}{(3V/4\pi N)^{1/3} kT} \quad (18)$$

is the ratio of the mean Coulomb energy to the thermal energy. Consequently, in this case too the nonideal part of the partition function is determined entirely by the parameter Γ , and if crystallization is occurring in the system we can write for the density of the coexisting phases:

$$\rho_{l,s} \sim (kT)^3. \quad (19)$$

There is no point in writing out further relations following from (17), since a system of point charges in a uniform compensating background is unstable (the pressure and compressibility are negative) and to obtain physical results it is necessary to consider the self-energy of the background (see below).

Thus, we have obtained a number of important relations characterizing the thermodynamics of transitions in simple model systems. However, the existence of phase transitions in these simple systems still needs to be proved, and, moreover, it is necessary to clarify their relation to phase transitions in real systems. As we shall see from the following, the combination of the data obtained by means of numerical and real experiments gives the information necessary for the solution of these problems and makes it possible to establish that the relations (5)–(8) and (19) also remain valid for real systems in the limit of very high temperatures and densities.

3. RESULTS OF COMPUTER EXPERIMENTS

By computer or numerical experiments, we mean methods for the numerical solution of many-particle problems in statistical physics, realized by means of high-speed computers. At present, two methods that can be used to perform numerical experiments are known: these are the Monte Carlo method^[13,14] and the molecular-dynamics method^[15,16]. Since a detailed consideration of these methods does not enter our problem, we shall give here only the necessary minimum of information. The interested reader will find a detailed account in the literature cited.

In both methods, as a rule, a cubic cell containing N particles is given. The number N of particles in the cell is limited by the capacity of present-day computers and does not exceed a few hundred. To eliminate surface effects, periodic boundary conditions are used.

Numerical experiments by the Monte-Carlo method are usually performed at constant volume and temperature. In the method there are practically no limitations on the form of the interaction potential, but the requirements of a finite calculation time force us, as a rule, to use a pair potential. After the initial configuration, which can be arbitrary, is chosen, the particles of the system are assigned random displacements and the energy of the new configuration is calculated. If the energy of the system is lowered, the new configuration is taken with a weight equal to unity; if the energy is raised, the new configuration is taken with a weight equal to $1 - \exp(-\Delta U/kT)$, where ΔU is the difference of the energies of the initial and final configurations of the particles. In the case when the specified displacement of the particles is forbidden, a return to the initial configuration occurs. As is proved in^[13,14], for such a system of calculation the frequency of appearance of the different configurations is proportional to the Boltzmann factor $\exp[-U(x_i)/kT]$. The mean value of any function of the coordinates can be calculated by means of the expression

$$\langle f \rangle = \sum_{i=1}^j f(x_i) u_i,$$

where $u_i = P(x_i) / \sum_j P(x_j)$ is the normalized probability of the i -th state; this is equivalent to averaging over the Gibbs canonical ensemble. Thus, by means of the Monte-Carlo method it is possible to calculate the energy, the specific heat, the equation of state, etc. Unfortunately, the Monte Carlo method is not effective for calculating the free energy and entropy.

The numerical experiments by the molecular-dynamics method are performed at constant volume and constant energy. After the initial configuration is chosen, arbitrary velocities are assigned to the particles and the classical equations of motion are solved. Ultimately, at each given moment of time the coordinates and velocities of the particles are known. In fact, the whole system moves along a certain trajectory in phase space, and the totality of points in the phase space can be regarded as a microcanonical ensemble. Equilibrium properties of the system (the energy, temperature and pressure) are calculated by averaging over the time.

To obtain reliable data, in both methods one studies the dependence of the results on the number of particles in the basic cell and makes estimates for $N \rightarrow \infty$. In most cases these estimates are entirely reliable.

One of the first important achievements of the numerical methods developed was the study of the equation of state of a system of hard spheres^[17,18]. It was found that the compression isotherm of a system of hard spheres in the high-density region consists of two nonintersecting branches. The investigation of the configurations of the particles and of the character of their motion indicated definitely that the two branches of the isotherm belong to the gas-liquid state and the crystalline state of the system. These were the first proofs of the existence of a first-order phase transition in a system of hard spheres. However, up to the present time, coexistence of phases in phase transitions in systems of artificial particles has not been obtained⁴⁾, and this is explained by the small number of particles in the basic cell. In view of this fact, the coordinates of the phase transition and, consequently, its thermodynamic properties, cannot be established directly.

The only possibility of establishing the coordinates of a phase transition lies in using the equality of the chemical potentials in the phase transition. However, neither the chemical potential nor the entropy can be calculated in the framework of the Monte Carlo method or of the molecular-dynamics method, but in the limit of low density the thermodynamic properties of practically any system can be calculated exactly. Therefore, the calculation of the necessary thermodynamic functions is carried out to be integrating the equation of state. This problem is trivial for the liquid or liquid-like phase, but it is impossible to expand the solid phase to arbitrary low density. In this case the problem is solved by introducing a periodic external field stabilizing the solid phase at low density^[23]. For systems of particles possessing a "soft" interaction potential, the calculation of the thermodynamic properties of the solid phase can be performed by means of the standard methods of lattice dynamics. The results of numerical experiments in this case are used to calculate the corrections for anharmonicity^[24].

Up to now, the Monte Carlo and molecular-dynamics techniques have been used to study the crystal-liquid transitions for a system of hard spheres and systems of particles interacting in accordance with the law $\Phi(r) \sim 1/r^n$, with $n = 4, 6, 9, 12$ ^[24-27]. In addition, in^[28] calculations were performed for a system of particles with a Lennard-Jones potential. In^[27] the effect of the energy of attraction on the thermodynamics of the melting was taken into account in the framework of perturbation theory. Figure 2 and Table I give data characterizing the thermodynamics of melting in systems of artificial particles with power-law repulsion.

The work on the investigation of crystallization in a system of point charges in a uniform compensating background requires special consideration. As we have already noted in Sec. 2, such a system possesses negative pressure and compressibility and is consequently unstable. In order that a system of point charges have physical characteristics, it is necessary to consider the self-energy and pressure of the background. For this it is sufficient to assume, e.g., that the uniform compensating potential is due to a degenerate electron gas.

It is easy to see that in the case of a phase transition allowance for the free energy of the background cannot alter the value $\Gamma = Z^2 e^2 / r_0 kT$ (cf. Sec. 2) at which the intersection of the two branches of the free energy in the subsystem of point charges occurs, but the thermodynamic properties of the transition will be determined to a certain extent by the nature of the compensating potential.

A system of point charges was one of the first systems studied by the Monte Carlo method. Crystalliza-

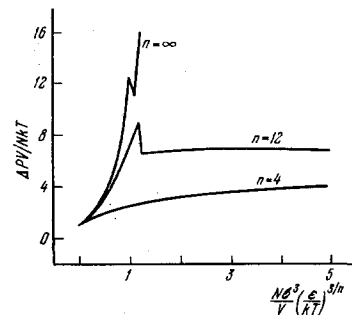


FIG. 2. Equation of state of model systems of particles with interaction $\Phi(r) = \epsilon(\sigma/r)^n$ ^[24]. The breaks in the slopes of the curves correspond to crystallization and melting.

TABLE I. Thermodynamic properties of the crystal-liquid phase transition in systems of particles with interaction $\Phi(r) = \xi(\sigma/r)^n$ [24]

	$n=4$	$n=6$	$n=9$	$n=12$	$n=\infty$
$\rho (\epsilon/kT)_s^{3/n}$	3.94	1.56	0.971	0.844	0.736
$\rho (\epsilon/kT)_l^{3/n}$	3.92	1.54	0.943	0.813	0.667
$\Delta F/NkT$	-0.45	-0.50	-0.63	-0.72	-1.16
$\Delta U/NkT$	0.35	0.25	0.21	0.18	0.00
$\Delta S/R$	0.80	0.75	0.84	0.90	1.16
$\Delta V/V_s$	0.005	0.013	0.030	0.038	0.103
$\frac{PV_0}{NkT} \left(\frac{\epsilon}{kT} \right)^{3/n}$	426	61	22	16	8.3

$\rho = N\sigma^3/\sqrt{2V}$, where V is the volume of the system. In the case of hard spheres ($n = \infty$) the parameter σ is taken to be equal to the diameter of the sphere.
 ΔF , ΔU and ΔS are the changes in the free energy, internal energy and entropy in the melting.
 $\Delta V/V_s$ is the relative volume discontinuity in the melting.

tion in this system was discovered in [29]. In this same paper an approximate estimate for the crystallization line was given ($\Gamma \approx 125$). The more exact results of [30] show that the intersection of the two free-energy branches corresponding to the liquid and solid phases occurs near $\Gamma = 158$, and, consequently, the equation of the melting curve in $(\rho - T)$ coordinates is of the form

$$T = \kappa \rho^{1/3},$$

where

$$\kappa = \frac{(Ze)^2 \sqrt[3]{4\pi/3}}{158k}. \quad (20)$$

The calculations performed in the paper for the thermodynamic parameters of the melting for a system of He^4 nuclei whose electrical neutrality is maintained by a nonrelativistic degenerate electron gas led to the following results:

$$\frac{\Delta V}{V_s} \approx 0.0004, \quad \frac{\Delta S}{R} \approx 0.82. \quad (21)$$

It is necessary to note that, as follows from the data of Table I and the values given above, the entropy discontinuity is a more stable characteristic of the melting than is the relative change of volume.

Thus, computer experiments give definite proofs of the existence of phase transitions in the simple systems considered in Sec. 2. However, it must be emphasized that these proofs do not possess the necessary rigor, and therefore certain doubts about the generality of the numerical results are natural.

In the following sections it will be shown that real experiments can be used as an independent source of proofs confirming the validity of the results of the computer experiments.

4. RESULTS OF REAL EXPERIMENTS

At the present stage of development of our knowledge of melting it is obvious that we must regard the basic problem of experiment to be the establishment of the trends in the behavior of the thermodynamic quantities characterizing the melting when the melting temperature or degree of compression is increased. In fact, knowledge of these trends can, firstly, constitute the necessary base on which it will become possible to develop the theory of melting, and, secondly, will facilitate the elucidation of certain fundamental problems in the

physics of melting on a purely empirical basis. Figure 3 shows different variants of the behavior of the melting curve of a simple substance as a consequence of specific trends in the behavior of the entropy of melting and of the relative volume discontinuity in the melting.

It may appear strange to the reader that, despite the conclusions of the preceding sections, which explicitly indicated the absence of a critical point on the melting curves and an unlimited increase of the melting temperature with compression in the case of simple model systems, we are nevertheless discussing these questions in this section. The point is that the adequacy of the model systems for real systems must be proved. In addition, we feel it important to emphasize that the experimental data should, as far as possible, be analyzed independently of any of these results, particularly as they do not follow from a faultless theory.

At first sight, it follows from Fig. 3 that the demands made on experiments in the study of the thermodynamics of melting are, in practice, unrealistic. Indeed, we are not in a position to perform experiments at arbitrarily high temperatures or unlimited compression, but there is often no necessity for this. For example, if we are concerned with a substance whose interaction potential looks like the pair potential represented in Fig. 4 and we wish to explain how this substance will behave in the limit of high temperatures, then, as follows from thermodynamic perturbation theory [3], it is sufficient to perform the experiments at temperatures exceeding the depth ϵ of the potential well. This condition is fully attainable in the case of the inert gases. Nevertheless, the experimental possibilities impose quite definite limitations on the choice of objects for study. The state of experimental technique at the present time means that it is only in the case of the inert gases and alkali metals (i.e., substances with low melt-

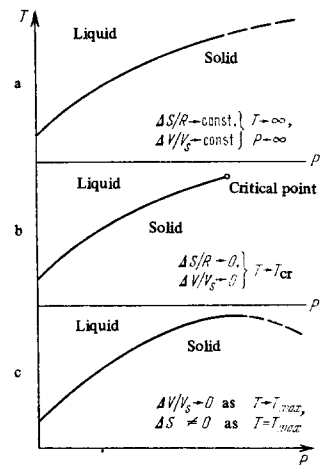


FIG. 3. Hypothetical variants of the behavior of the melting curve of a simple substance as a consequence of definite tendencies in the behavior of the entropy of melting and of the relative volume discontinuity in the melting. a—Unlimited increase of the melting temperature; b—critical point on the melting curve; c—a maximum melting temperature.

