Entropy, disorder, melting

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Usp. Fiz. Nauk **154**, 93–122 (January 1988)

The connection of geometric or spatial disorder and entropy is examined. The formulation of the problem of the entropy of a geometrically disordered system is asserted to make no sense if one does not stipulate the method of "preparing" it. The nonergodicity of geometrically disordered systems and the conditionality of their thermodynamic analysis are stressed. The relative constancy of the entropy of melting of simple classical substances is explained by the weak dependence of the entropy of a simple liquid on the number of particles involved in collective motion and collectively utilizing the accessible space. Certain features of quantum and low-dimensional sytems are discussed.

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INTRODUCTION

The concept of "entropy" is associated in our minds with disorder. However, we rarely consider the content of the concept of "disorder" itself, and in hard cases we intuitively resort to images of spatial or geometric disorder. Yet in fact, entropy, which by definition is the mean logarithm of the statistical distribution function, can serve only as a measure of the uncertainty of our knowledge of the microscopic state of a system of many particles. The term "disorder", often associated with the concept of entropy, should be understood only in the sense that the microscopic state of a system of many particles is fixed by a set of random quantities that can be calculated on the basis of probability laws. The total entropy of a system, while characterizing the statistical "disorder", is not always directly connected with spatial or any other order of the material. For this reason an overall thermodynamic analysis cannot replace the analytical methods based, e.g., on the concept of the order parameter. However, owing to the fundamental nature of entropy and the possibility of studying it experimentally, the study of the problem of the connection of entropy with concrete disordering phenomena seems very important. Here the problem of spatial or geometric disorder merits special attention in connection with the vigorous development of studies in the field of amorphous and vitreous materials, liquid crystals, and materials of low dimensionality.

A convenient starting point for discussing the problem as a whole is the problem of the entropy of melting, to which this article is mainly devoted. At the same time we shall take up other questions that bear upon the problem being treated.

We should add that several monographs[1–5] at different levels have appeared in recent years that discuss to some degree problems close to the theme of this article. The interested reader will find much supplementary information there.

1. ENTROPY OF MELTING OF SIMPLE SYSTEMS

As is known, the entropy of melting of simple substances (i.e., substances consisting of particles having a spherically symmetric interaction) undergoes relatively small variations, and has a value of the order of the gas constant R, or 1.95 cal/mole (Richard's law).[6,7] An attempt to explain this law was undertaken by Hirschfelder, Stevenson, and Eyring in 1937 within the framework of concepts of "collective" entropy[8] (see Sec. 3), but it was criticized in a study by Rice[9] (see also Ref. 48). Rice's main argument involved the results of early thermodynamic studies of the melting of simple substances at high pressures, which appeared to indicate that the entropy of melting varies substantially upon compression.

Interest in the problem of melting arose again in the 60s in connection with the technique of "numerical" experiments based on fast computers and new experimental studies at high pressures.[10,11] The real and the "numerical" experiments confirmed the remarkable constancy of the entropy of melting of simple systems.[11,12]

In 1973 a group of authors from the Institute of Crystallography of the Academy of Sciences of the USSR[13] studied the interrelation of the entropy of melting ΔS and the relative volume discontinuity $\Delta V/V_S$ for argon and sodium, and established that: 1) the $\Delta S(\Delta V/V_S)$ relationship is universal in form; and 2) the limiting value of the entropy of melting as $\Delta V/V_S \to 0$ equals $\approx 0.7R$ or $\approx R \ln 2$ (Fig. 1). Subsequently this observation has been confirmed for other examples and has been discussed in Refs. 14–24. An attempt was undertaken[16,21,24] to extend the "ln 2 law" to the melting of alkali-halide crystals and the melting of the halide sublattice in superionic phase transitions in the halides of the alkaline-earth metals.

A very interesting situation was found in studying the melting of the hydrogen (deuterium) sublattice in the hy-

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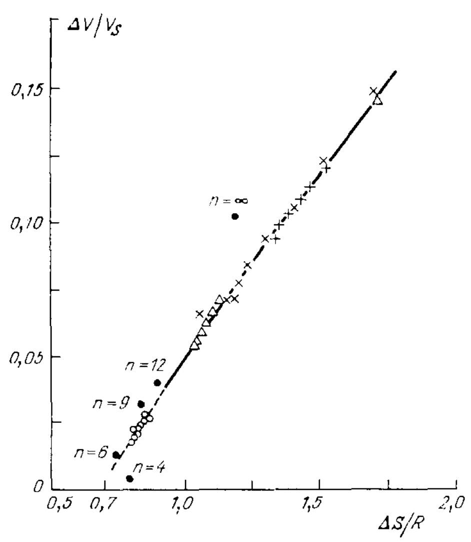

FIG. 1. Interrelation of the relative volume jump $\Delta V/V_S$ and the entropy of melting $\Delta S/R$ for Ar and Na.[11,13] The solid dots denote the results of "numerical" experiments in systems with an interaction of the form $\Phi(r) \sim r^{-n}$.[12]

drides (deuterides) of the transition metals. In the systems V–D and Ta–D as the metal-deuterium ratio approaches unity, the entropy of disordering (melting) approaches a value of the order of 0.7 R.[25,26] Curiously, the entropy of "melting" of the electronic subsystem in magnetite Fe_3O_4 also proves to be very close to 0.7 R or R ln 2 (0.65 R [27]).[1)]

The presented examples indicate that apparently the problem of the entropy of melting is not local, but is closely connected with a multitude of other phenomena of configurational disorder.

Thus the fifty years of development that have elapsed from the time of the hypothesis of Hirschfelder *et al.*[8] have led only to replacing the "ln e" problem with the "ln 2" problem. Yet we must stress that the degree of closeness of the experimentally determined asymptotic value of the entropy of melting to the value ln 2 remains unclear. In other words, the approximate estimate $\sim 0.7\ R$ can imply with equal success either $\ln 2 = 0.69$ or, e.g., $2/3 \approx 0.66$ (on this topic see Ref. 18). The fundamental importance of this problem is evident. Indeed, if we nevertheless are dealing with an ln 2 law, rather than simply with a number ≈ 0.7, then a liquid is nothing other than a two-level system, and the solution of the ln 2 problem reduces to seeking a satisfactory picture of two different states of particles in a simple liquid.

2. LIQUID, GLASS, AND "RESIDUAL" ENTROPY

It is logical to seek clarification of whether the existence of an excess entropy as compared with the crystal is a necessary property of any spatially disordered state of matter.

One of the best known examples of disordered substances differing from a liquid is a glass. Formation of a vitreous phase occurs easily in a number of inorganic and organic compounds and metal alloys. Simple substances do not form glasses under real conditions. However, in "numerical" experiments, where extremely large rates of supercooling are attainable, glasses can be formed also in very simple model systems.[19,29-34]

It is often stated that a glass possesses a quite finite so-called "residual" entropy at a temperature of absolute zero. What is this residual entropy? Let us study as an example the behavior of the heat capacity of ethanol in the temperature region of crystallization and vitrification[34] (Fig. 2). Figure 3 shows also the corresponding data for a model system of particles having an interaction of the form $\Phi(r) \sim r^{-12}$ from the data of "machine" experiments.[32]

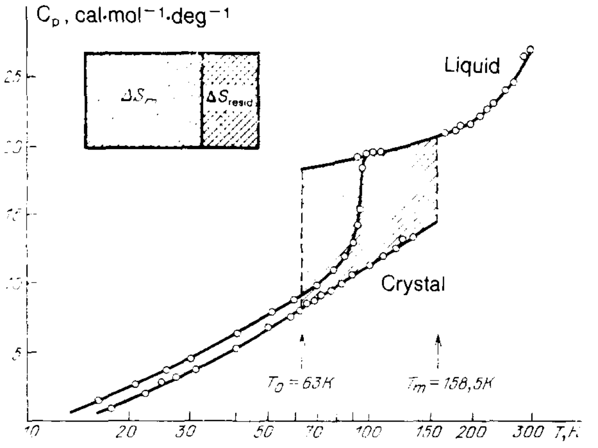

FIG. 2. Heat capacity of ethanol in the region of melting and vitrification.[34]

As we see from Figs. 2 and 3, the heat capacity of the liquid is always larger than that of the crystal in the supercooling region, while the difference in heat capacities rises with decreasing temperature. As was first noted by Kauzman,[35] this fact imposes a strong lower bound on the region of existence of the liquid phase. Actually, the higher heat capacity of the liquid implies a high rate of decline of the entropy of the liquid upon cooling. Upon extrapolating the heat capacity of the supercooled liquid into the low-temperature region and calculating its entropy, we must conclude that a certain temperature T_c exists where the heat capacity of the system must decline sharply. In the converse case, unless something happens with the system on further temperature decrease (crystallization or vitrification), the entropy of the system at $T = 0$ will be less than that of the crystal obtained by equilibrium crystallization (Kauzman's

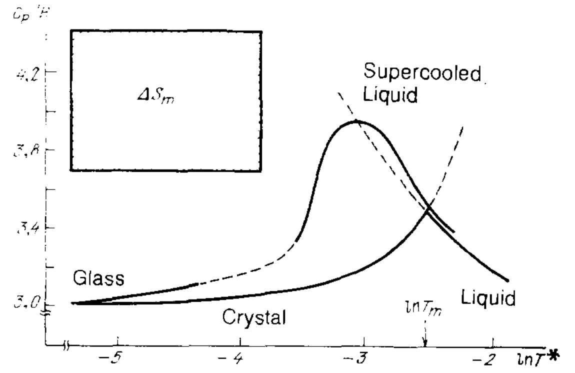

FIG. 3. Heat capacity of a model system of soft spheres with $\Phi r \sim r^{-12}$ in the region of melting and vitrification.[32]

paradox). In fact the vitrification temperature is always higher than Kauzman's temperature T_c (see Fig. 2). Consequently the overall entropy change throughout the path of cooling the liquid and glass from the melting point to $T = 0$ proves smaller than the entropy of the liquid at the melting point. To maintain balance, we must consider that the entropy of the glass at $T = 0$ has a nonzero value. This value has been called the "residual" entropy. In order of magnitude the "residual" entropy of the glass amounts to an appropriate fraction of the entropy of melting, but its concrete value depends on the prehistory of the specimen (Table I).