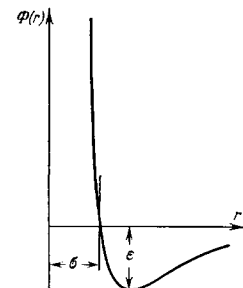


FIG. 4. Schematic form of an interparticle pair interaction potential of the type $\Phi(r) = \epsilon f(\sigma/r)$.

ing points and high compressibilities) that we can rely on obtaining sufficiently representative results in the study of the thermodynamics of melting.

But what is the essence of an experiment to study the thermodynamics of melting? In the general case, it is necessary to study the behavior of the volume, energy and entropy along the melting curve. This problem requires that a combination of dilatometric, piezometric and calorimetric measurements be performed. However, if the thermodynamic properties of the substance have been well studied at atmospheric pressure, it is sufficient to know only the equation of state $\varphi(P, V, T) = 0$ and the equation of the melting curve, $P = f(T)$. Everything else can be calculated easily by means of known thermodynamic relations.

If we set ourselves the more limited task of studying only the change of the thermodynamic quantities on melting, the experiment is simplified and we can confine ourselves to measuring the $(P - T)$ -coordinates of the melting curve and one of the quantities appearing in the Clausius-Clapeyron equation, i.e., the heat of melting or the volume change in the melting. Since calorimetric measurements at high pressures cannot be performed with high precision, measurement of the volume discontinuity ΔV must be preferred.

The demands on the experimental accuracy are very great. Indeed, if the volume change in the melting is a quantity of the order of a few per cent, to determine the volume discontinuity accurate to one per cent it is necessary to measure the volume with an accuracy of about 0.01%. Furthermore, since the derivative dP/dT appears in the Clausius-Clapeyron equation, the coordinates of the melting curve should be determined with an accuracy no worse than a few hundredths of a degree and a few atmospheres.

Modern means of measurement and automation make it possible to maintain and measure the temperature and pressure with the necessary precision (we do not consider here the problems associated with the pressure and temperature scales) in the region of pressures of the order of 3×10^4 kgf/cm² and at temperatures not exceeding 600–700°K and bounded below by the melting curve of helium. However, none of the progress in modern techniques has had any substantial influence on the development of methods of measuring the volume of a substance, especially in the region of the crystal-liquid transition under conditions of high pressures. This fact partly explains the inadequacy of the experimental data characterizing the thermodynamics of melting.

Nevertheless, despite the existing difficulties, the position has changed in recent years and at the present time we have fully representative results on the thermodynamics of melting of argon, sodium and cesium, giving an experimental basis for the discussion of the problem of melting as a whole. We now turn to examine these results.

a) Argon. Argon plays a significant role as an object of investigation in many fields of physics. The popularity of argon is explained primarily by the small magnitude of the quantum effects, owing to which many properties of argon can be treated in a purely classical approximation and with a relatively simple form of inter-particle interaction function. As is well known, the potential energy of argon can be written in the form of a sum of pair terms

$$U(r_1, \dots, r_N) = \sum_{1 \leq i < j \leq N} \Phi(r_{ij}), \quad (22)$$

where $\Phi(r_{ij})$ is the pair-interaction potential, which can be approximated with good accuracy by the Lennard-Jones (6:12) model potential^[31] (see Fig. 4):

$$\Phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (23)$$

Successful investigations of the thermodynamics of melting of argon have been carried out by three independent groups in Canada^[34], the USA^[35,36] and the USSR^[37,38]. The Canadian and American investigators used practically the same method of measurement. The essence of this method can be described in the following way (Fig. 5). A high-pressure vessel of calibrated capacity is weighed on a precision balance and linked with a generator of compressed gas by a thin flexible capillary. During the experiment the temperature, pressure and mass of the gas are measured. In the processing of the results of the measurement it is necessary to take into account the deformation of the vessel, the displacement of the zero of the balance, and a number of other effects. However, the principal difficulty in this method is obviously associated with blocking of the capillary on crystallization of the argon, and with the impossibility of penetrating sufficiently far into the region of stability of the solid phase in order to "squeeze out" macro-defects of different kinds (see, in this connection, the very interesting observations on the crystallization of helium in^[39]). Therefore, it is not ruled out that the values obtained for the volume of the solid phase of argon in these experiments may be somewhat too low.

Figures 6 and 7 illustrate the method of measuring the volume of argon as realized in the Crystallography Institute of the USSR Academy of Sciences. Here, a piston piezometer immersed in the high-pressure cell is used to measure the argon volume. The piston of the piezometer plays the role of a divider, separating the compressed argon from the liquid transmitting the pressure, and serves as an indicator of the level of the compressed argon (for more details of the technique, see^[40]). The medium used to transmit the pressure is benzene, and therefore the range of attainable temperatures is bounded by the solidification curve of the latter. The main sources of errors in this experiment are leakage of the gas and penetration of the benzene into the piezometer cavity. However, comparison of measurements performed on raising and lowering the

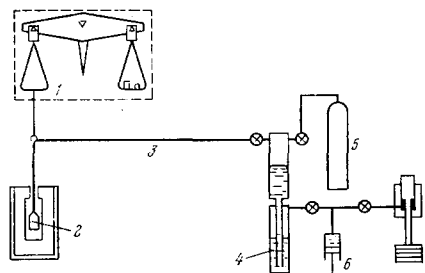


FIG. 5. Scheme of the apparatus used by the Canadian group^[34] to study the thermodynamics of melting of argon. Fundamentally similar apparatus was used in the experiments of the American investigators^[35,36]. 1—Balance; 2—high-pressure vessel; 3—flexible capillary; 4—mercury separator; 5—cylinder with argon; 6—pump; 7—load-piston manometer.

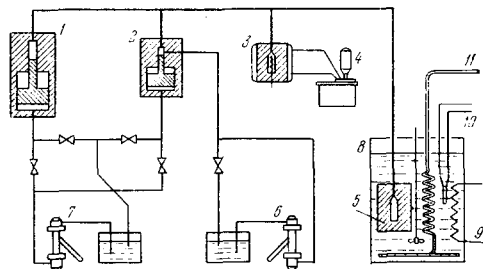


FIG. 6. Scheme of the high-pressure apparatus at the Institute of Crystallography of the USSR Academy of Sciences, designed to study the thermodynamics of melting of substances with low melting points [40]. 1—Pressure booster; 2—initial-pressure valve; 3—vessel containing manganin resistance manometer; 4—thermostat to stabilize the temperature of the manganin manometer; 5—vessel designed to house the piezometer; 6—pump to supply compressed benzine to the high-pressure system; 7—oil pump to supply the hydraulic cylinders of the pressure booster and valve; 8—thermostat; 9—heater; 10—resistance thermometer; 11—refrigerator.

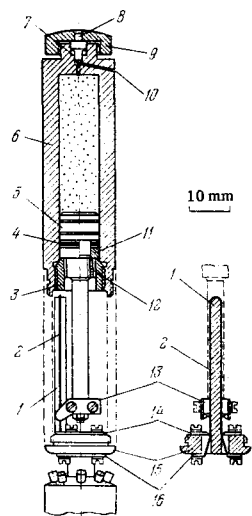


FIG. 7. Piston piezometer used to measure the volume of compressed argon in the Institute of Crystallography of the USSR Academy of Sciences. 1—Column of the displacement gauge; 2—constantan wire; 3, 11, 12—components of the sealing unit; 4—gasket of fluorosilicon resin; 5—piston; 6—casing; 7—resin sealing washer; 8—valve needle; 9—nut; 10—channel for filling the piezometer; 13—mobile potential contacts; 14—fixed potential contacts; 15—panel; 16—current contacts.

pressure practically always makes it possible to recognize these effects. By means of this method, it has been possible to carry out reliable measurements of the volume of solid and liquid argon at pressures up to 17×10^3 kgf/cm².

Table II gives a summary of the results of the measurements and thermodynamic calculations characterizing the thermodynamics of melting of argon, from the data of different authors. Comparison of the results of the measurements shows that the maximum difference observed in the volume values from the data of [35, 38] does not exceed 1%; the difference in the values of the volume discontinuity is much smaller. On the whole, it must be acknowledged that the agreement between the measurements performed by the three independent groups, by different methods, is highly satisfactory.

Before proceeding to discuss the experimental data, we shall recall briefly a number of propositions from thermodynamic perturbation theory [2], which are important for the following account.

The energy of a system of particles interacting in accordance with a potential of the type (23) can be represented under certain conditions as

$$U(r_1, \dots, r_N) = U_0(r_1, \dots, r_N) + U'(r_1, \dots, r_N), \quad (24)$$

where

$$U'(r_1, \dots, r_N) \ll |U_0(r_1, \dots, r_N)| \quad (25)$$

$$U_0 = \sum_{i < j} \Phi_0(r_{ij}), \quad U' = \sum_{i < j} \Phi'(r_{ij}).$$

It can be seen that representing the potential energy of the system in the form (24) implies separating the inter-particle interaction function into two parts, i.e.,

$$\Phi(r) = \Phi_0(r) + \Phi'(r). \quad (26)$$

The form of the functions $\Phi_0(r)$ and $\Phi'(r)$ depends on the way in which the total potential is separated: one of these ways is illustrated in Fig. 8. Expanding the perturbing part of the partition function in powers of the ratio U'/kT , we obtain the free energy of the system in the form [3]

$$F = F_0 + \langle U' \rangle - \frac{\langle (U' - \langle U' \rangle)^2 \rangle}{2kT}, \quad (27)$$

or, at high temperatures,

$$F = F_0 + \frac{N^2}{2V} \int \Phi'(r) g_0(r) (4\pi r^2) dr, \quad (28)$$

where F_0 is the free energy of the unperturbed system, and

$$\langle U' \rangle = \frac{N^2}{2V} \int \Phi'(r) g_0(r) (4\pi r^2) dr$$

is the mean value of the perturbing energy, expressed by means of the radial distribution function $g_0(r)$ of the unperturbed system [43].