For simple model systems in numerical experiments the following values of the residual entropy of a vitreous phase were obtained: system of hard spheres $0.5\,R$ [33]; R [30]; system of Lennard-Jones particles at constant pressure $\approx 0.7\,R$ [31]; the same system under isochoric conditions ≈ 0[19];[2)] system of soft spheres ($\Phi \sim r^{-12}$) $\approx 0.3\,R$.[32]

Thus, apart from the numerical experiment of Ref. 19, the real and numerical experiments reveal that glasses possess an appreciable residual entropy. The impression arises that actually a static (apart from zero-point vibrations) spatially irregular system of particles possesses a nonzero entropy.

Let us write the Boltzmann expression for the entropy

$$S = k \ln W, \tag{1}$$

where W is the number of microstates corresponding to a given macroscopic state of the system.

In our case we should take W to be the number of distinguishable configurations of the particles compatible with the given energy. However, at $T = 0$ the particles constituting the glass practically do not move, and their mutual arrangement in the given concrete specimen is just as unique as the distribution of particles in a crystal. The possibility in principle of realizing a multitude of other energetically equivalent configurations plays no role here, owing to their unattainability.

Thus it would seem that we have no other recourse than to accept that for a glass $W = 1$ at $T = 0$, and hence, $S = 0$. Apparently this contradicts the conclusion of nonzero entropy of a disordered system of particles.

Let us try again to analyze this problem by rewriting the expression for the entropy in another, yet equivalent form:

$$S = k \ln \Delta\Gamma. \tag{2}$$

Here $\Delta\Gamma = \Delta p \cdot \Delta q / (2\pi\hbar)^2$ is the statistical weight, and $\Delta p \cdot \Delta q$ is the phase volume occupied by the system.

This expression offers us nothing new as compared with Eq. (1) in observing the evolution of a vitreous phase in time. If the chosen configuration of particles is separated from the energetically equivalent configurations by impenetrable barriers, then the phase trajectory of the systems will be enclosed in a phase volume practically equal to that of the corresponding crystalline phase.

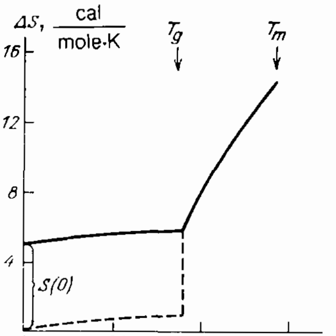

FIG. 4. Entropy difference of supercooled and crystalline glycerol.[37] T_m—melting temperature; T_g—vitrification temperature; $S(0)$—"residual" entropy. Dotted line—behavior of the entropy difference under the assumption that the entropy of supercooled glycerol decreases jumpwise at the vitrification point.

However, if one prepares an ensemble of corresponding systems, i.e., in our case a sufficiently large number of macroscopically equivalent specimens of glass, then their image in phase space will be represented by a cloud of points filling a substantially greater volume than the volume obtained upon studying the time evolution of one specimen.

This seemingly paradoxical result involves a very simple fact. The point is that the liquid that is the starting material for preparing the glass constitutes an essentially degenerate system. That is, a particular energy in the given case corresponds to a multitude of different spatial configurations. However, since we have no way each time to control the concrete configuration in preparing the systems of the ensemble, each frozen system (glass) inherits only the configuration of particles, to a certain degree random, that corresponds to a certain instantaneous configuration of the mother liquid.

Thus, in the given case averaging over time and averaging over the ensemble lead to different results. This indicates the nonergodicity, or if appropriate, the nonequilibrium of the system. The difference between nonergodicity and nonequilibrium is not essential in our discussion, since the relaxation time of the vitreous state is in any case very large on the laboratory time scale.

The nonstandard situation that has arisen directly bears on the problem of the residual entropy and generally requires a nonstandard approach to the interpretation of the thermodynamic experiment.

The usual way to analyze the experimental data (Fig. 4) reduces to a formal interpretation of the heat capacity of

TABLE I.[36]

	Silica	Ethanol	Glycerol
$S(0)/R$	0,45	1.3	2.3
$S(0)/\Delta S_m$	0.9	0.3	0.3

$S(0)$—value of the "residual" entropy; ΔS_m—entropy of melting.

the metastable liquid and the glass within the range from the melting point down to absolute zero, which yields a deficit of entropy as compared with its overall change in heating and melting of the crystalline phase.

Let us examine the situation that arises in vitrification in greater detail.

Upon cooling the metastable or supercooled liquid, the system proves to be trapped in a certain restricted volume of configuration space that corresponds to practically a single, randomly chosen configuration of particles. In general, one might close the discussion with this, assuming that the system has become nonergodic, and it makes no sense to formulate the problem of the entropy of the ensemble from its single realization. However, one can treat a restricted ensemble that includes only the configuration of the particles fixed in the sense of the mean value of the coordinates.

In this case we must assume that the "configurational" entropy of the system declines to zero at the point (region) of vitrification. This view involves purely psychological difficulties, since we always expect the decline in entropy to be accompanied by the release of the corresponding amount of heat. In the given case this does not happen, since the system, while lying in a configurational "trap", cannot relax to a configuration of lesser energy, at least within the time of a standard thermodynamic experiment. The only observable result of the described process must be a rather sharp decline in the heat capacity owing to "freezing out" of the configurational degrees of freedom. Following this logical schema, the break in entropy that arises upon integrating the experimental heat capacity must be referred to the vitrification temperature (see Fig. 4), which frees us from the need to attribute a finite value to the entropy of a spatially disordered system at $T=0$.

Consequently we must conclude that the "numerical" values of the "residual" entropy are not a characteristic of statistical disorder, but can serve as a measure of the number of configurations in the mother liquid at the instant preceding vitrification (see also the discussion in Refs. 36 and 38).

Thus the entropy of the liquid, which is large in comparison with the crystal, is not at all caused by the lack in it of translational symmetry, but arises from the concrete physical situation, which enables realizing a large number of microstates.[31] We shall see below that situations can occur in which the liquid has an entropy lower than that of a crystal existing at the same temperature and density.

Above we have assumed implicitly that the atomic configuration in the glass is stationary and does not vary in time. In this case the only type of motions accessible to the particles of the glass amounts to small vibrations with respect to the equilibrium positions. Naturally, here the low-temperature heat capacity of the glass must be described by the Debye law $C\sim T^3$. However, as it has turned out, to describe the experimental data has required introducing an additional term linear in the temperature.[39] The theory of the low-temperature heat capacity of a glass constructed in Refs. 40 and 41 based on a model of tunneling states indicates that a fraction of the barriers separating the energetically close configurations is penetrable.

The standard two-level variant of the model of tunneling states is apparently not exhaustive. Yet, in general it correctly predicts a number of observable effects, including the approximate logarithmic dependence of the heat capacity on the time of observation.[42] The observed low-temperature phenomena are common to a broad class of the so-called "nonergodic" systems, including dielectric and metallic glasses,[42,43] "frozen" orientationally disordered systems,[42] spin glasses,[44] etc.

We should assume that also superbarrier transitions can occur at high temperatures that couple different configurational states in disordered systems. The early measurements of the heat capacity of vitreous glycerol at temperatures several degrees below the vitrification point showed that, if the time of measurement is as much as tens of hours, then the heat capacity acquires values corresponding to extension of the liquid curve.[45] However, on further lowering of the temperature, the relaxation times become so great that such experiments become practically impossible.

Evidently, by measuring time in historical segments, e.g., millennia, we might extend the region of stability of the liquid state to lower temperatures. The result of further expansion of the time scale substantially depends on the character of the energy barriers that separate the different configurational states. If at least some of these barriers are infinite, then the corresponding relaxation times are infinite, which leads to a nonergodicity in principle of the system as a whole.

In the case of "configuration" glasses and "configurationally" amorphous systems, we must also introduce the time of relaxation to the crystalline state, which apparently is finite. Therefore, if we measured the time on geological scales, then the problem of certain amorphous and vitreous substances simply would not exist. Instead the problem would arise of short-lived nonequilibrium states—precursors of metastable crystallization. In this sense a completely different situation exists in the case of systems where the ordered state cannot be realized in principle; they include, e.g., spin glasses. Naturally, such a system will be "amorphous" at any scales of the time of observation.

3. "COLLECTIVE" ENTROPY AND ENTROPY OF MELTING

"Collective" entropy is defined as the difference in entropy of two systems, in one of which the motion of the N particles in the volume V is in no way restricted, whereas in the other each particle is enclosed in a cell with impenetrable walls of volume V/N.[46]

Although the concept of "collective" entropy is somewhat artificial, nevertheless it can be usefully employed in the context of this article. Actually, as is implied by the definition, collective entropy is directly associated with large-scale density fluctuations, which actually determine the geometric disorder in a liquid. In the case of a system of noninteracting particles the "collective" entropy can be calculated directly.

Actually the partition function of a classical system of noninteracting particles in a volume V has the form

$$Z_1=\frac{\lambda^{-3N}V^N}{N!}, \tag{3}$$

where $\lambda=h/(2\pi mkT)^{1/2}$.

Correspondingly we have the following expressions for the entropy:

$$S=-\frac{\partial F}{\partial T}=-\frac{\partial}{\partial T}(-kT\ln Z), \tag{4}$$

$$S_1=R\ln\frac{V}{N}+R+\frac{3}{2}R\ln\frac{mkTe}{2\pi\hbar^2}, \tag{5}$$

where $R = kN$ is the gas constant.

The partition function of a system of noninteracting particles whose motion is restricted to cells of volume V/N is written in the form

$$Z_2 = \lambda^{-3N} V^N N^{-N}. \qquad (6)$$

Hence, upon taking account of (4), we obtain the following expression for the entropy:

$$S_2 = R \ln \frac{V}{N} + \frac{3}{2} R \ln \frac{mkTe}{2\pi\hbar^2}. \qquad (7)$$

Equations (5) and (7) imply that the difference in entropy of the two systems is

$$\Delta S = S_1 - S_2 = R. \qquad (8)$$

The quantity R in (8) amounts to the collective entropy of the system of noninteracting particles.

As we see from Eqs. (3) and (6), the appearance of this quantity formally arises from the difference of the values of $\ln N!$ and $N \ln N$. In this connection the impression can arise that the appearance of the collective entropy R in the system of noninteracting particles substantially involves the nonzero probability of very large density fluctuations restricted only by the total number N of particles in the system. We can easily convince ourselves that this is not true. Let us use Poisson's formula, which describes the fluctuation of the number of particles in a given volume of an ideal gas.[47] We shall calculate the probabilities of the corresponding fluctuations for the volume V/N. In this case Poisson's formula acquires the form $W_n = (eN)^{-1}$. Table II gives the probabilities of fluctuations in the number of particles in a volume V/N and their corresponding contribution to the entropy, which is calculated as $S_n/R = -W_n \ln W_n$.

As we see from the table, the probability of finding even three noninteracting particles in a single small volume of space is rather small. Therefore, as we shall see below, a "collective" entropy in practically the complete volume arises in systems divided into cells containing a large, albeit microscopic number of particles.

Let us write the partition function of a system of noninteracting particles divided into clusters of volume nV/N, each of which contains n particles:

TABLE II. Fluctuations of the numbers of particles in the volume V/N of an ideal gas (V—total volume of the system; N—total number of particles).

W_n	$-W_n \ln W_n$
$W_0 = 0{,}367879$	0.367879
$W_1 = 0{,}367879$	$0{,}367879$
$W_2 = 0{,}1839397$	$0{,}311437$
$W_3 = 0{,}0613132$	$0{,}1711717$
$W_4 = 0{,}0153283$	$0{,}0640425$
$W_5 = 0{,}0030657$	$0{,}00177427$
	$\sum\limits_n = S_n/R \approx 1{,}2$

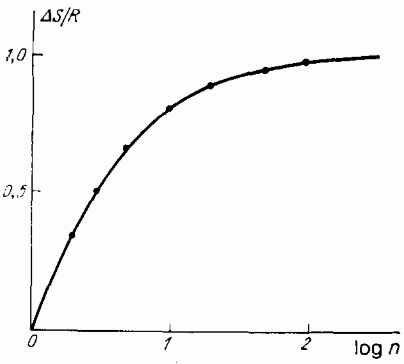

FIG. 5. Dependence of the "collective" entropy on the number n of particles per cluster.

$$Z_n = \lambda^{-3N} \left[\frac{(nV/N)^n}{n!} \right]^{N/n}. \qquad (9)$$

The change in entropy in going from the cellular system described by the partition function in the form (6) to the cluster system will be

$$\Delta S_n = k \ln \frac{n^N}{(n!)^{N/n}}. \qquad (10)$$

In Fig. 5 ΔS_n is shown as a function of the number of particles in the cluster.

We see that, even at $n = 100$, the collective entropy of the cluster system is very close to R.

Let us call attention to the fact that the "collective" entropy R of an ideal gas differs numerically from the entropy that we have obtained on the basis of the Poisson formula (see Table II). This involves the fact that not nearly all the density fluctuations contribute to the collective entropy, but only a fraction of them (see Fig. 6).

The closeness of the collective entropy of a system of noninteracting particles and the entropy of melting of simple substances was used at one time as evidence of the identity of these two quantities.[8] However, owing to the remarks of Rice[8] and the study of Hoover and Ree,[48] this idea has been discredited to a considerable degree. Hoover and Ree[48] calculated the collective entropy for systems of hard particles and showed that the collective entropy in systems close to real ones is a function of the density and attains its maximum

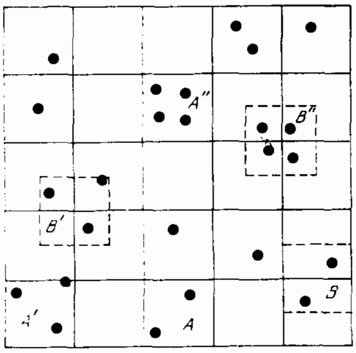

FIG. 6. Illustration of the physical concept of "collective" entropy A and B are equivalent configurations. The B configurations do not contribute to the "collective" entropy.

value R only in the ideal-gas limit (Fig. 7). According to Hoover and Ree the contribution of the collective entropy to the entropy of melting of hard spheres amounts to less than 30% ($\Delta S_m = 1.16$,[12] while the jump in $S_{col} \approx 0.3$ (see Fig. 7)). However, we note that the collective entropy of systems having interaction is ambiguously defined. In the calculations of Hoover and Ree,[48] in calculating the entropy of the cellular system, the impenetrable walls limited only the motion of the center of gravity of the particles, so that the particles could penetrate into adjacent cells.

Under high-density conditions this suffices for realization of a considerable fraction of the configuration inherent in unbounded systems in general. However, one can easily show that the result will differ if one excludes even an insignificant penetration of the particles into adjacent cells.

Actually, let us study a one-dimensional system of hard particles. The partition function of this system can be calculated exactly and has the form[49]

$$Z^{1D} = \lambda^{-N} \frac{(L - Nl_0)^N}{N!}. \qquad (11)$$

Here L is the length of the system, and l_0 is the length of a particle. In contrast to the corresponding expression (3) for an ideal gas, the partition function in (11) contains the renormalized or "free" volume (length) of the system. We can conveniently rewrite Eq. (11) in the form

$$Z^{1D} = \lambda^{-N} (l - l_0)^N e^N. \qquad (12)$$

Here $l - l_0 = (L - Nl_0)/N$ is the single-particle "free" volume (here we use the approximation $N! \approx N^N e^{-N}$).

The form of Eq. (12) implies that the collective entropy of the one-dimensional system of hard particles in the given case is $kN = R$ at any density (it is interesting to compare this with the result of Hoover and Ree[48]; see Fig. 7).

Thus the calculations of Hoover and Ree[48] apparently do no exhaust the entire problem of the collective entropy. Moreover, if we return to the original definition of the collective entropy as the entropy that arises from the communal sharing of the volume,[8] then we should suppose that the collective entropy of a gas-liquid system of realistic particles is rather close to R at any density (see also Fig. 5).

On the basis of the conclusions presented above, we can write the following for the entropy of melting of a simple substance:

$$\Delta S = k \ln \left(\frac{v_f^l}{v_f^s} \right)^N e^N. \qquad (13)$$

Here v_f^l and v_f^s are respectively the one-particle "free" volumes of the liquid and the crystal (see Refs. 46 and 50 for the "free" volume in systems of interacting particles).

Unfortunately the calculation of the free volume v_f for two-and three-dimensional systems cannot be performed so simply as in the one-dimensional case. However, we can assume that the ratio $v_f^l/v_f^s < 1$ in the limit as $\Delta V/V_S \to 0$. This conclusion is based on elementary geometric considerations and consists in the idea that the irregular structure of a liquid defines just as irregular a system, generally nonisometric, of internal cavities, which are not always accessible to the particles constituting the liquid.

In connection with the statement that we have made, the behavior of the entropy of a system of hard spheres in the melting-crystallization region is of interest (Fig. 8),[51] and besides, refutes the naive view of the connection of entropy with geometric disorder. As is implied by the form of the free energy of a system of hard spheres $F = (3/2)\, NkT - TS$, the phase transition in this system is controlled exclusively by the entropy component of the free energy. We see from Fig. 8 that the entropy of an even slightly supercooled liquid of hard spheres is always smaller than the entropy existing with the same volume and temperature. Apparently the intersection of the two branches of the free energy in this case suppresses large-scale density fluctuations in the liquid phase, and hence, causes the disappearance of the term e^N in the partition function. In this case the entropy difference of the supercooled liquid and the crystal is determined by the difference between the logarithms of the single-particle "free" volumes.

The calculations performed in Ref. 52 actually show that the "free" volume in the liquid phase of a system of hard spheres at a density close to crystallization proves to be smaller than that in the crystalline phase at the same density.[4)]

Thus the asymptotic result for the entropy of melting of a simple substance (the "ln 2" rule) (see Fig. 1) can be interpreted as

$$\Delta S \approx k \ln (0.74)^N e^N \approx R \ln 2, \qquad (14)$$

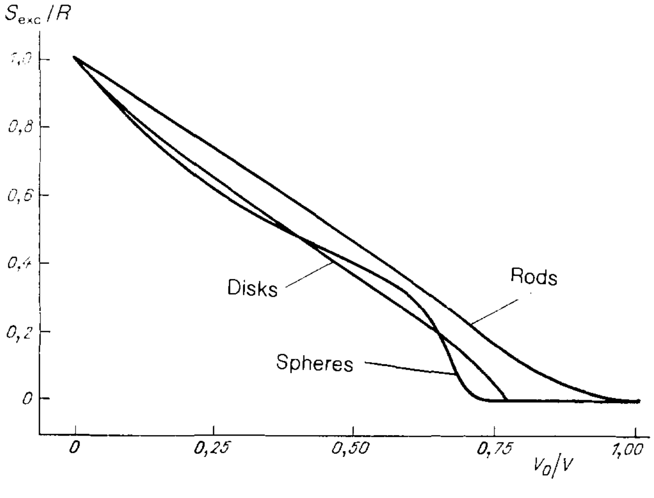

FIG. 7. The "collective" entropy in the systems of hard particles.[48]

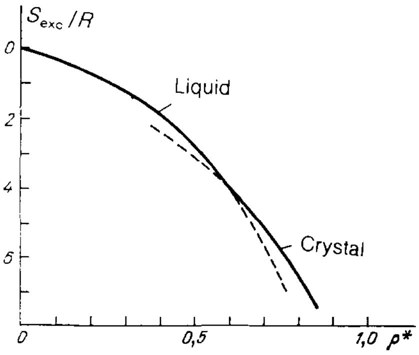

FIG. 8. Behavior of the excess entropy S_{exc}, i.e., the entropy minus the ideal-gas component, in the crystallization of a system of hard spheres.[51]

where $0.74 \approx v_f^l/v_f^s$.