It is important here to emphasize two aspects. First, the perturbing energy gives an appreciable contribution to the thermodynamic properties of the system at all temperatures, and, consequently, a potential of the form

TABLE II. Thermodynamics of the melting of argon (experimental data)

T	P	ΔV	V_s	$\Delta V/V_s$	$\Delta S/R$	ΔH	ΔU	Literature
83.78	0.7	3.53	24.61	0.144	1.686	281	281	41
96.41	450.1	2.91	24.36	0.120	1.530	293	256	34
101.11	752.5	2.72	24.18	0.113	1.469	295	247	
105.81	970.9	2.57	24.04	0.107	1.432	301	243	
110.55	1197.1	2.45	23.88	0.103	1.398	307	238	
115.30	1429.6	2.33	23.75	0.098	1.358	311	233	
120.08	1669.3	2.20	23.62	0.093	1.316	314	228	
94.73	460	2.96	24.34	0.122	1.523	287	255	35
108.12	1072	2.50	24.02	0.104	1.413	303	241	
120.85	1707	2.20	23.65	0.090	1.313	315	227	
140.88	2761	1.92	23.04	0.083	1.246	349	225	
160.40	3880	1.72	22.54	0.076	1.207	385	228	
180.15	5098	1.57	22.08	0.071	1.175	420	233	
180.20	5102	1.55	22.11	0.070	1.161	416	230	
204.32	6460	1.41	21.69	0.065	1.063	425	212	
156.39	3644	1.76	22.64	0.078	1.214	377	227	36
181.28	5161	1.54	22.01	0.070	1.148	413	227	
224.41	7835	1.32	21.18	0.062	1.089	479	237	
253.49	10156	1.20	20.63	0.058	1.058	533	248	
197.78	6261	1.495	21.470	0.070	1.133	445	226	38
221.61	7929	1.360	—	—	1.101	487	234	
222.87	7947	1.364	20.964	0.065	1.106	489	236	
247.77	9727	1.263	—	—	1.086	534	247	
247.94	9734	1.261	20.554	0.061	1.084	534	247	
273.00	11594	1.181	20.167	0.059	1.072	581	261	
273.12	11604	1.183	20.122	0.059	1.074	583	261	
297.93	13573	1.114	19.768	0.056	1.062	628	274	
298.00	13579	1.110	19.805	0.056	1.058	626	273	
298.16	13569	1.100	19.808	0.056	1.049	621	272	
322.83	15630	1.052	—	—	1.049	673	288	
323.15	15657	1.050	19.410	0.054	1.047	672	287	

T is the melting temperature in °K, P is the melting pressure in kgf/cm², ΔV is the volume discontinuity in the melting, in cm³/mole, V_s is the volume of the solid phase at the melting point, ΔS is the entropy of melting, ΔH and ΔU are the changes in the enthalpy and internal energy in the melting, in cal/mole, and R is the gas constant.

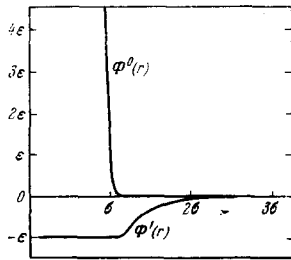


FIG. 8. Method proposed in [42] for decomposing a potential of the form $\Phi(r) = \epsilon f(\sigma/r)$ into two parts $\Phi_0(r)$ and $\Phi'(r)$. At high densities and temperatures, the energy due to the interaction $\Phi'(r)$ can be regarded as a perturbation.

$\Phi(r) = \epsilon(\sigma/r)^n$ is not, as is often stated, the high-temperature form of the more general potential $\Phi(r) = \epsilon[(\sigma/r)^n - (\sigma/r)^m]$. In fact, neglect of the attractive part of the potential (23) is possible only at very high densities. Secondly, it may be hoped that for intermediate densities the mean value of the perturbing energy is, in view of the sufficiently long range of the perturbing potential (see Fig. 8), almost independent of the concrete configuration of the particles, and the correction to the free energy of the system will have the van der Waals form, i.e.,

$$F \approx F_0 + \frac{a}{V}, \quad (29)$$

where a is a constant.

It is clear that these remarks clarify the viewpoint outlined earlier about the possibility of separating out a single term, depending on the configuration of the particles, in the energy of substances of the inert-gas type.

We turn again to consider the experimental data. The material presented in Table II and in Figs. 9–11 complete thermodynamic information about the melting of argon in the temperature range from the triple point (83.81°K) to 323°K. We recall that the critical temperature of argon, which can serve as a measure of the depth of the interaction potential, equals 151°K.

We shall consider Fig. 9, which depicts the temperature dependences of the entropy discontinuity $\Delta S/R$ and of the relative volume discontinuity $\Delta V/V_S$ in the melting of argon. It can be seen in Fig. 9 that the quantities $\Delta S/R$ and $\Delta V/V_S$, while decreasing rapidly in the low-temperature region, become practically constant at temperatures above 200°K. It seems highly probable that $\Delta S/R$ and $\Delta V/V_S$ remain finite at all temperatures and pressures. More informative from the point of view of establishing the asymptotic values of $\Delta S/R$ and $\Delta V/V_S$ is Fig. 11, where $\Delta S/R$ and $\Delta V/V_S$ are presented as functions of the volume discontinuity ΔV . It follows from Fig. 11 that as ΔV tends to zero, which is equivalent to the degree of compression and the temperature tending to infinity, $\Delta S/R$ and $\Delta V/V_S$ tend to finite values. Graphical extrapolation leads to the following asymptotic values:

$$\left. \begin{aligned} \frac{\Delta S}{R} &\rightarrow \sim 0.9, \\ \frac{\Delta V}{V_S} &\rightarrow \sim 0.03 \end{aligned} \right\} T \rightarrow \infty. \quad (30)$$

Thus, we have obtained extremely important results, enabling us to state that: 1) the melting temperature of substances of the argon type increases without limit on increase of the degree of compression; 2) the melting is a first-order phase transition at all temperatures and pressures, i.e., there is no critical point on the melting curve. We remark that these conclusions are in agreement with those of Sec. 2.

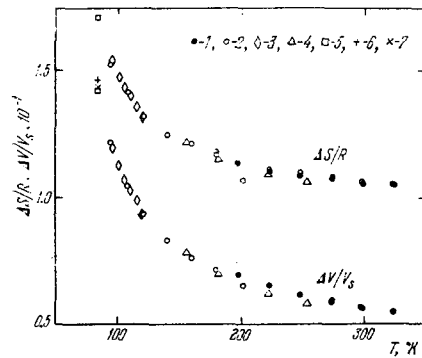


FIG. 9. Temperature dependence of the relative volume discontinuity $\Delta V/V_S$ and entropy discontinuity $\Delta S/R$ in the melting of argon, from the data of different authors. 1—[38]; 2—[35]; 3—[34]; 4—[36]; 5—[41]; 6—[44]; 7—calculated from the data of [45–46].

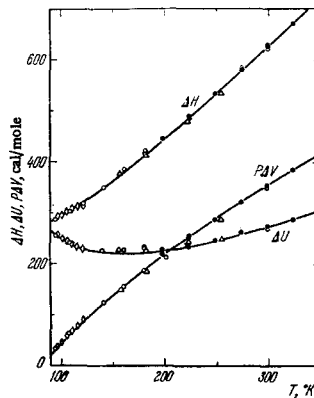


FIG. 10

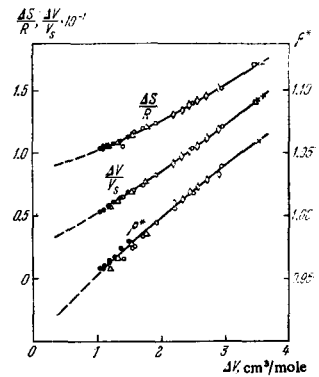


FIG. 11

FIG. 10. Changes in the enthalpy (ΔH), internal energy (ΔU) and free energy ($\Delta F = -\Delta F$) in the melting of argon, as functions of temperature (for the symbols, see Fig. 9).

FIG. 11. Relative volume discontinuity $\Delta V/V_S$, entropy discontinuity $\Delta S/R$ and reduced density of the solid phase ($\rho^* = \rho(\epsilon/kt)^{1/4}$) in the melting of argon, as functions of the volume discontinuity ΔV ($\Delta V \rightarrow 0$ corresponds to $P \rightarrow \infty$). $\rho = N\sigma^3/\sqrt{2V}$, where V is the molar volume of solid argon along the melting curve. For the quantities σ and ϵ in the calculation of ρ^* , the values of the corresponding parameters of the Lennard-Jones (6:12) potential of [31] were taken (for the symbols, see Fig. 9).

It is interesting to compare the relations (30) with the results of the computer experiments. From the data of Table I, in the melting of a model system of particles interacting in accordance with the law $\Phi(r) = \epsilon(\sigma/r)^{12}$ the entropy discontinuity and the relative volume discontinuity are equal to

$$\frac{\Delta S}{R} = 0.89, \quad \frac{\Delta V}{V_S} = 0.038. \quad (31)$$

Comparison of (30) and (31) shows the extremely close correspondence between the computer experiments and real experiments.

Additional information can be extracted from Fig. 11, which demonstrates the dependence of $\rho(\epsilon/kt)^{3/n}$ for solid argon on the volume discontinuity ΔV along the melting curve (for the symbols see Fig. 11). The quantity $\rho(\epsilon/kt)^{3/n}$ depends on the ratio of the repulsive energy to the temperature and is a constant for "soft" spheres with power-law repulsion. In fact, in this case, the relation $\rho(\epsilon/kt)^{3/n} = \text{const}$ is the melting curve in the coordinates $(\rho - T)$ (see Table I). For melting of a real substance, the $(\rho - T)$ coordinates of the melting curve depend both on the van der Waals corrections and

also on the other structure-sensitive terms in the potential energy apart from the energy of repulsion. However, in the limit, we may expect that the ratio $\rho(\epsilon/kT)^{3/n}$ will be close to the corresponding ratio for a system with a purely repulsive interaction. As can be seen from Fig. 11 and Table I, the ratio $\rho(\epsilon/kT)^{3/n}$ for argon tends to the characteristic value for a system of particles with repulsion described by the law $\Phi(r) \sim 1/r^{12}$.

The set of results obtained above makes it possible to conclude that the "characteristic" energy determining the crystallization of argon at high temperatures is indeed the energy of repulsion. We note that the numerical agreement between the relations (30) and (31) gives us the necessary proofs of the adequacy of the computer experiments for the real situation.

We shall consider the behavior of the quantities $\Delta V/V_S$ and $\Delta S/R$ in the low-temperature region, in which it differs substantially from the behavior in the case of systems of particles with repulsion only. It is clear that the explanation of this fact must be sought in the influence of the attractive interaction. A qualitative understanding of the effects associated with the influence of the attractive interaction on the thermodynamics of melting can be obtained in the framework of van der Waals theory, i.e., by considering the attraction in the spirit of mean-field theory^[47]. In fact, Fig. 12 demonstrates that the van der Waals corrections to the free energy ($-a/V$) and pressure ($-a/V^2$) lead to a decrease of the transition pressure and to an increase of the volume discontinuity ΔV as compared with the corresponding characteristics of the phase transition in the system without attraction. An increase in the entropy of the transition (the effect of increase of the "free" volume) should also appear as a consequence of the increase of the volume discontinuity^[43]. With increasing density and melting temperature, the contribution of the attractive interaction to the free energy and pressure of the system will decrease, and, consequently, a reasonable explanation is found for the qualitative aspects of the behavior of $\Delta V/V_S$ and $\Delta S/R$ in the melting of a real system (see Fig. 9). A calculation of the effect of attraction on the phase transition in a system of "soft" spheres, performed in^[28] by means of perturbation theory, is in complete agreement with these conclusions.

On the basis of the qualitative arguments given, it is possible to obtain approximate analytic relations characterizing the behavior of the relative volume discontinuity $\Delta V/V_S$ and entropy discontinuity $\Delta S/R$ along the melting curve for a real case.

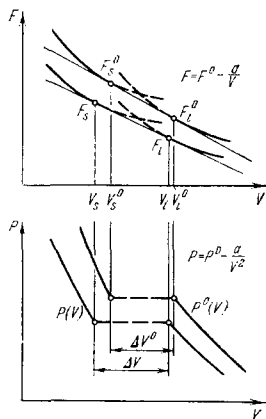


FIG. 12. Scheme illustrating the effect of an attractive interaction on the parameters of the phase transition.

We shall consider a system of Lennard-Jones particles at the melting temperature T . We remark that compression or expansion of this model system, which simulates the properties of the inert gases, is equivalent to changing the weight parameter of the attractive interaction^[6]. We write the nonideal free energy of the system in the form of a function of the thermodynamic variables and of the interaction weight parameter ξ :

$$\frac{\Delta F}{kT} = f\left(\frac{\rho^{n/3}\epsilon}{kT}\right) + \xi\varphi\left(\frac{\rho^{m/3}\epsilon}{kT}\right), \quad (32)$$

where ρ is the dimensionless density and ξ is the attractive-interaction weight parameter, taking values from zero to unity.