Curiously, one can obtain this result from the extremely simplified model studied in Ref. 11.

We shall assume that the partition function of the crystal can be represented by an expression of the form of (6) describing a system of N particles, each of which is enclosed in a cell of volume V/N, where

V is the total volume of the system:

$$Z = \lambda^{-3N}\left(\frac{V}{N}\right)^N.$$

Within the framework of the present analysis it is immaterial whether we consider the particles to be point particles or attribute any dimension to them. In the latter case we must replace the volume of the cell V/N by the free volume v_f, which does not alter our conclusions.

Further, we must write and calculate the partition function of a system of particles whose motion is not restricted by artificial cells. Evidently this problem cannot be solved exactly for a system of interacting particles. Instead we shall propose the following trick. While keeping the division of space into cells of volume V/N, we shall let the particles migrate from cell to cell. In this case we must take account of the probability of multiple occupancy of cells. However, since we are treating a state of limiting compression, we shall take account of the probability of only double occupancy.

Upon allowing for the smallness of the fluctuations in general, we can suppose that a cellular system with the possibility of double occupancy of cells can describe the overwhelming fraction of the configurations of particles inherent in a continuous system. Evidently a cell will be considered doubly occupied when the centers of gravity of two particles fall inside it (Fig. 9). Consequently we must count the number of ways of distributing M single particles and $(N - M)$ pairs of particles over N positions as M varies from zero to N and allow for the motion of single particles and pairs of particles within the bounds of a single cell. If we assume that the "free" volume of a particle lying in a doubly occupied cell is smaller by a factor of f than the "free" volume of a single particle and we assume the probability of all distributions to be the same, we obtain the following expression for the partition function of the disordered system:

$$Z = \lambda^{-3N}\sum_{M=0}^{N}\frac{N!}{M!\,\{[(N-M)/2]!\}^2}\left(\frac{V}{N}\right)^M\left(\frac{V}{fN}\right)^{N-M}. \tag{15}$$

The change in entropy in going from a system of single occupancy of cells to a system with the possibility of double occupancy, with account taken of (6) and (15), will be

$$\frac{\Delta S}{k} = \ln\sum_{M=0}^{N}\frac{N!}{M!\,\{[(N-M)/2]!\}^2 f^{N-M}}. \tag{16}$$

Figure 10 demonstrates the dependence of the transition entropy on the parameter f. When $f = 2$ the maximum term of the summation in (16) corresponds to the condition $M = N/2$. The latter implies that half of the particles exist in the "pair" state. Hence the mean single-particle "free" volume in the disordered phase amounts to a value of the order of 75% of the "free" volume of a particle in the "crystal". A concrete calculation for $f = 2$ yields

$$\Delta S = k\ln(2^{3/2N}\cdot 2^{-1/2N}) = k\ln 2, \tag{17}$$

or

$$\Delta S \approx k\ln(0.707)^N\cdot 2.82^N. \tag{18}$$

We can easily see that the corresponding numbers in (14) and (18) are rather close.

Thus it seems that the specifics of the melting of a real substance arise to a considerable extent from the character of the high-frequency motions of the particles, which are ultimately determined by the single-particle "free" volume of the system. In turn the "high-frequency" behavior of a real system is directly associated with the interparticle interaction potential.

On the basis of the data presented in Fig. 11, and simply from physical considerations, we should expect that the entropy of melting of a simple system can increase upon weakening of the interparticle repulsive forces. It is difficult to establish this effect from real experimental data (in this regard we should call attention to the entropy of melting of cesium at high pressures; see below). Moreover, even in the case of "numerical" experiments, such an effect is masked by the increase in volume on melting. However, as is implied by Fig. 9, this effect apparently begins to be manifested somewhere in the region $n \geqslant 6$, where n is the exponent in the law $\Phi(r) \sim r^{-n}$ describing the interparticle repulsion.

Thus it is not ruled out that the estimate $\Delta S/R \approx 0.7$ generally does not correspond even to the hypothetical situation, while the minimum value of the entropy of melting of a simple substance is close to the value $\approx 0.8\,R$.

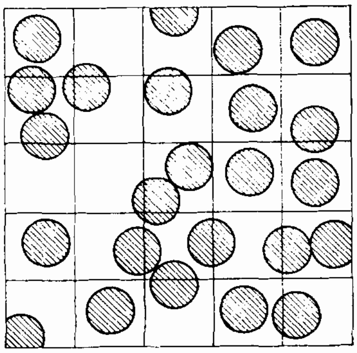

FIG. 9. Illustration of the cellular model with the possibility of double occupancy of cells.

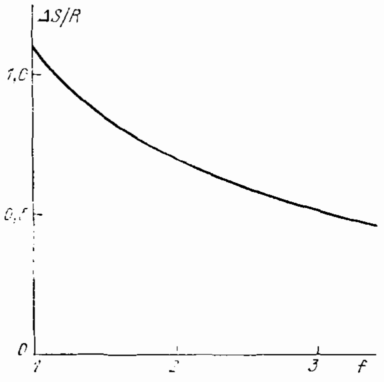

FIG. 10. Dependence of the entropy of "melting" of the cellular model on the parameter f that takes account of the change in the single-particle free volume in double occupancy of a cell.

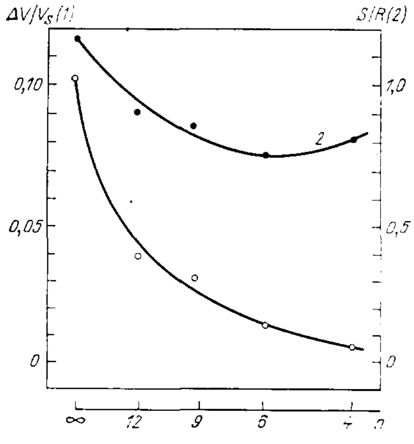

FIG. 11. Dependence of the entropy of melting and the relative volume jump in the melting of model systems on the exponent n ($\Phi(r) \sim r^{-n}$).[12]

4. MELTING OF HELIUM

As is known, helium (more exactly, its isotopes ^{3}He and ^{4}He) does not crystallize at atmospheric pressure down to absolute zero. The crystalline phases of ^{3}He and ^{4}He can be obtained only at elevated pressures ($^4\text{He} \sim 25$ kg/cm^2; $^3\text{He} \sim 34$ kg/cm^2 as $T \to 0^{54}$). This behavior of helium is explained by the instability of crystalline helium at low pressures owing to the large amplitude of the zero-point vibrations of the atoms. Apparently it is more correct to speak of the stabilization of the liquid phase of helium at low pressures owing to its lower kinetic (zero-point) energy as compared with the crystalline phase. However, in this section we shall not be interested in the details of quantum melting (on this topic, see, e.g., Refs. 55 and 56). We are interested in the evolution of the entropy of melting of the isotopes of helium with varying temperature. Figure 12 shows experimental data[57] characterizing the behavior of the entropy of melting of ^{3}He and ^{4}He down to temperatures ~ 30 K. For comparison this same diagram shows the corresponding results for argon.[11] We see from Fig. 12 that, as we should have expected, the entropies of melting of helium and argon apparently have a common "classical" high-temperature limit. Let us call attention to the fact that the quantum effects in the melting of helium are still important even at temperatures ~ 30 K (compare the curves for ^{3}He and ^{4}He in Fig. 12).

Actually, we can easily convince ourselves by using the data of Refs. 57 and 58 that the ratio of the thermal de Broglie wavelength to the mean interatomic distance λ_T/d for helium along the melting curve is a quantity of the order of 1.3 at 30 K and 0.85 at 97 K ($\lambda_T = (2\pi\hbar^2/mkT)^{1/2}$; $d = (V/N)^{1/3}$).

Evidently at low temperatures the role of quantum effects in melting must increase in accord with the increase in the thermal wavelength λ_T, which ultimately determines the features of behavior of the entropy of melting.

We should assume that an increase in the thermal wavelength λ_T diminishes the number of different configurations, and hence diminishes the number of states in general. Naturally, this effect ultimately determines the decrease in the entropy jump upon melting of helium down to the temperatures of quantum degeneracy.[5] One can say that, as the temperature decreases, the entropy becomes an ever less sensitive characteristic of the state of aggregation of the material.

Figure 13, which demonstrates the dependence of the entropy of melting of ^{3}He and ^{4}He on the ratio d/λ_T calculated along the melting curve, can illustrate what we have said. As we see from Fig. 13, the use of the ratio d/λ_T as a coordinate makes the difference between the behaviors of the entropy of melting of ^{3}He and ^{4}He vanish throughout the temperature range down to the temperature of the λ-transition in ^{4}He (cf. Figs. 12 and 13).

Curiously, as is implied by Fig. 13, if we ignore the λ-transition in ^{4}He, we still obtain a zero value of the entropy of melting of helium at $T = 0$, which indicates the lack of a causal connection between the phenomena of quantum degeneracy and the Nernst heat theorem.

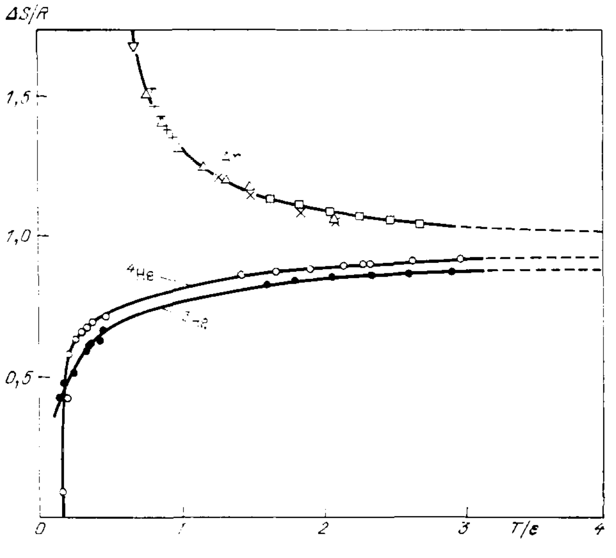

FIG. 12. Entropy of melting of Ar and He as a function of the reduced temperature.[11,57] $\varepsilon_{Ar} = 119.3$ K, $\varepsilon_{He} = 10.22$K.

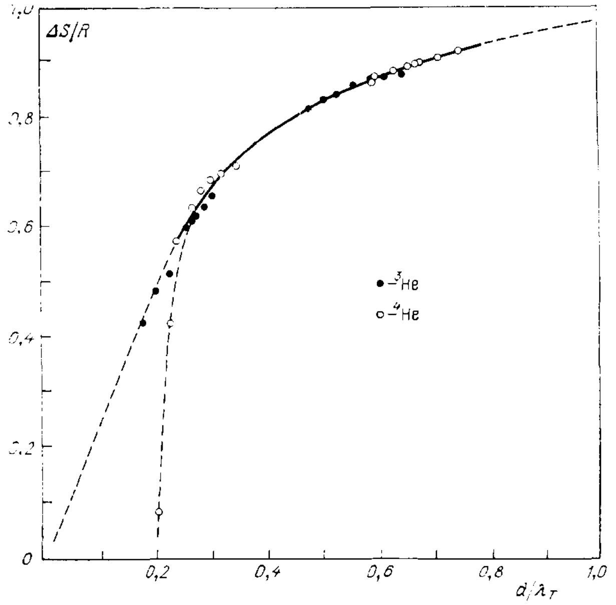

FIG. 13. Entropy of melting of ^{3}He and ^{4}He as a function of the ratio d/λ_T. d-mean interparticle distance; $\lambda = h/(2\pi mkT)^{1/2}$-thermal de Broglie wavelength. Calculated from the data of Ref. 57.

Turning again to Fig. 12, we note that, at temperatures somewhat exceeding the temperature of the λ-transition in ^{4}He, the difference between the entropy of melting of argon and helium amounts to a value of the order of the gas constant R. In all likelihood this is not fortuitous, but is due to the disappearance of the "collective" entropy in the limiting quantum case. Moreover, this is not amazing, since the concept of "collective" entropy is in spirit purely classical.

Thus the increase in entropy of melting of helium with increasing temperature can be interpreted as the result of a gradual rise in the "collective" entropy from zero to the limiting value.

5. MELTING OF TWO-DIMENSIONAL AND QUASI-TWO-DIMENSIONAL SYSTEMS

As is known, the positional order in a crystal is described by a two-component order parameter. In this case, with a spatial dimensionality $D = 2$, such strong fluctuations in the order parameter arise that its mean value is zero at any temperatures above absolute zero. In the given case the spatial dimensionality $D = 2$ is the lower critical dimensionality. As it has turned out, many two-dimensional systems undergo a specific phase transition accompanied by establishment of topological long-range order.[60]

In this sense two-dimensional crystallization or melting constitutes a characteristic example and can arise via a phase transition of continuous type[61] (more exactly, two phase transitions[62]). In the absence of long-range positional order, the well-known arguments of Landau on the impossibility of crystallization-melting via a continuous phase transition lose force.[63]

It has been known since the time of the studies of R. Peierls[64] and L. D. Landau[63] that the r.m.s. deviations of the atoms from the equilibrium positions in a two-dimensional crystal increase without bound (logarithmically) with increasing dimension of the system (the logarithmic increase in the r.m.s. displacements of the atoms is actually very weak. To observe displacements of the order of the interatomic distance requires a crystal of astronomic dimensions[65]). This implies that long-range positional order is absent in a two-dimensional crystal, and hence, a two-dimensional crystal in the strict sense of this word does not exist. However, as Mermin first showed, a two-dimensional crystal possesses long-range topologic or orientational order[66] (orientational order is defined as order in the system of bonds linking adjacent particles with one another). It was found subsequently that this property ensures a finite shear modulus in a two-dimensional crystal, which distinguishes it from a two-dimensional liquid. The existence of a phase transition in a two-dimensional system of interacting particles has been proved in an number of studies (for a review of the corresponding results, see Refs. 60, 67). A general mechanism of phase transitions involving topological defects has been proposed by Kosterlitz and Thouless.[61] Nelson and Halperin[62] used the ideas of Kosterlitz and Thouless to detail the pattern of melting of a two-dimensional substance. According to Nelson and Halperin two-dimensional melting occurs in two stages. First the two-dimensional crystal possessing orientational long-range order transforms to a so-called hexatic phase having algebraic decay of orientational order, and then to a true liquid phase where positional and orientational order decay exponentially.

Naturally the two-stage continuous transition amounts to a possibility in principle of how the events develop. It does not rule out an alternative course, i.e., a first-order transition. Unfortunately, true two-dimensional objects are unattainable to experimental study. Electrons on the surface of liquid helium, adsorbed monomolecular layers, and monomolecular films of liquid crystals are still two-dimensional objects in the three-dimensional world. Numerical experiments seem ideally suited for solving "two-dimensional" problems. However, the restricted number of particles and too short times of "experiment" do not allow one to draw categorical conclusions.

The results of the numerical experiments performed up to now lead to the conclusion that two-dimensional melting is a first-order phase transition (see Refs. 68–73 and Table III). However, indications exist that, with increasing dimension of the system and decreasing hardness of the interaction potential, the "first-order" character of the phase transition somewhat declines.[74–76]

The studies of the phase transitions in monomolecular films of smectic liquid crystals also as yet indicate a jumpwise character of melting in these systems.[77]

Cogent proofs exist of the continuity of melting in incommensurable monolayers of Xe on a graphite substrate, although the problem of the influence of the substrate on the properties of the phase transition is not absolutely clear.[78]

The question of the thermodynamic nature of two-dimensional melting is unquestionably highly interesting, but it is not important in principle for the presentation below. Rather, from considerations of convenience we shall assume

TABLE III. Change in the volume (area) and entropy in melting of simple systems from the data of numerical experiments.[69]

Model	Parameter* n	$\frac{\Delta V}{V_S}$ (3 D), %	$\frac{\Delta A}{A}$ (2 D), %	$\frac{\Delta S}{R}$ (3 D)	$\frac{\Delta S}{R}$ (2 D)
Hard spheres (disks)	∞	10,3	4,0	1,16	0,41
Soft spheres (disks)	12	3,8	2,1	0,89	0,25
Lennard-Jones (T^*) = 0.8	12—6	13,1	4,76	1,75	0,49
One-component plasma	1	0,05	0,5?	0,82	0,2?

---

*Parameter n—exponent in the interaction law $\Phi(r) \sim r^{-n}$. The two exponents characterizing repulsion and attraction are given for the Lennard-Jones system.

that two-dimensional melting is a first-order phase transition.

Thus, we are interested in the relation between the dimensionality of the space and the entropy of melting. The "experiments" favor the existence of such a relationship. The data of Table III show that the entropy of melting of two-dimensional systems is always less than that of the corresponding three-dimensional analogs. Figure 14 also merits attention, where the heat capacity of 3-D and 2-D systems having an interaction of the form $\Phi(r) \sim r^{-12}$ in the melting region is shown.[69] As we see from Fig. 14, both $C_P(T)$ curves behave similarly, and they can be superposed on one another with good accuracy by a scale transformation with the coefficient 3/2, which corresponds to the ratio of numbers of degrees of freedom of 3-D and 2-D systems. However, it is not clear whether a direct relation exists between the entropy of melting and the number of degrees of freedom.

Let us try to analyze this problem within the framework of the concept of "collective entropy".

We convinced ourselves above that the collective entropy of a system of noninteracting particles is close to the entropy of melting of simple substances, and hence we can hope that an analysis within the framework of this very simple model can yield useful results.

Apparently there is no need to write again the partition function of a system of noninteracting particles (see (3)). Instead we shall write directly the expressions for the entropy of the 3-D and 2-D systems:

$$S^{3\mathrm{D}} = R \ln \frac{V}{N} + R + \frac{3}{2} R \ln \frac{mkTe}{2\pi\hbar^2}, \tag{19}$$

$$S^{2\mathrm{D}} = R \ln \frac{A}{N} + R + R \ln \frac{mkTe}{2\pi\hbar^2}. \tag{20}$$

Here A is the area occupied by the two-dimensional system; $R = kN$ is the gas constant.

Comparison of Eqs. (19) and (20) shows that the dimensionality of the space explicitly determines the value of the numerical coefficient in the temperature component of the entropy that arises from integration of the momentum of the partition function. However, the configurational component of the entropy in (19) and (20) cannot be compared directly. Let us transform the coordinate component of the partition function for a two-dimensional ideal gas $Z_c = A^N/N!$ to a form that allows direct comparison with the expression (3) for the three-dimensional case. Let us define the area A in such a way that the mean distance between the N particles would be equal to $(V/N)^{1/3}$. In other words, we shall require the linear density of particles in the 2-D and 3-D systems to be the same. In this case we have

$$A = \left(\frac{l}{N^{1/3}} N^{1/2}\right)^2, \tag{21}$$

where $l = V^{1/3}$. Then we have[6)]

$$Z_K^{2\mathrm{D}} = \frac{(l^2 N^{1/3})^N}{N!}, \tag{22}$$

$$S^{2\mathrm{D}} = \frac{2}{3} R \ln \frac{V}{N} + R. \tag{23}$$

Comparison of (19) and (23) shows that the coefficient of the configuration term of the entropy is also determined by the dimensionality of the space, but the value of the "collective" entropy, in this case R, remains invariant! (see Sec. 3).[7)]

Since we insist that the entropy of melting is a quantity of the same order of magnitude as the collective entropy, this result contradicts the data of Table III.