As follows from (32), for $\xi = 0$ the system under consideration goes over into a system of "soft" spheres with known melting characteristics. For non-zero values of ξ , the changes in the thermodynamic functions on melting no longer correspond to the case of soft spheres. However, if the energy of attraction is treated in the van der Waals approximation, the increments in the dimensionless thermodynamic quantities must be assumed to be proportional to the increment in the interaction weight parameter, the coefficients of proportionality being functions of the varying dimensionless quantities. The general form of these functions is not known, but in a number of cases we can make use of the smallness of the quantities being studied. Thus, we shall characterize the change in the relative volume discontinuity on variation of ξ by the relation

$$d\frac{\Delta V}{V_S} = \gamma\left(\frac{\Delta V}{V_S}\right) d\xi. \quad (33)$$

In view of the smallness of the quantity $\Delta V/V_S$, we shall expand $\gamma(\Delta V/V_S)$ in a series in powers of $\Delta V/V_S$. It follows from physical considerations that the expansion of $\gamma(\Delta V/V_S)$ has the form $\sum a_i(\Delta V/V_S)^i$. Retaining only the first-order term in the expansion, we have

$$d\frac{\Delta V}{V_S} = \zeta(T^*)\frac{\Delta V}{V_S} d\xi, \quad (34)$$

where T^* is the dimensionless temperature. Next, taking into account that the interaction weight parameter appears in the partition function only in combination with the temperature, we shall assume that

$$\zeta(T^*) = \frac{\alpha}{T^*}, \quad (35)$$

where α is a dimensionless constant. Finally, from (34) and (35) it follows that

$$\frac{\Delta V}{V_S} \approx \left(\frac{\Delta V}{V_S}\right)_0 \exp\left(\frac{\alpha\xi}{T}\right), \quad (36)$$

where $(\Delta V/V_S)_0$ is the relative volume discontinuity for melting in a system without attraction.

The formula (36) can be obtained in a certain approximation on the basis of purely thermodynamic arguments. We shall illustrate this with the example of a highly compressed substance.

For a system of repulsive particles at the melting temperature T we write the thermodynamic equality

$$P\Delta V = -\Delta F. \quad (37)$$

We shall introduce attraction in the van der Waals sense, i.e., we shall assume the energy of attraction to be equal to $-\epsilon V_0/V$. We shall regard ϵ as a variable. Then, by means of (37), we have

$$P d\Delta V = \frac{\Delta V}{TV_S} V_0 d\epsilon. \quad (38)$$

Here we are neglecting the influence of the attraction on the pressure and absolute volumes of the coexisting phases, which is possible in view of the high density of the system. Next we take into account that $P \sim T^{1+(3/n)}$ and $V_{l,s} \sim T^{-n/3}$. The volume of the effective sphere of interaction also depends on the temperature according to $V_s \sim T^{-n/3}$, since there are no temperature-independent characteristic quantities with the dimensions of volume in the system. Then from (38) we obtain a differential relation equivalent to (34):

$$d \frac{\Delta V}{V_s} \approx \frac{\alpha}{T} \frac{\Delta V}{V_s} d\epsilon.$$

Calculations show that the set of experimental data characterizing the behavior of the relative volume discontinuity in the melting of argon as a function of temperature (see Table II) is described with good accuracy by formula (36), with the following parameter values:

$$\left(\frac{\Delta V}{V_s}\right)_0 = 0.0385, \quad \alpha\epsilon = 109.33^\circ\text{K}. \quad (39)$$

We note that the numerical value of the quantity $(\Delta V/V_s)_0$, equal to the asymptotic value of $\Delta V/V_s$ for $T \rightarrow \infty$, agrees with the estimate (30) and agrees surprisingly well with the corresponding quantity (31)⁷⁾ obtained in the computer experiment for a system of particles with interaction potential $\Phi(r) \sim 1/r^{12}$. The parameter $\alpha\epsilon$ was found to be close to the Lennard-Jones potential depth, equal to $\sim 120^\circ\text{K}$ ^[31], i.e., the constant α is a quantity of order unity.

Table III contains the results of a calculation, by means of formula (36), of the quantity $\Delta V/V_s$ at the triple points of the inert gases; the value 0.038 was taken for $(\Delta V/V_s)_0$, and the Lennard-Jones potential depth was taken as the parameter $\alpha\epsilon$. As can be seen from Table III, the calculated values agree well with the experimental data.

One of the conclusions that can be drawn on the basis of the analysis given above is that the energy of attraction in the inert gases can be treated to a good approximation in the framework of van der Waals theory. It follows from this that the energy of attraction does not lead to qualitative changes in the character of the interparticle correlations. In this case, the dependence $\Delta S/R = f(\Delta V/V_s)$ can be represented in the form of an expansion in powers of $\Delta V/V_s$:

$$\frac{\Delta S}{R} = a + b \left(\frac{\Delta V}{V_s}\right) + c \left(\frac{\Delta V}{V_s}\right)^2 + \dots \quad (40)$$

In view of the smallness of the quantity $\Delta V/V_s$, in the expansion (40) we can retain the zeroth- and first-order terms only. As follows from Fig. 13, the dependence between $\Delta S/R$ and $\Delta V/V_s$ in the case of argon is indeed close to linear (for additional information on the entropy of melting, see below).

b) Sodium. As an object of study, sodium plays the same prominent role in metal physics as that of argon in molecular physics. The spherical Fermi surface and the negligibly small contribution of the direct short-range ion-ion interaction to the energy make sodium an ideal model of the metallic state of matter.

The total energy of a metal of the sodium type, excluding the thermal excitations, can be written as^[7]

$$E - E_{\text{therm}} = E_e + E_i, \quad (41)$$

where E_e is the energy of the electrons in the field of fixed ions and E_i is the electrostatic energy of the ions

TABLE III

	T, °K	ϵ , °K	$(\Delta V/V_s)_{\text{exp}}$	$(\Delta V/V_s)_{\text{calc}}$
Ne	24.57	36.3	0.153	0.166
Kr	115.95	159	0.151	0.150
Xe	161.36	228	0.151	0.156

T is the temperature at the triple point [41].
 ϵ is the energy parameter of the Lennard-Jones (6:12) potential [31].
 $(\Delta V/V_s)_{\text{exp}}$ are the experimental values of the relative volume discontinuity in the melting at the triple point [41].
 $(\Delta V/V_s)_{\text{calc}}$ are the calculated values of the relative volume discontinuity.

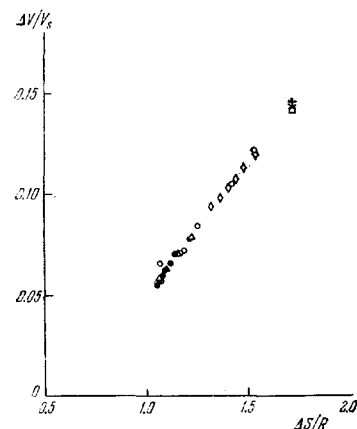


FIG. 13. Relationship between the relative volume discontinuity $\Delta V/V_s$ and entropy discontinuity $\Delta S/R$ in the melting of argon, from the data of [34-36, 38, 41, 44-46].

in a background of neutralizing uniform charge (the Madelung energy). The Madelung energy of a system of point ions has the form

$$E_l = \frac{Z^2 e^2}{r_a} \eta(s_1, \dots, s_N), \quad (42)$$

where $\eta(s_1, \dots, s_N)$ is a function of the dimensionless coordinates of the ions and r_a is the radius of an atomic sphere.

A physically visualizable interpretation of the electron energy can be obtained with the aid of the pseudo-potential concept^[48,49]. According to^[48,49], the electron energy E_e in second-order perturbation theory has the form

$$E_e = E_e^{(0)} + E_e^{(1)} + E_e^{(2)}, \quad (43)$$

where $E_e^{(0)}$ is the energy of the interacting electron gas and $E_e^{(1)} = \sum_{\mathbf{k}} \langle \mathbf{k} | W | \mathbf{k} \rangle$ is the mean value of the non-Coulomb part of the electron-ion interaction. For a local pseudo-potential $W(r)$,

$$E_e^{(1)} = \frac{c r_0^3}{V}, \quad (44)$$

where c and r_0 are the parameters of the pseudo-potential. It is not difficult to see that the expression for $E_e^{(1)}$ can be rewritten in the form

$$E_e^{(1)} = \frac{\epsilon' V_0}{V}; \quad (45)$$

where ϵ' is the characteristic energy, equal to $Z^2 e^2 / r_0$ in order of magnitude. We shall need this form of $E_e^{(1)}$ later on. $E_e^{(2)}$ the energy corresponding to the indirect pair interaction of the ions via the conduction electrons. In the one-electron approach to the problem of scattering of electrons by a collection of ions, $E_e^{(2)}$ can be written in the form

$$E_e^{(2)} = \sum_q |S(q)|^2 F(q), \quad (46)$$

where $S(q) = (1/N) \sum e^{-iqr}$ is the structure factor and $F(q)$ is the characteristic function, depending on the form factor of the isolated ion and on the screening properties of the electron gas.

It is important to emphasize that of all the components of the total energy only the ion energy E_i and the indirect pair interaction energy $E_e^{(2)}$ depend on the ion configuration, and, as we should expect, the contribution of the energy $E_e^{(2)}$ to the total energy of the metal is extremely small (Fig. 14).

Thus, the ion energy E_i makes the overwhelming contribution to the structural energy of the alkali metals.

The first experiments to study the thermodynamics of the melting of sodium were carried out by Bridgman at pressures up to 12,000 kgf/cm² [50]. These experiments were repeated many years later in the Institute of Crystallography of the USSR Academy of Sciences [51]. However, for a number of reasons, the accuracy of the data of [50, 51] has turned out to be inadequate for a reliable calculation of the changes in the thermodynamic functions on melting.

New results characterizing the thermodynamics of melting of sodium at pressures up to 22×10^3 kgf/cm² have now been obtained at the Institute of Crystallography [52]. Just as in the case of argon, the thermodynamic data were calculated on the basis of (P-V-T) measurements.

The measurements of the volume of sodium as a function of temperature and pressure were carried out by means of a piston piezometer, the general scheme of which is given in Fig. 15. The chief source of error

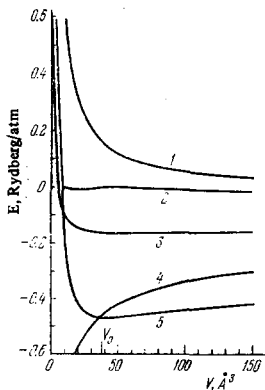


FIG. 14. Total energy of crystalline sodium and its separate components at $T = 0$, as function of the volume [7]. 1— $E_e^{(0)}$; 2— $E_e^{(2)}$; 3— $E_e^{(0)}$; 4— E_i ; 5— E ; V_0 is the sodium volume at $P = 0$.

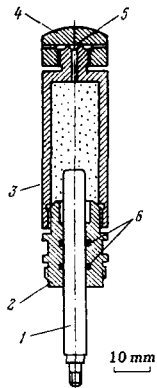


FIG. 15. Piezometer for measuring the volume of liquid and solid sodium. 1, 2—Piston pair; 3—casing; 4—sealing nut; 5—orifice for filling; 6—viscous grease. A screw thread on the piston 1 and the sleeve 2 serve as a mounting for the displacement gauge. In the measurements, the piezometer is situated inside a thick-walled high-pressure vessel (see Fig. 6).

is the possibility of loss of the substance, or of penetration of the medium transmitting the pressure into the piezometer cavity. This defect is characteristic, generally speaking, of all piston methods of measuring the volume, but, as we noted in Sec. 4(a), it is possible to avoid it if the measurements are carried out carefully.