We can imagine a number of reasons why the entropy of melting of a two-dimensional system can have a lower value than for its three-dimensional analog. We recall that in Sec. 3 we concluded that one can write the entropy of melting of a simple substance as (13):

$$\frac{\Delta S}{k} = \ln \left(\frac{v_f^l}{v_f^s}\right)^N e^N.$$

Here v_f^l and v_f^s are the single-particle "free" volume of the liquid and the crystal, respectively; e^N is the fluctuation term that determines the "collective" entropy of the liquid.

We stress that Eq. (13) envisages that the "collective" entropy of the crystal is identically equal to zero. In taking account of Eq. (13), we should study the following causes that give rise to the "anomalously" low entropy of melting of two-dimensional systems:

a) the ratio v_f^l/v_f^s has a smaller value for two-dimensional than for three-dimensional systems;

b) the "collective" entropy of a two-dimensional liquid is smaller than $k \ln e^N$ or R, in line with the geometric restrictions on the scale of the density fluctuations;

c) the "collective entropy of a two-dimensional crystalline phase has a nonzero value owing to its "pathological" properties.

Below, in analyzing the melting of quasi-two-dimensional systems, we shall see that the possibility exists of a definite choice between the stated variants.

In treating the melting of quasi-two-dimensional systems, we shall restrict the topic to a single, yet quite instructive example of a phase transition: crystalline smectic crystal B to smectic crystal A. The class of smectic liquid crystals can be defined as a system consisting of parallel layers periodically distributed in space consisting of elongated, rigid molecules that generally lie at a large angle to the plane of the layer (Fig. 15). The simplest of the smectic liquid crystals (smectic A) is an example of a one-dimensionally ordered substance and can be described as a system of two-dimensional liquid layers regularly arranged in space.[79 8)] A smectic B amounts to a more ordered type of liquid crystals and is known in two forms. One of them possesses crystalline

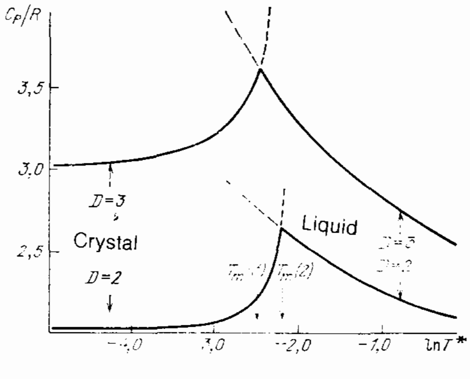

FIG. 14. Heat capacity of 2-D and 3-D systems of soft spheres ($\Phi(r) \sim r^{-12}$) in the melting region.[69]

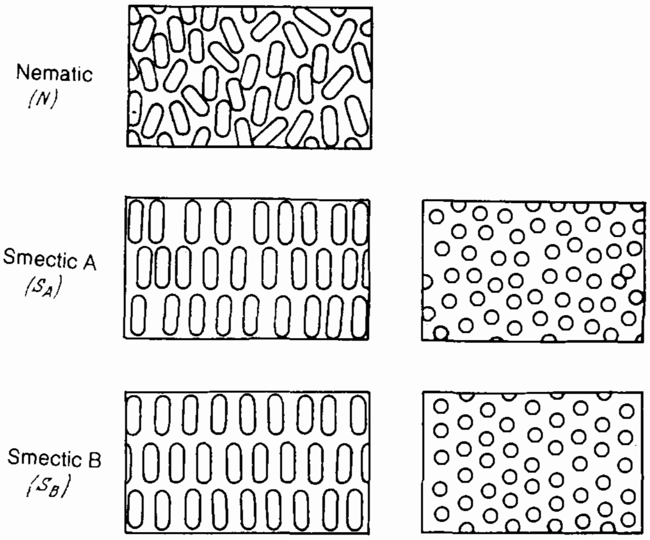

FIG. 15. Schemtic diagram of liquid-crystalline phases.

packing of the molecules in the layers and an appreciable interlayer correlation. The interlayer shear modulus in a crystalline smectic B has a finite value, although extremely small.[81,82] In essence a crystalline smectic B amounts to a true three-dimensional crystal. The other form of smectic has only topological long-range order and amounts to a three-dimensional analog of the hexatic phase of Nelson and Halperin.[83]

We shall be most interested in the crystalline smectic B to smectic A phase transition, which is actually an example of two-dimensional melting in a three-dimensional system.

Figure 16 shows part of the phase diagram of a substance with the abstruse name of *N*-(4-*n*-butyloxybenzylidene)-(4-*n*-octylaniline) or BBOA for short, which undergoes a cr. $S_B - S_A$ phase transition according to the data of Ref. 84 (here S is the generally accepted notation for smectic phases, while cr. S_B denotes a crystalline smectic B).

The phase transition cr. $S_B - S_A$ that we are interested in is a clearly marked first-order phase transition, whereas the S_A-N transition amounts to a continuous-type transition. Along the S_B-S_A equilibrium line the amplitude of the one-dimensional density wave continuously declines with increasing pressure and vanishes at the final critical point (FCP), above which the S_B melts directly to the nematic phase.

The distinguishing feature of the thermodynamics of the $S_B - S_A$ phase transition in the given case is the increase in the entropy of transition with increasing pressure (Fig. 17).

We shall show that this behavior of the entropy of melting can be explained with elementary calculations in the noninteracting-particle approximation. We shall write again the coordinate component of the partition function of N ideal particles in the volume V, with $Z_c = V^N/N!$. Let us order our system in such a way that it has the form of a stack of sheets. We shall assume that the area of each sheet is $A = l^2 = V^{2/3}$ and it contains $N^{2/3}$ particles. Evidently the number of such sheets must be $N^{1/3}$ (Fig. 18).

The coordinate component of the partition function of such a system has the form

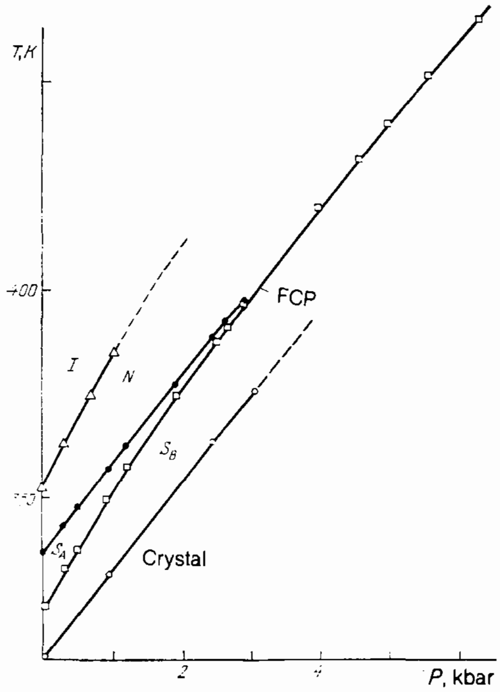

FIG. 16. Phase diagram of BBOA.[84]

$$Z_{\kappa}^{2(3D)} = \left[\frac{(V^{2/3})^{N^{2/3}}}{N^{2/3}!}\right]^{N^{1/3}} = \frac{V^{2/3N}}{(N^{2/3}!)^{N^{1/3}}}. \qquad (24)$$

Correspondingly we have the following expression for the configurational component of the entropy

$$S_{\kappa}^{2(3D)} = \frac{2}{3} R \ln \frac{V}{N} + R^{9)\,10)} \quad . \qquad (25)$$

As we see from (23) and (25), we have obtained a result fully analogous to the two-dimensional case. However we must remember that the temperature component of the entropy will be three-dimensional in this case, owing to the possibility of bending vibrations.

Thus, upon taking acount of (19) and (25), we have the following expression for the difference in entropies of the normal and the one-dimensionally ordered systems:

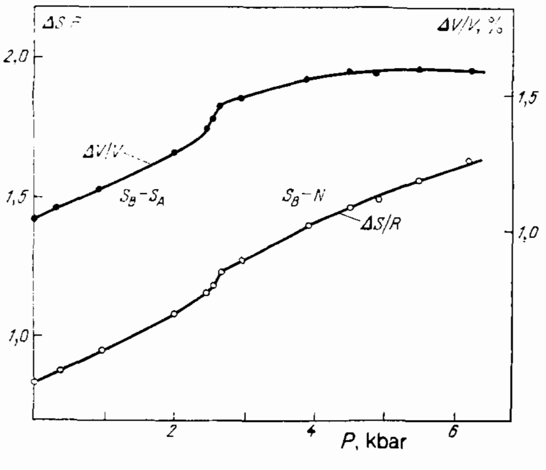

FIG. 17. Change in volume and entropy upon melting of the crystalline smectic B in BBOA.[84]

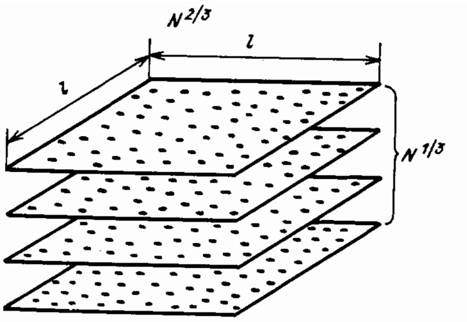

FIG. 18. Illustration of the calculation of the entropy of a layered system of noninteracting particles.

$$S^{3D}-S^{2(3D)}=\frac{R}{3}\ln\frac{V}{N}. \tag{26}$$

Further, let us write the coordinate component of the partition function for the quasi-two-dimensional crystal in the form

$$Z_K=\left[\left(\frac{V^{2/3}}{N^{2/3}}\right)^{N^{2/3}}\right]^{N^{1/3}}. \tag{27}$$

Then we obtain for its configurational entropy

$$S_K=\frac{2}{3}R\ln\frac{V}{N}. \tag{28}$$

Equations (26)–(28) imply that the entropy of transition of a quasi-two-dimensional crystal to a quasi-two-dimensional liquid is $\approx R$, whereas the entropy of melting of a quasi-two-dimensional crystal to a three-dimensional liquid is $\approx R + (1/3)R\ln(V/N)$.