Figures 16 and 17 and Table IV contain the results characterizing the thermodynamics of melting of sodium. The first thing that strikes one is the surprising similarity in the character of the behavior of the thermodynamic functions in the melting of sodium and argon (see Figs. 9, 10, 16 and 17); and although the asymptotic limit for $\Delta V/V_s$ as $\Delta V \rightarrow 0$ is not established here as distinctly as in the case of argon, the corresponding limit for $\Delta S/R$ undoubtedly exists and amounts to a quantity of the order of 0.7 (we note that $0.7 \approx \ln 2$; for the significance of this fact, see below). These results undoubtedly convince one that the concrete nature of the inter-particle forces exerts no substantial influence on the characteristics of the crystal-liquid phase transition, and, consequently, only certain general properties of the interaction energy are important for melting. As noted earlier, the structure-sensitivity of the total potential energy of any real system is clearly a qualitative property of this type [8]. In the specific case of sodium, the structure-sensitivity of the potential energy is determined principally by the ion energy E_i . In view of

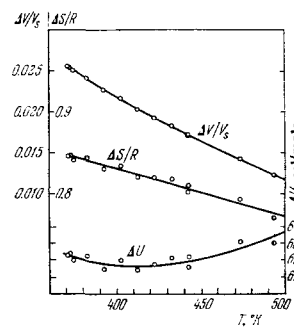


FIG. 16

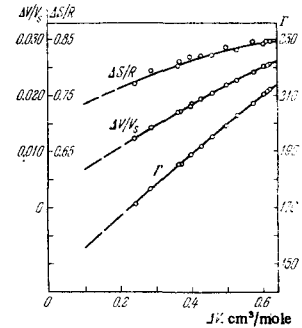


FIG. 17

FIG. 16. Temperature dependence of the relative volume discontinuity $\Delta V/V_s$, entropy discontinuity $\Delta S/R$ and internal-energy discontinuity ΔU in the melting of sodium [52].

FIG. 17. Entropy of melting ($\Delta S/R$), relative volume discontinuity $\Delta V/V_s$ and the parameter $\Gamma = e^2/r_0 kT$ as functions of the volume discontinuity ΔV in the melting of sodium ($\Delta V \rightarrow 0$ corresponds to $P \rightarrow \infty$). r_0 is defined from the condition $4\pi r_0^3/3 = V_s/N$, where V_s is the volume of solid sodium along the melting curve [52].

TABLE IV. Thermodynamics of the melting of sodium [52] (experimental data)*

T	P	ΔV	V_s	$\Delta V/V_s$	ΔH	$\Delta S/R$	ΔU
371.26	35	0.617	24.15	0.0255	624	0.846	623
372.53	183	0.613	24.11	0.0254	627	0.847	624
374.54	420	0.601	24.02	0.0250	627	0.842	621
382.63	1420	0.572	23.68	0.0242	645	0.845	624
392.50	2670	0.528	23.28	0.0227	648	0.831	615
402.36	4050	0.496	22.87	0.0217	668	0.835	620
412.33	5514	0.457	22.48	0.0203	673	0.822	614
422.34	7106	0.426	22.07	0.0193	688	0.821	618
432.16	8801	0.396	21.66	0.0183	703	0.819	622
442.11	10635	0.366	21.30	0.0172	713	0.811	622
442.58	10644	0.363	21.23	0.0171	706	0.804	616
473.15	17088	0.287	20.15	0.0142	747	0.794	632
493.15	22148	0.240	19.42	0.0124	755	0.771	631

*For the notation and units of measurement, see Table II.

this it is interesting to compare the crystallization of sodium with the phase transition in the model of the one-component Coulomb plasma (see Sec. 3). In fact, since the relative contribution of the pair interaction energy $E_e^{(2)}$ decreases on compression (see Fig. 14), and the purely volume terms $E_e^{(0)}$ and $E_e^{(1)}$ do not affect the coordinates of a phase transition with $\Delta V = 0$, the asymptotic value of the parameter $\Gamma = Z^2 e^2 / r_a kT$ as $\Delta V \rightarrow 0$ (here r_a is the radius of the atomic sphere of sodium at the melting temperature and T is the melting temperature) should be close to the corresponding value characterizing the crystallization of the one-component classical plasma. As can be seen from Fig. 17, the parameter Γ along the melting curve of sodium tends to a value ~ 150 , which is in agreement with the data of [30].

As regards the limiting values of the relative volume discontinuity $\Delta V/V_S$ and of the entropy discontinuity $\Delta S/R$, an extremely unusual situation arises.

It is well known that the stability of the alkali metals at moderate pressures is ensured exclusively by the non-Coulomb part of the electron-ion interaction, i.e., by the non-pointlike nature of the ions. The electron energy $E_e^{(0)}$ is almost independent of the volume of the system under moderate compression, and in practice can be regarded as an additive correction to the total energy. Therefore, the equilibrium volume at atmospheric pressure, the equation of state and the thermodynamics of the melting of sodium are functions of only two components of the total energy: the mean value of the non-Coulomb part of the electron-ion interaction $E_e^{(1)} \sim 1/V$ and the ion energy $E_i \sim 1/V^{1/3}$. Obviously, at high pressures the general character of the volume dependence of the free energy of sodium is determined principally by the energy $E_e^{(1)}$, while the existence of the phase transition (crystallization) is ensured by the structure-sensitive ion energy E_i .

Thus, the asymptotic values of the quantities $\Delta V/V_S$ and $\Delta S/R$ as $P \rightarrow \infty$, about which information can be obtained on the basis of the experimental data, will not correspond, generally speaking, to the values characterizing the crystallization of a classical one-component plasma.

It can be shown that, from a formal point of view, the limiting values of the quantities $\Delta V/V_S$ and $\Delta S/R$ in the melting of sodium correspond more closely to a hypothetical substance with a pair interaction of the form $\Phi(r) \sim 1/r^3$ (the divergence of the integral in the calculation of the energy of a system with interaction of the form $\Phi(r) \sim 1/r^3$ need not worry us, since we are concerned with a purely formal similarity, and, moreover, we can always add a small positive number to the power exponent). For this, we write the free energy of a metal of the sodium type, after subtraction of the ideal-gas and electronic components, in a form analogous to (32):

$$\frac{\Delta F}{kT} = f\left(\frac{\rho \epsilon'}{kT}\right) + \xi \varphi\left(\frac{\sqrt[3]{\rho} \epsilon'}{kT}\right); \quad (47)$$

in this formula ρ is the dimensionless density, ϵ' is the characteristic energy (the parameters determining ρ and ϵ' are obvious from (45)), and ξ is the weight parameter of the ion interaction.

It should be emphasized that, in contrast to the case of argon, the interaction weight parameter ξ cannot be equal to zero, but varies in a range from a very small

value δ to 1 (when $\xi = 0$ the phase transition disappears).

Thus, for $\xi \approx \delta$, which is equivalent to high density, the thermodynamic properties of the system depend almost exclusively on the single combined variable $\rho \epsilon' / kT$, and consequently, in the limit of very high pressures, the thermodynamics of the crystallization is determined by the relations

$$V_l \approx \frac{c}{T}, \quad V_s \approx \frac{c'}{T}, \quad P \approx bT^2, \quad (48)$$

$$\frac{\Delta V}{V_s} = \text{const}, \quad \frac{\Delta S}{R} = \text{const}.$$

Finally, the formal analogy between the thermodynamic characteristics (48) of melting for a model of an alkali metal and the corresponding properties of a system of particles interacting in accordance with the law $\Phi(r) \sim 1/r^{3+\Delta}$ is obvious (see Sec. 2).

It is interesting to compare the asymptotic value of the quantity $\Delta V/V_S$ (as $P \rightarrow \infty$) for sodium with the quantity $\Delta V/V_S$ that is characteristic of the melting of a hypothetical substance with interaction $\Phi(r) \sim 1/r^{3+\Delta}$. Direct information about the latter is unobtainable, but from the data of Table I this quantity can be assumed equal to 0.0025–0.0030. Extrapolation of the experimental data (see Fig. 17) agrees with this estimate⁹⁾.

Going over to the analysis of the behavior of $\Delta V/V_S$ as a function of temperature in the melting of sodium, we note that if we confine ourselves to representing the free energy of sodium in the form (47) we obtain an exponential formula of the type (36) for the dependence $\Delta V/V_S = f(T)$. However, despite the smallness of the second-order terms $E_e^{(2)}$ in the expansion of the electron energy, it is necessary to take account of their influence on the thermodynamic properties of the melting. The reasons for this necessity are connected with the obvious fact that the thermodynamics of a phase transition is determined not by the absolute values of the various quantities, but by the difference in their values in the coexisting phases. In the specific case of sodium, the difference in the energies $E_e^{(2)}$ in the solid and liquid phases at pressures close to atmospheric is comparable with the difference in the ion energies E_i ^[53]. Since the energy $E_e^{(2)}$ is a negative quantity and has a large absolute value for a disordered state of a substance, it is obvious that its influence on the phase transition reduces to an increase in the transition pressure and a decrease in the volume discontinuity. The correction that takes into account the effect of $E_e^{(2)}$ on the volume discontinuity has the form

$$\delta \Delta V \approx \frac{\Delta E_e^{(2)}}{P}, \quad (49)$$

where $\Delta E_e^{(2)}$ is the difference in the second-order electron energies in the solid and liquid phases.

Taking (49) into account and assuming that $\Delta E_e^{(2)} = \text{const}$,¹⁰⁾ we obtain for the correction to the relative volume discontinuity:

$$\delta \frac{\Delta V}{V_s} \approx -\frac{\text{const}}{T}. \quad (50)$$

The final expression for the temperature dependence of the relative volume discontinuity in the melting of sodium is

$$\frac{\Delta V}{V_s} \approx \left(\frac{\Delta V}{V_s}\right)_0 \exp\left(\frac{A}{T}\right) - \frac{B}{T}, \quad (51)$$

where $(\Delta V/V_S)_0$ is the asymptotic value for $\Delta V/V_S$ for $T \rightarrow \infty$, and A and B are constants. The calculations

show that the experimental values of $\Delta V/V_S$ characterizing the melting of sodium are described with good accuracy by the expression (51) with the following values for the constants:

$$\left(\frac{\Delta V}{V_S}\right)_0 = 0.0034, A = 847.6^\circ\text{K}, B = -2.69^\circ\text{K}. \quad (52)$$

We call attention to the fact that the quantity obtained for the asymptotic value of $\Delta V/V_S$ and the sign of the constant B correspond to the estimates given above.

Thus, just as in the case of argon, the analysis of the behavior of the thermodynamic quantities characterizing the melting of sodium leads to the conclusion that there is an unlimited increase in the melting temperature on compression, and no critical point on the crystal-liquid equilibrium curve.

To conclude this section, we note that at very high pressures the analysis of the thermodynamic properties of sodium, as well as the properties of other alkali metals, should include consideration of the energy of the short-range ion-ion repulsion, and the energy of the electron gas.

In the limiting case of complete ionization the model of the substance is again simplified, and we can confine ourselves to considering the ion energy E_i and the Fermi energy E_f of the electron gas. In these conditions, the behavior of the substance is determined to a substantial degree by the energy E_f , and the relations (48) undergo certain changes; in particular, in accordance with the dependence $E_f \sim V^{-2/3}$ the equation of the melting curve will have the form $P \sim T^{5/2}$, and the relative volume discontinuity $\Delta V/V_S$ hardly exceeds a few ten-thousandths (see Sec. 2 and^[30]).

c) **Thermodynamics of melting of cesium and nature of the maxima in the melting curves.** The discovery of temperature maxima in the melting curves of a number of substances (cf., e.g.,^[1,54]) has violated long-standing ideas about the shape of melting curves, built up under the influence of the experimental work of Bridgman. This discovery has been a powerful stimulus for the development of experiments to study melting, since it is precisely in the attempts to explain the nature of the maxima that the full weakness of the existing theoretical viewpoints has been revealed. A number of authors^[55,56] have effectively reactivated the old hypothesis of Tamman (cf.^[1]) about the existence of a universal temperature maximum for all substances, which, generally speaking, reduces to an assertion about the limited field of stability of the crystalline state of matter. It must be specially stressed that here we are not concerned with quantum phenomena and the associated "cold" melting of matter.

In this connection, it is necessary to recall that in considering simple models of matter with a power-law interaction we convinced ourselves of the existence of universal relations between the "characteristic" energy and the melting temperature:

$$\frac{\epsilon_0(V)}{kT} = \text{const} > 1, \quad (53)$$

which follow from the self-similarity of the partition function. The statements that there is a one-to-one relationship between the density of a substance and the melting temperature (cf. (5) and (19)) and that there is an unlimited rise in the melting temperature on compression are a rigorous consequence of (53). For melting of a real substance, the relation (53) is not valid in the

general case. However, as we have been able to see, for simple substances of the argon and sodium types there exist relations of the type (cf. Figs. 10 and 17)

$$\frac{\epsilon_0(V)}{kT} \rightarrow \text{const} \text{ as } P \rightarrow \infty. \quad (54)$$

It is not difficult to conclude that the hypothesis of a universal maximum is in contradiction with (54), since it requires an unlimited increase of $\epsilon_0(V)/kT$ on compression.

Thus, we can conclude that, for given constant parameters of the inter-particle interaction function, temperature maxima (like other anomalies) in the melting curves are impossible.

However, we can imagine a situation in which the relation of the type (54) will be violated. Primarily, this refers to those cases in which the character of the inter-particle interaction changes on compression.

We shall consider the characteristic case of cesium, the phase diagram of which possesses a number of remarkable features, including a double maximum in the melting curve^[57-59]. It is well known that at pressure 4×10^4 kgf/cm² a phase transition occurs in solid cesium without change of the crystal structure, and is usually associated with a transition of the valence electron from the s to a d state^[60-61]. There are grounds for assuming that a similar transition also occurs in liquid cesium, but, in view of a specific feature of the liquid state, this transition occurs continuously and begins at pressures of the order of 10^4 kgf/cm²^[58,59]. It is obvious that a change of the wavefunction of the valence electron should lead to a sharp change of the electron-ion interaction parameters and, consequently, to violation of the conditions under which limiting relations of the type (54) are valid.

The thermodynamics of the melting of cesium has been studied in the Institute of Crystallography of the USSR Academy of Sciences^[62]. The volume of the cesium was measured by means of a special piston piezometer with an intermediary liquid^[63] (Fig. 18). The cesium sample investigated was placed in a hermetic ampoule of stainless steel, with a well thickness of 0.05 mm. As can be seen from Figs. 15 and 18, the technique for measuring the volume of cesium was substantially more complicated than in the case of sodium; this was a consequence of the extremely high reactivity of cesium.

The results of the investigations are set out in Table V and are illustrated in Fig. 19. Analysis of the results obtained shows that at low pressures the behavior of the

TABLE V. Thermodynamics of the melting of cesium (smoothed data)^{[62]*}

T	P	ΔV	$\Delta V/V_S$	$\Delta S/R$	ΔH	ΔU
301.52	1	1.691	0.0243	0.8477	507.7	507.7
323.23	1 000	1.408	0.0210	0.8272	531.1	498.1
341.85	2 000	1.188	0.0194	0.8104	550.3	494.7
372.08	4 000	0.888	0.0146	0.7904	584.2	501.0
395.75	6 000	0.707	0.0124	0.7852	647.3	517.9
415.08	8 000	0.587	0.0108	0.7854	647.6	537.6
431.25	10 000	0.493	0.0096	0.7853	672.8	557.3
444.76	12 000	0.410	0.0083	0.7895	697.5	582.4
455.70	14 000	0.331	0.0069	0.8103	733.5	625.0
463.95	16 000	0.250	0.0054	0.8618	794.2	700.5
469.34	18 000	0.158	0.0036	0.9525	888.0	821.4
471.76	20 000	0.042	0.0012	1.0746	1007.0	987.3
471.20	22 000	-0.101	-0.0023	1.1864	1110.4	1162.7

*For the notation, see Table II.

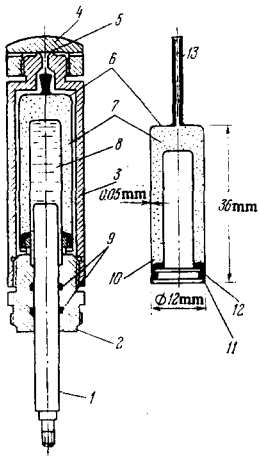


FIG. 18. Piezometer for measuring the volume of liquid and solid cesium [63]. This piezometer is analogous in many respects to the piezometer for measuring the volume of sodium (see Fig. 15), but differs from the latter by the presence of an inner hermetic ampoule, containing the cesium. The space between the walls of the piezometer cavity and the ampoule is filled with mercury. To calculate the volume of the substance being investigated at high pressures it is necessary to know the equation of state of mercury. 1,2—Piston pair; 3—casing; 4—sealing nut; 5—orifice for filling the piezometer with mercury; 6—ampoule containing cesium; 7—cesium; 8—mercury; 9—viscous grease; 10—deformable part of the ampoule; 11—welded joint; 12—base of the ampoule; 13—orifice for filling the ampoule with cesium.

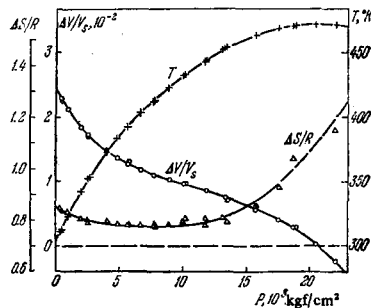


FIG. 19. Pressure dependence of the melting temperature T , relative volume discontinuity $\Delta V/V_S$ and entropy discontinuity $\Delta S/R$ in the melting of cesium [62].

thermodynamic quantities characterizing the melting of cesium agree, from a qualitative point of view, with the known results for argon and sodium. Moreover, it should be noted that the initial portion of the dependence $\Delta V/V_S = f(T)$ for cesium is well described by formula (51) with constants equal to $(\Delta V/V_S)_0 = 0.0032$, $A = 698.8^\circ\text{K}$ and $B = -2.39^\circ\text{K}$. We call attention to the fact that, as we should expect in this case, the value of the constant $(\Delta V/V_S)_0$ is practically the same for cesium and sodium. At high pressures, however, this agreement disappears. The sharp increase in the entropy of melting and the change in the character of the behavior of ΔV and $\Delta V/V_S$ along the melting curve are undoubtedly evidence of a fairly sharp change in the properties of compressed cesium.

Thus, the experimental data indicate explicitly that the appearance of the maximum in the melting curve of cesium is not a reflection of general tendencies, but, on the contrary, is an "anomalous" phenomenon. In fact, as is well known, at pressures above $(40-45) \times 10^3 \text{ kgf/cm}^2$, after the series of phase transformations has been completed, the situation in cesium becomes normal and the melting curve again acquires the "usual" form [57-59].

5. SPECIAL PROBLEMS

a) Entropy of melting. By analyzing the results of computer and real experiments, it is not difficult to conclude that the numerical values of the entropy of melting experience relatively small variations from substance to substance and, on average, amount to a quantity of the order of the gas constant R ($R \approx 2 \text{ cal/mole}$). To explain this fact, the hypothesis of a discontinuous increase in the "communal" entropy from zero to R on melting was formerly invoked [64, 65]. The essence of

this hypothesis is easily elucidated using a simple example.

We consider a system of N noninteracting particles in a volume V . The partition function of this system is $Z_1 = \lambda^{-3NVN}/N!$. We enclose each of the particles in a cell of volume V/N with impenetrable walls, and then obtain for the partition function: $Z_2 = \lambda^{-3N}(V/N)^N$. The difference in the entropies of the two systems equals

$$S_1 - S_2 = k \ln \frac{N^N}{N!} = Nk = R. \quad (55)$$

This hypothesis is certainly beautiful, but it is incorrect, since the liquid cannot be identified with a system similar to an ideal gas. Nevertheless, the result (55) is of undoubted interest as an upper limit for the entropy of disordering at constant volume. It seems probable that, together with this, there exists a certain minimum value for the entropy of disordering, responsible for the disappearance of only the long-range order in any given system of particles. Indeed, if this were so, the relative constancy of the values of the entropy of melting for different substances would not seem surprising.

Unfortunately, these considerations cannot be reinforced by a calculation of the number of states for a real disordered system of particles. However, the experimental results at our disposal shed some light on this important problem.

As we have seen in Sec. 4(a), the entropy of melting of argon can be represented in the form (40):

$$\frac{\Delta S}{R} = a + b \frac{\Delta V}{V_s} + c \left(\frac{\Delta V}{V_s} \right)^2 + \dots$$

An analogous expression can also be written for sodium. The constant a in the expression (40) corresponds to the change of entropy in melting without change of volume, which is not realizable physically. However, by varying the parameters of the inter-particle interaction and the conditions of melting (see Table I and Sec. 3), we can make the volume change in the melting sufficiently small. The question is: does the constant a in the expression (40) have any physical meaning?

This question is not unimportant, since in the hypothetical melting of a substance under conditions of constant V it is possible that the disappearance of the long-range order in the system is achieved in the most economical way, i.e., with the minimum change in the number of states. Thus, it is not ruled out that the entropy of melting for $\Delta V/V_S = 0$ characterizes the minimum "disorder" compatible with the absence of long-range order in a continuous system. However, it is not clear to what extent the value of the constant a depends on the specific properties of a real system of particles.

We call attention to Fig. 20, which demonstrates the inter-relationship between the discontinuity $\Delta S/R$ in the entropy of melting and the relative volume discontinuity $\Delta V/V_S$ for argon and sodium. It follows from the figure that the form of the functions $\Delta S/R = f(\Delta V/V_S)$ is the same for these two substances [11]. In this connection it is necessary to emphasize that the crystal structures of argon and sodium are different. For the asymptotic value of the entropy of melting we obtain the surprising result $\sim 0.7R$, [12] or [66]

$$\frac{\Delta S}{R} \rightarrow \ln 2 \quad \text{as} \quad \frac{\Delta V}{V_s} \rightarrow 0. \quad (56)$$

We recall that such a result for the entropy of disordering is characteristic for systems of particles whose

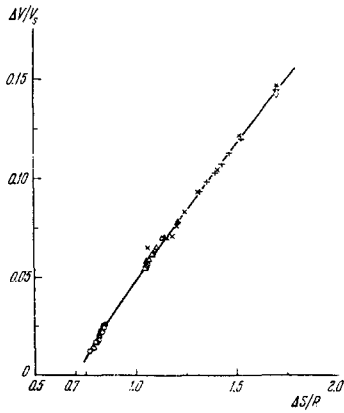


FIG. 20. Relationship between the relative volume discontinuity $\Delta V/V_S$ and entropy discontinuity $\Delta S/R$ in the melting of argon and sodium [66].

state is determined by a variable that can take only two values, e.g., for a system of spins with spin-value $1/2$. However, in the present case, the concept of two states of a particle in a dense system is clearly inadmissible. Below we shall attempt to show that the result (56) for the entropy of disordering can be obtained, with certain special assumptions, in the framework of a cell model.

We consider a system of N indistinguishable particles in a volume V divided into N numbered cells. The trivial state of the system with singly-occupied cells (Fig. 21a) is naturally identified with the ordered or crystalline state. It is clear that disordering of the system is possible in the framework of this model only when cells become multiply occupied. Inasmuch as we are attempting to model a system of high density, we shall take only double occupation into account (Fig. 21b).