Thus we have obtained a result qualitatively agreeing with the behavior of the entropy jump upon melting of BBOA (see Fig. 17).

Further we shall try to use the results of our analysis and the experimental data on the melting of BBOA to elucidate the nature of the "low" values of the entropy of melting of two-dimensional systems.

Let us examine the case of pure "quasi-two-dimensional" melting. While taking account of (13), (25), and (28), we shall write the entropy of melting in a quasi-two-dimensional system of interacting particles in the form

$$\Delta S=R+\frac{2}{3}R\ln\frac{v_f^l}{v_f^s}. \tag{29}$$

Allowing for the fact that the change in volume in melting of BBOA is small, we shall use the value ~ 0.75 for the ratio v_f^l/v_f^s as an approximation, which arises from analyzing the real, and hence three-dimensional data (see (14)). Upon substituting this value into (29), we obtain $\Delta S/R \approx 0.81$ for the entropy of melting of the quasi-two-dimensional system. Remarkably, this value coincides practically absolutely exactly with the entropy of melting of BBOA at atmospheric pressure (see Fig. 17).

The attained agreement is unquestionably too good for fully trusting the obtained value. Nevertheless, the estimate that we have made renders unlikely the variants a) and b) proposed above for explaining the "low" entropy of melting of two-dimensional systems. Thus we cannot but conclude that a two-dimensional quasicrystal has a nonzero "collective" entropy. In other words, the large-scale fluctuations make a more substantial contribution to the entropy of a two-dimensional crystal than happens in the three-dimensional case. We can easily see that this conclusion fully agrees with those first made by Peierls[63] and Landau[64] and it favors the possibility of realizing two-dimensional melting via a phase transition of continuous type.[61,62]

6. "EXOTIC" MELTING CURVES

As has been established by the experimental studies, the melting point of different substances at high pressures can behave in an unusual manner (Fig. 19).[7,11] Below we shall concentrate on analyzing melting curves having temperature maxima as in the most general case. Since, as experiment shows, the entropy of melting is always positive (there are two exceptions to this rule involving the melting of ^{3}He and ^{4}He at low temperatures), then, as is implied by thermodynamics, the volume jump ΔV in melting is negative for a curve with a negative slope dT/dP, and changes sign on a melting curve having a maximum. At the maximum point, naturally, we have $\Delta V=0$ (see Fig. 19).

We emphasize that melting curves of types (2) and (3) cannot be obtained in the class of systems having an interaction of the form $\Phi(r)\sim r^{-n}$. Actually, as one can easily show,[11] the following relationships hold for the melting of systems with a power-function interaction:

$$P\sim T^{1+(3/n)},\quad \frac{\Delta V}{V_S}=\text{const},\quad \Delta S=\text{const}. \tag{30}$$

Here P and T are the coordinates of the melting curve, $\Delta V/V_S$ is the relative volume jump in melting, and ΔS is the entropy jump in melting.

When we include an attractive interaction the relationships of (30) acquire the meaning of high-temperature asymptotic relationships,[11] which naturally rules out the equations $dT/dP=0$ and $\Delta V=0$ for any finite temperatures and pressures.

Figure 11 showed the behavior of $\Delta V/V_S$ and ΔS in the melting of systems having a repulsive power-function interaction as a function of the value of the exponent n. We note that the volume jump in melting declines very rapidly with

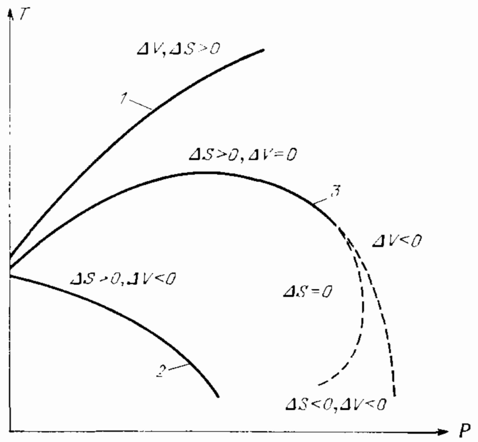

FIG. 19. Variants of the behavior of melting curves at high pressures.

decreasing n. We should call attention to the character of the behavior of the entropy of melting at small n. The impression is created that somewhere in the region of $n = 5$ the entropy of melting begins to increase with decreasing n, although the error of determination of ΔS in this region of n values is too large for drawing categorical conclusions.

It would seem that melting curves of forms (2) and (3) are generally impossible for any reasonable pair potential. Actually, by introducing the effective index $n_{\text{eff}}(r) = -\,\mathrm{d}\ln\Phi(r)/\mathrm{d}\ln r$, it appears as though we could describe each region of the melting curve by a power-function potential, which rules out the appearance of melting curves 2 and 3 (see Fig. 19). In fact this conclusion can be valid only in case of concave potentials, but does not hold if the potential is convex.

Let us study Fig. 20, which shows the behavior of the free energy and the pressure P in the region of a maximum on the melting curve. Evidently the appearance of a maximum requires a double crossing of the free-energy curves of the liquid and the crystal. Consequently it turns out that the pressure of the liquid in the region of the maximum unavoidably must become less than the pressure of the crystal.

Let us write the expression for the pressure in a system having the pair potential $\Phi(r)$ as implied by the classical virial theorem:

$$P = \frac{RT}{V} - \frac{1}{6}V^2 \int r\Phi'(r)\, g(r)\, dr. \tag{31}$$

As we see from Eq. (31), the nonideal component of the pressure is determined by the convolution of the derivative of the potential $\Phi'(r)$ with the radial distribution function $g(r)$.

Figure 21 illustrates some situations that arise with differing behavior of the derivatives $\Phi'(r)$. We see that, if $\Phi'(r)$ declines nonlinearly with decreasing distance r, the pressure of the liquid is always greater than the pressure of the crystal, and vice versa, the pressure of the liquid can be less than the pressure of the crystal if the derivative $\Phi'(r)$ increases nonlinearly.

Figure 22 shows several potential curves as compared with the power-function potential $\Phi(r) \sim r^{-n}$, which in principle can give rise to the sought effect. "Numerical" experiments in systems having a potential of the type depicted in Fig. 22 actually show maxima on the melting curves.[86-89]

The behavior of the entropy of melting in the case being discussed is nontrivial and is of great interest. Let us study again Fig. 20, which shows the isotherms of the free energy of the liquid and the crystal for a substance having a maximum on the melting curve. For the intersection points of the free energy we can write

$$F_l = F_s,$$

$$U_l - TS_l = U_s - T\quad ,$$

or

$$\frac{\Delta U}{\Delta S} = T.$$

Here U is the internal energy of the phase. Since we are treating isothermal compression, the following equation holds:

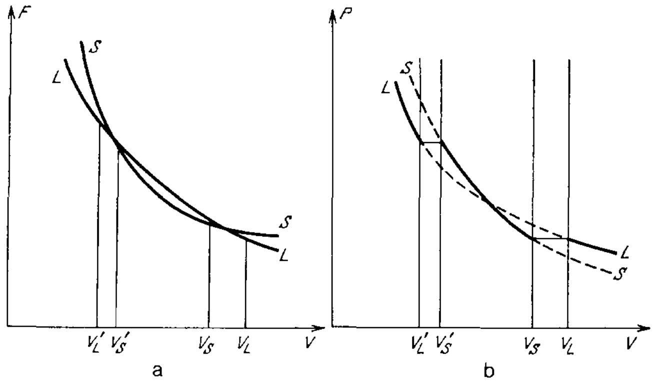

FIG. 20. Schematic diagram of the behavior of the free energy (a) and the pressure (b) in the region of a maximum on the melting curve.

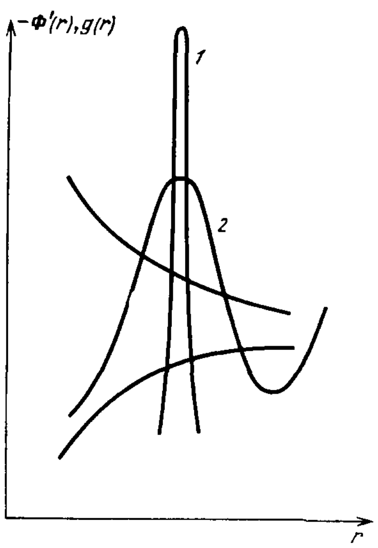

FIG. 21. Illustration of possible variants of the behavior of the derivative $\Phi'(r)$. $g(r)$—radial distribution function for the crystal (1) and the liquid (2).

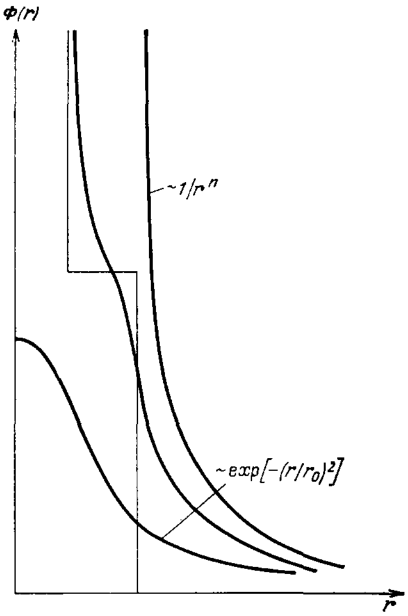

FIG. 22. Hypothetical interaction potentials.

$$\left(\frac{\Delta U}{\Delta S}\right)_{V_1} = \left(\frac{\Delta U}{\Delta S}\right)_{V_2}. \qquad (32)$$

Here the subscripts V_1 and V_2 denote the coordinates of the intersection points of the curves F_l and F_s. We should remember that ΔU and ΔS in this case amount to the differences of the internal energy and the entropy at constant volume, rather than constant pressure. However, this is not essential to the current treatment.