The partition function of our system has the form

$$Z = \lambda^{-3N} \sum_{M=0}^N \frac{N!}{M! \{(N-M)/2\}!^2} \left(\frac{V}{N}\right)^M \left(\frac{V}{2N}\right)^{N-M}, \quad (57)$$

where M is the number of single particles and the combinatorial factor under the summation sign is the number of ways of distributing M particles and $(N-M)/2$ pairs of particles over N positions.

It is easy to see that the entropy change in the transition from the ordered state with $M = N$ to the disordered state is

$$\frac{\Delta S}{k} = \ln \sum_{M=0}^N \frac{N!}{M! \{(N-M)/2\}!^2} 2^{N-M}, \quad (58)$$

or, replacing the sum in (58) by its maximum term with $M = N/2$, we obtain for large N :

$$\frac{\Delta S}{R} = \ln 2. \quad (59)$$

Clearly, this discussion is not a solution, but rather a formulation, of the problem. Nevertheless, it can serve as a useful illustration of such ill-defined concepts as the long-range order and the order-disorder transition in a continuous system of coordinates.

b) Equation of the melting curve. In 1927, Simon proposed for the equation of the melting curve an empirical equation of the form [67]

$$\frac{P-P_0}{a} + 1 = \left(\frac{T}{T_0}\right)^c, \quad (60)$$

where P_0 and T_0 are the pressure and temperature of the triple point, and a and c are constants. At high pressures, the quantity P_0 can be neglected and (60) acquires the simpler form

$$P = AT^c + B \quad (61)$$

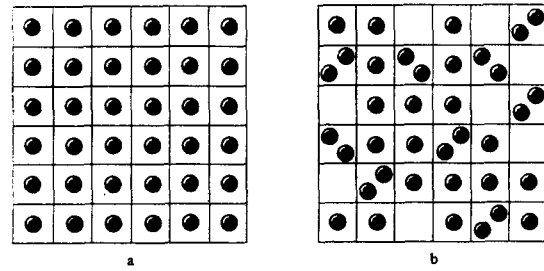


FIG. 21.

with three constants A , B and c . Equation (61) describes the experimental melting curves with good accuracy and is widely used for interpolation and extrapolation of experimental data [1, 68]. The numerous attempts to justify Eq. (61) have been mainly semi-empirical in character and have not led to positive results (see the bibliographies on this question in the reviews [1, 68]).

We shall show that Simon's equation cannot be rigorously justified for real substances, even in the limit of very high pressures.

As we have seen in Sec. 2 (Eq. (6) and Table I), the equation of the melting curve for a system of particles interacting in accordance with the law $\phi(r) \sim 1/r^n$ is

$$P = \alpha T^{1+(3/n)}, \quad (62)$$

where α is a constant. We shall take the attraction into account in the framework of perturbation theory (see Sec. 4(a)).

The first-order correction to the melting pressure will be equal to the ratio $\Delta \langle U' \rangle / \Delta V$ of the difference in the perturbation-energy values in the liquid and solid phases to the volume discontinuity in the melting in the unperturbed system (see Fig. 12). With the first-order correction taken into account, we obtain for the equation of the melting curve:

$$P = \alpha T^{1+(3/n)} - \frac{\Delta \langle U' \rangle}{\Delta V}, \quad (63)$$

or, using the van der Waals approximation for the perturbation energy, we shall have, using the relations (5),

$$P = \alpha T^{1+(3/n)} - \beta T^{6/n}. \quad (64)$$

Thus, we have convinced ourselves that Eqs. (52) and (53) should be regarded only as interpolation formulas. In practice, this means that the constants of Simon's equation are in fact pseudo-constants, and their numerical values should depend on the region of temperatures being investigated. As an example, in Table VI numerical values, calculated by the least-squares method for different temperature regions, are given for the constants of the Simon equation approximating the melting curve of argon. As can be seen from Table VI, the results of the calculation correspond to our expectations. On the other hand, the coefficients of Eq. (64), calculated for the same parts of the melting curve of argon with the assumption that $n = 12$, turn out to be sufficiently stable (Table VII).

In conclusion, we note that application of the Simon equation to describe the melting curves of metals, ionic crystals and other substances does not have even the slightest theoretical justification. As an example, we point out that at low pressures the equation of the melt-

TABLE VI. Parameters of the Simon equation $P = AT^c + B$ for the melting curve of argon (P is in kgf/cm^2 and T in $^\circ\text{K}$)

T	A	B	c	Literature
83.8—117.6	1.87462	-2158.883	1.591781	45
97.8—272.9	2.72620	-2338.475	1.52299	69
197.8—322.8	3.15742	-2390.0	1.49694	38*)

*In the calculation, the coordinates of the triple point are included in the data of [38].

TABLE VII. Parameters of the equation $P = \alpha T^{1.25} + \beta T^{0.5}$ for the melting curve of argon (P is in kgf/cm^2 and T in $^\circ\text{K}$)

T	α	β	Literature (experiment)
83.8—117.6	17.749	-491.288	45
97.8—272.9	17.879	-498.514	69
197.8—322.8	17.997	-504.096	38*

*In the calculation, the parameters of the triple point are included in the data of [38].

ing curve of an alkali metal has, in accordance with the results of Sec. 4(b), the form

$$P \approx -AT^{4/3} + BT^2 + CT, \quad (65)$$

where the first term is due to the ion energy E_i , the second arises from the mean energy of the electron-ion interaction $E_e^{(1)}$, and the third arises from the pair-interaction energy $E_e^{(2)}$.

c) Lindemann's melting criterion and some thermodynamic properties of coexisting phases. Lindemann's melting criterion states that the ratio of the mean amplitude of vibration of the atoms to the interatomic distance in the solid is a constant at the melting point^[1,70], i.e.,

$$\gamma = \frac{V \langle (\Delta R)^2 \rangle}{R} = \text{const.} \quad (66)$$

In the Debye approximation the relation (66) is usually written in the form¹³⁾

$$\frac{mV^{2/3}\Theta^2}{T_m} = C^2, \quad (67)$$

where m is the atomic weight, V is the molecular volume, Θ is the Debye temperature, T_m is the melting temperature, and C is a constant.

Despite its purely empirical origin, the Lindemann relation is widely used in geophysical and astrophysical applications, in the study of the Wigner crystallization of electrons, of the "cold" melting of highly compressed matter, etc. Naturally, the question arises of the theoretical justification of Lindemann's rule and its limits of applicability.

It can be shown that the Lindemann relation is a rigorous consequence of the self-similarity of the nonideal part of the partition function for a system of particles with interaction $\Phi(r) \sim 1/r^n$. In fact, in this case (see Sec. 2) the partition function has the form (3)

$$Z = \frac{V^N}{N! \lambda^{3N}} \int_{s_1} \dots \int_{s_N} \exp \left(- \frac{\rho^{n/3} \epsilon \sum_{i < j} s_i^{-n}}{kT} \right) ds_1 \dots ds_N,$$

where $s_i = r_i (N/V)^{1/3}$ are dimensionless coordinates and, since $\rho^{n/3} \epsilon / kT = \text{const}$ on the melting curve, the probability distribution function of the dimensionless coordinates is constant along the melting line for both

the liquid and the solid phases. This conclusion immediately leads to the result that the nonideal parts $S - S_i$ of the entropy and the mean values of the dimensionless coordinates of the particles in the liquid and crystalline states are constant along the melting curve. It is not difficult to see that this is precisely the essence of the Lindemann rule. We remark that the analog of the Lindemann rule for the liquid phase is the statement that the reduced pair distribution function $g(s_i, s_j)$ of the particles is unvarying.

To illustrate the above arguments we shall obtain the Lindemann relation from the constancy of the ratio of the potential and thermal energies along the melting curve for a system of particles with an inverse-power-law interaction. Thus, we have

$$\frac{U(r_1, \dots, r_N)}{kT} = \text{const.} \quad (68)$$

In the case of the crystalline phase, (68) can be rewritten in the form

$$\frac{Ar^{-n}}{kT} = \text{const.} \quad (69)$$

The temperature in (69) can be expressed in terms of the vibration amplitude of the atoms, from the expression

$$\langle \Delta R^2 \rangle = \frac{3kT \langle \omega^{-2} \rangle}{m}. \quad (70)$$

Assuming an Einstein spectrum, we have for the frequency:

$$\omega_E^2 = \frac{1}{m} \frac{\partial^2 \Phi}{\partial r^2} \sim \frac{1}{m} n(n+1) R^{-(n+2)}. \quad (71)$$

From (69), (70) and (71) we obtain

$$\frac{V \langle (\Delta R)^2 \rangle}{R} = \text{const.}$$

When we go over to consider the experimental data, we must emphasize that even in the case of a simplified model of a real substance, in which terms depending only on the volume are present, together with the structure-sensitive term, in the potential energy, the relations that follow from the self-similarity of the partition function lose their validity, generally speaking. But inasmuch as a uniform field applied to the system does not change the coordinate distribution function, changes in the nonideal entropy and in the mean dimensionless coordinates of the particles on the melting curve can only be the result of a change in the phase volumes at the coexistence point (see Fig. 12). The latter effect is not large, and we may expect that the nonideal entropy of the coexisting phases and the Lindemann constant will be practically constant along the melting curve for substances such as argon and sodium. Figures 22 and 23 and Tables VIII and IX clearly confirm the validity of the assumptions made.

Thus, we have verified that the Lindemann relation is a consequence of the self-similarity of the classical partition function of a system of particles with an interaction potential of the form $\Phi(r) \sim 1/r^n$ and cannot be regarded as a universal criterion of melting. Naturally, the limits of applicability of the Lindemann relation, just as for all other scaling relations following from (3), are determined primarily by the limits of applicability of classical statistics.¹⁴⁾ In view of this, attempts to determine the coordinates of "cold" melting, which is essentially a quantum phenomenon, on the basis of the Lindemann rule are unsound^[74] (concerning "cold melting", see^[2,74]).

6. FINAL REMARKS AND CONCLUSIONS

Thus, melting or crystallization is a universal physical phenomenon, characteristic of practically all substances. It is obvious that the responsibility for this phenomenon, which appears as a first-order phase

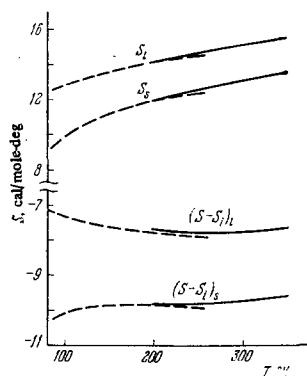


FIG. 22

FIG. 22. Entropy S and nonideal entropy $S - S_l$ of the solid and liquid phases of argon along the melting curve, as functions of temperature [72].

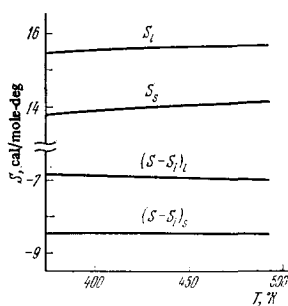


FIG. 23

FIG. 23. Entropy S and nonideal entropy $S - S_l$ of the solid (s) and liquid (l) phases of sodium along the melting curve, as functions of temperature.

TABLE VIII. Volume, entropy and Lindemann's constant along the melting curve of argon

T_m	V_l	V_s	S_l	S_s	$(S-S_l)_l$	$(S-S_l)_s$	Θ^*	c	γ	Literature
83.806	28.24	24.63	12.53	9.14	-3.632	-5.205	70.0	140.6	0.084	73
90	27.66	24.46	12.67	9.50	-3.648	-5.125	70.6	138.5	0.086	
100	27.00	24.24	12.83	9.91	-3.702	-5.064	72.9	133.3	0.087	
120	25.89	23.66	13.24	10.53	-3.763	-5.003	78.7	130.4	0.090	
140	25.00	23.08	13.47	11.01	-3.809	-4.949	84.7	128.8	0.092	
180	23.60	22.04	13.99	11.70	-3.869	-4.950	96.8	127.9	0.092	
220	22.54	21.20	14.38	12.20	-3.924	-4.962	108.7	128.2	0.092	
260	21.69	20.50	14.66	12.55	-3.966	-4.999	120.9	129.7	0.091	
198.15	22.931	21.437	14.224	11.963	-3.863	-4.934	101.5	126.5	0.093	72
223.15	22.339	20.977	14.473	12.274	-3.890	-4.934	108.5	126.6	0.093	
248.15	21.810	20.549	14.716	12.559	-3.903	-4.930	114.9	126.3	0.093	
273.15	21.331	20.150	14.950	12.858	-3.907	-4.903	120.1	125.0	0.094	
298.15	20.889	19.778	15.194	13.094	-3.895	-4.897	126.0	124.7	0.094	
323.15	20.479	19.428	15.446	13.369	-3.869	-4.862	130.3	123.2	0.095	
348.15	20.093	19.091	15.704	13.643	-3.832	-4.818	134.1	121.4	0.097	

T_m is the melting temperature in $^{\circ}\text{K}$, V_l and V_s are the volumes of the liquid and solid phases in cm^3/mole , S_l and S_s are the entropies of the liquid and solid phases in $\text{cal}/\text{mole. deg}$, $(S - S_l)_l$ and $(S - S_l)_s$ are the nonideal entropies of the liquid and solid phases in units of R ($S_l = (5R/2) + R \ln V + 3R \ln [mkt/2\pi h^2]/2$) Θ^* is the Debye temperature in $^{\circ}\text{K}$ (determined from the entropy with the aid of Tables of Debye functions), and $\gamma = (\Delta R)^{1/2}/R$ (in the calculation of γ it is assumed that $(\omega^2) = 5\omega_D^2/3$ and $(\omega^2) \approx 1/(\omega^2)$).

TABLE IX. Volume, entropy and Lindemann's constant along the melting curve of sodium*

T_m	V_l	V_s	S_l	S_s	$(S-S_l)_l$	$(S-S_l)_s$	Θ^*	c	γ
373.15	24.691	24.083	15.460	13.786	-3.436	-4.254	140.4	100.6	0.120
383.15	24.227	23.661	15.485	13.818	-3.444	-4.260	143.4	100.8	0.120
393.15	23.773	23.247	15.508	13.850	-3.452	-4.264	146.4	101.0	0.119
403.15	23.329	22.840	15.530	13.882	-3.460	-4.268	149.2	101.1	0.119
413.15	22.893	22.440	15.551	13.916	-3.467	-4.270	152.0	101.2	0.119
423.15	22.466	22.045	15.570	13.948	-3.474	-4.272	154.9	101.3	0.119
433.15	22.045	21.655	15.588	13.981	-3.482	-4.273	157.7	101.2	0.119
443.15	21.631	21.270	15.604	14.013	-3.489	-4.273	160.4	101.2	0.119
453.15	21.222	20.888	15.619	14.045	-3.496	-4.272	163.1	101.2	0.119
463.15	20.819	20.510	15.630	14.074	-3.504	-4.272	166.0	101.2	0.119
473.15	20.421	20.136	15.637	14.099	-3.512	-4.273	168.9	101.3	0.119
483.15	20.028	19.764	15.647	14.126	-3.519	-4.272	171.7	101.3	0.119
493.15	19.639	19.395	15.663	14.159	-3.523	-4.268	174.2	101.1	0.119

*For the symbols, see Table VIII.

transition, should be attributed to an equally universal property of the inter-particle interaction.

Regarding melting as the most general example of an order-disorder transition, it is natural to assume that the required universal property of the interaction is manifested in the structure-sensitivity of the potential energy. Generally speaking, this is a property of any realistic system of particles. In view of this, it is not surprising that the ability to crystallize is displayed or can be displayed in systems (molecules, atoms, atomic nuclei, neutrons, etc.) at the most diverse levels of the hierarchy of the material particles.

Thus, the highly general character of the problem of melting is obvious.

It is well known, however, that a theory of melting does not exist, and one of the principal reasons impeding its creation is the impossibility of an adequate description of the configuration space of a system with high density in the framework of lattice models with a large mesh. Nevertheless, in a certain sense it is possible to formulate an axiomatic approach to the problem of melting, making it possible to link together the conclusions following from statistical mechanics and the results of the real and computer experiments. The logical outline of this approach is described briefly below.

As is well known, in a number of the simplest systems (inert gases, alkali metals), the structure-sensitive or "characteristic" energy can be represented in the form of a power function of the particle coordinates. By considering the properties of model systems with a Hamiltonian in which the potential part contains only the "characteristic" energy (the "soft-sphere" model and the classical one-component plasma model) and postulating the existence of a first-order phase transition in these systems, it is not difficult, using the scaling relations, to obtain a number of rigorous relations characterizing the thermodynamics of the melting. The derivations of the impossibility of a critical point on the melting curve, of the unlimited increase of the melting temperature on compression, etc., are consequences of these relations. But confidence in the validity of the results obtained can be achieved only when the existence of the phase transition in the model systems studied is proved. Direct comparison with experiment is ineffective here, inasmuch as the numerical coefficients in the relations following from the scaling theorem are unknown. However, by bringing the results of the computer experiments into the analysis, we obtain simultaneously the necessary proof of the existence of phase transitions in the model systems and a proof of the validity of identifying the "characteristic" energy responsible for the melting with the energy of repulsion (in the case of the inert gases) and with the ion energy (in the case of the alkali metals).

The analysis of the experimental data characterizing the melting of argon and sodium are in complete accordance with the interpretation of the melting as an order-disorder transition, and demonstrates that the qualitative trends in the behavior of the thermodynamic functions along the melting curve are independent of the nature of the "characteristic" energy. The actual nature of the "characteristic" energy determines the temperature and heat of melting and the magnitude of the volume change, but, as we should expect, the value of the entropy of melting is a highly stable characteris-

tic of the melting. Moreover, all the existing data force us to assume that there exists a limit determining the minimum value of the entropy of melting, equal to $\sim R \ln 2$. It is obvious that this quantity is closely connected with the disappearance of the long-range order on melting and characterizes the minimum "disorder" consistent with loss of long-range order in a continuous system. It appears that an explanation of this fact could shed new light on the nature of the liquid state.

We shall say a few words about maxima in melting curves. It follows from the material cited in this review that a universal maximum in the melting curve is impossible in the case of given constant parameters determining the form of the "characteristic" energy (here we do not consider quantum effects, the influence of which can be important only at astrophysical pressures). From this point of view, maxima in the melting curves of simple substances must be regarded as "temporary" transient phenomena, arising as a result of a change in the inter-particle interaction function.

It should be emphasized that in the study of anomalies in melting curves a general approach is evidently impossible, and each case must be treated specifically. This remark applies to a still greater degree to substances with covalent interaction, which are not considered in the present article.

In conclusion, the author thanks L. V. Keldysh, A. P. Levanyuk and S. A. Pikin for discussion of a number of the problems described in this article. The author is also grateful to Ya. B. Zel'dovich, D. A. Kirzhnits and I. N. Makarenko, who read the entire article and made many valuable comments. In addition, the author would like to record that discussions with V. A. Abovskii facilitated the elucidation of the question of the influence of attraction on the form of the melting curve.

¹⁾As is well known, it follows from the Landau theory that a line of second-order phase transitions cannot exist for a crystal-liquid transition [20]. We remark that this conclusion was reached by considering the order parameter to be the one-particle distribution function, which, in the case of a liquid or gas, is a quantity proportional to the macroscopic density, and in the case of a crystal is a periodic function with maxima at the lattice sites. It is clear that, in principle, this supposes the possibility of existence of crystals with an infinitesimally small amplitude of oscillation of the one-particle distribution function, which is unlikely.

²⁾We note that in the "compressible-lattice" model [9,10] it is possible to avoid the basic difficulty of the theory of Lennard-Jones and Devonshire—the appearance of a critical point on the equilibrium curve.

³⁾It is interesting to note that decrease of the mesh size in an order-disorder transition in two-dimensional lattice systems of hard particles leads to a change of the type of phase transition [11]. This leads to the thought that the nature of melting as a first-order phase transition is somehow related to the continuous nature of space.

⁴⁾The discovery of a van der Waals loop in a system of 870 hard disks [19] is considered to be the only direct proof of the existence of a phase transition in a system of artificial particles. However, in view of the well-known theorem of Peierls (see [20-22]) on the instability of a two-dimensional crystal at $T \neq 0$, the nature of this transition is not entirely clear.

⁵⁾It is necessary to emphasize that in fact the many-particle interaction in the inert gases, including argon, is not negligibly small [32,33]. Therefore, the potential (23) should be regarded only as an "effective" pair potential, which indirectly takes the contribution of the many-particle forces into account.

⁶⁾The introduction of a weight parameter for the attractive interaction means, in the present case, that the inter-particle interaction potential of the system is written in the form $\Phi(r) = \epsilon[(\sigma/r)^n - \xi(\sigma/r)^m]$, where ξ is a dimensionless coefficient taking values from zero to unity.

⁷⁾In view of the substantial approximations made in the analysis of the

behavior of $\Delta V/V_S$, the very precise agreement between the quantities $\Delta V/V_S$ from (31) and (39) must be admitted to be fortuitous.

⁸⁾In discussions we often start implicitly from the statement that the potential energy is always a minimum for an ordered state of a substance. We note that there is no general proof of this statement [6].

⁹⁾It should be kept in mind that, since the contribution of the energy of the interacting electron gas to the thermodynamics of melting of sodium is extremely small in the region of moderate pressures, the extrapolation to infinite pressure gives properties that are characteristic not of sodium itself but of the model taken to describe the properties of sodium in the region of moderate pressures.

¹⁰⁾The quantity $\Delta E_g^{(2)}$ depends primarily on the mean configurations of the particles in the liquid and in the solid state (cf. (46)), which can be regarded as given along the melting curve.

¹¹⁾We remark that a universal relation between $\Delta V/V_S$ and $\Delta S/R$ represents a kind of "scaling" for melting.

¹²⁾The results of the computer experiments do not contradict the conclusion cited above (see Table I). However for the sake of objectivity, we should point out that the experimental results for polyvalent metals do not follow the dependence shown in Fig. 20. But in these cases a substantial contribution to the entropy of melting from the electronic component is possible. It is important, for us, to emphasize only the fact that cases in which the entropy of melting is smaller than $0.7R$ have not yet been recorded. The interested reader can verify this by making use of any handbook of physical and chemical constants.

¹³⁾The general expression for the mean-square amplitude of the vibrations is [71]

$$\langle \Delta R^2 \rangle = \frac{1}{Nm} \int \frac{\epsilon(\omega, T)}{\omega^2} g(\omega) d\omega,$$

where $\epsilon(\omega, T)$ is the vibrational energy of the mode with frequency ω and $g(\omega)$ is the frequency distribution function. In the Debye approximation the Lindemann melting criterion for $T > \Theta$ has the form

$$\gamma = \sqrt{\frac{9T_m \hbar^2}{m \Theta^2 k R^2}} = \text{const.}$$

For a frequency spectrum of arbitrary forms at high temperatures, we have

$$\gamma = \sqrt{\frac{3kT \langle \omega^{-2} \rangle}{m R^2}}.$$

¹⁴⁾It is easy to see that in the quantum case one more dimensionless parameter determining the properties of the system and including Planck's constant appears ($\hbar^2 \rho^{2/3} / mkT$), and thus the scaling relations that follow from the classified partition function for a system of particles with a power-law interaction (cf. Sec. 2) do not hold for a quantum system of particles.

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