As Eq. (32) implies, several ways to realize a temperature maximum on the melting curve are possible. However, in analyzing any of them we must take into account the fact that in the initial ("normal") region of the melting curve the difference of internal energies ΔU increases with the pressure, but the entropy of melting ΔS does not increase (for the power-function potential $\Delta U \sim V^{-n/3}$ we have $\Delta S = \text{const}$).

One of the possible ways to obtain a maximum reduces to an increase in the entropy of melting in a certain pressure interval, or in general, a monotonic behavior of the difference in potential energies.

The thermodynamic data characterizing the melting of cesium (Fig. 23) graphically illustrate this variant of behavior, although we must remember that the possibility of describing cesium within the framework of a pair potential of interaction is not evident.

The reason for the "anomalous" behavior of the entropy of melting undoubtedly must be sought in a "softening" of the potential in some range of densities. In this case the volume accessible for motion of particles in the liquid phase can be substantially increased without an extreme increase in the internal energy.

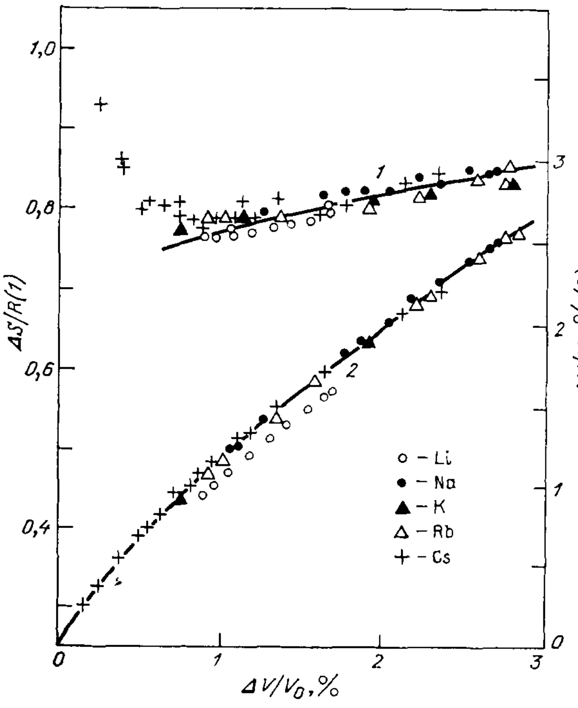

FIG. 23. Entropy of melting and relative volume jump as functions of the normalized volume jump in melting of the alkali metals.[90]

On the other hand, as is implied by the results of "numerical" experiments in the specific system of "Gaussian" particles,[89] a situation can occur in which the difference of internal energies ΔU and the entropy of melting ΔS decrease upon compression. In this system the internal energy and the entropy of each of the phases increases along the melting curve. The causes of the decline in the magnitude of ΔU for a Gaussian system upon compression are more or less clear. The point is that the "softening" of the potential makes the energy of the system less and less sensitive to the character of the arrangement of the particles. It is far more difficult to explain the decrease in entropy of melting ΔS along the melting curve of a Gaussian system. As the data of Ref. 89 imply, the decrease in entropy of melting involves the faster increase in entropy of the crystalline phase as compared with the liquid. We should assume that the relative amplitudes of vibration of the particles in a Gaussian crystal increase with decreasing density. The existing data show that the relative amplitude of the vibrations in a Gaussian crystal is actually anomalously large.[91] However, there is no information on the dependence of the quantity in which we are interested on the density.

Let us turn our attention to the fact that the entropy of melting in a Gaussian system at a density $\rho^* = 1$ is ≈ 0.64,[89] which is already lower than the "limiting" value $\Delta S = 0.7R$ (see Sec. 1). This can mean that the "collective" entropy of a compressed "Gaussian" crystal at high temperature is not zero.

The problem of the evolution of the entropy of melting of a Gaussian system upon further compression is extremely interesting. If we allow for the fact that part of the "liquid" configurations of particles can freeze out on lowering the temperature (the possibility of glass formation in a Gaussian system permits us to expect this effect), then it is not ruled out that the entropy of melting in a Gaussian system can become zero and even change sign (see Fig. 19).[11]

We stress that the material presented in this section does not contradict the general principles of Sec. 3, although the discussed examples do not lead us to expect that the "0.7 rule" will be obeyed. Evidently the analysis given in Sec. 3 is restricted to the case of systems with a rather "stiff" interaction. However, the particles of natural systems always have a "stiff" core. The sole exception here is hydrogen. Therefore it is precisely in the case of metallic hydrogen that unusual phase diagrams can arise (see Ref. 95).

In closing this section we note that the exotic potentials shown in Fig. 18 apparently can arise only as a consequence of multiparticle effects, the influence of electronic transitions, etc. For this reason these potentials must be treated only as an "effective" pairwise representation of complex interactions.

With this we close our review, which is devoted to spatial disorder and entropy. The author realizes that he has not been able to solve the problems treated in the article completely, but then his claims did not extend so far. What has been obtained is the view of an experimenter expressing his viewpoint in graphic physical images or categories of the measurable, since thus one creates the premises for formulating new experiments. Nevertheless the author hopes that the formulation of the problem as a whole and the discussions that have been advanced can be of general interest. We can summarize the fundamental conclusions of the article as follows.

Geometric disorders and entropy are interrelated nonuniquely. It makes no sense to pose the problem of the entropy of a geometrically or spatially disordered system without stipulating the method of "preparing" it. As a rule, geometrically disordered static systems are nonergodic and their thermodynamic analysis is highly arbitrary, or at least, requires a special approach. The "residual" entropy is not a characteristic of the static disorder of a geometrically disordered system, but can serve as a measure of the number of states in the corresponding system at high temperatures.

The relative constancy of the entropy of melting of simple classical substances does not result from the existence of a certain entropy of disorder in general, but is a consequence of the small dependence of the entropy of a simple liquid on the number of particles drawn into collective motion and collectively utilizing the accessible space.

The concept of collective utilization of space or "collective" entropy loses meaning in analyzing the melting of quantum systems, owing to the wave properties of the particles. The small value of the entropy of melting of quantum systems at low temperatures corresponds to the overall reduction in the number of distinguishable states.

The specifics of the melting of two-dimensional systems bears the imprint of the anomalous properties of the two-dimensional "crystalline" phase. The relatively low entropy of melting of two-dimensional systems is determined by the "liquidlike" character of a two-dimensional quasicrystal.

The melting of "exotic" systems at high pressure gives grounds for assuming that the entropy of melting substantially depends on the character of the interparticle interaction, and its behavior can serve as an indicator of the peculiarities of the phase diagram of the substance.

In closing the author thanks A. F. Andreev and V. A. Somenkov for discussions and valuable remarks, and L. A. Fal'kovskiĭ for reading the manuscript.

The author expresses especial indebtedness to D. A. Kirzhnits for the patience with which he heard out the often contradictory arguments of the author and for constructive criticism.

V. A. Somenkov and A. Sh. Shil'shteĭn drew the author's attention to the hydrides of the transition metals as an example bearing on the topic of this article.

Naturally, none of the cited persons bears responsibility for the article as a whole.

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1) We emphasize that the usual treatment of the "electronic" transition in magnetite[28] assumes that the N electrons are statistically distributed over the $2N$ lattice positions in the melting of the electronic subsystem. We point out that in this case the entropy of the transition would be $2R \ln 2 \approx 1.4$.

2) This result seems somewhat strange and obviously requires verification.

3) We can imagine a situation in which the choice of the same given geometrically disordered configuration of particles would be assured, e.g., in the adsorption of gases on a special substrate at low temperatures or in the trapping of electrons by a randomly distributed impurity in a crystal matrix. In this case the corresponding system will be fully ergodic and its heat capacity and entropy at low temperatures will not differ from the corresponding properties of a system built of the same particles regularly distributed in space.

4) Interestingly, a phase transition of the melting-crystallization type in a quantum system of hard spheres at $T = 0$ is exclusively determined by the competition of the kinetic energies of the corresponding phases, which in turn are closely associated with the localization of the particles. As the very existence of crystallization implies, in such a system[53] the particles in the supercooled liquid phase of quantum hard spheres are more localized than in a crystal of the same density.

5) Evidently, with a small value of the entropy of melting, the appearance in the liquid phase of even a small fraction of "condensate", i.e., particles with zero momentum, can cause sign inversion of the entropy of melting. Apparently this occurs in ^{4}He at a temperature of ~ 0.8 K.[26] A similar effect is observed in ^{3}He at a temperature of ~ 0.4 K.[26] However, in this case the sign inversion of the entropy of melting results from the ordering of the nuclear spins in liquid ^{3}He (the Pomeranchuk effect[59]).

6) Curiously, if we are not concerned with maintaining a linear density, but define the area as $A = V^{2/3}$, then we have $S^{2D} = (2/3)R \ln (V/N) + R[1 - (1/3)\ln N]$.

7) One can obtain this result much more simply by substituting the area A instead of the volume V into the corresponding expressions of Sec. 3. However, we lose information here on the variation of all the other contributions to the entropy.

8) The given definition of a smectic A is somewhat simplified. We should note that the r.m.s. displacements of the particles in a direction perpendicular to the surface of the layer diverge logarithmically with increasing distance,[47] while one should describe the layered structure in terms of a practically sinusoidal density wave.[80]

9) The value of the "collective" entropy in this case is again R, although particle exchange between the sheets is forbidden. This is a direct consequence of the low probability of large density fluctuations.

10) Analogously we can write for a two-dimensionally ordered system of non-interacting particles $S_c = (1/3)R \ln(V/N) + R$. This result is related to the problem of discotic liquid crystals.[85]

11) In this case the physics of melting of a classical system of Gaussian particles will be highly reminiscent of what one expects for a quantum system of "soft", e.g., Coulomb particles under conditions of strong compression, when the contribution of the "zero-point" energy to the overall energy of the system becomes appreciable.[92–94] In quantum melting the difference of internal energies ΔU of the two phases declines along the melting curve because the zero-point energy in the liquid phase is always less than in the solid. The relative amplitudes of the vibrations in the crystal also increase upon compression.

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Translated by M. V. King