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Stability and first-order phase transitions

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An approach is formulated to the problem of first-order phase transitions. It states that these transitions are caused by processes of stability loss at the microscopic level. A formal attribute of the loss of stability is the vanishing of the solution to the system of equations for distribution functions. Calculations for a model equation confirm this hypothesis. It is shown that the phase transition on the crystallization curve is caused by the instability of the system with respect to small perturbations of the distribution function at the first (the deepest) minimum of the thermal potential. The loss of stability on the liquid-evaporation curve is caused by the decay of the asymptotic behavior of the distribution function, while on the vapor-condensation curve it is again caused by the instability of the first minimum of the thermal potential. Criteria of stability loss are established. The results are generalized to the case of phase transitions in crystalline materials.

I. INTRODUCTION

As a rule, curves of first-order phase transitions are found from the conditions of coexistence of phases:

$$P(n_A,\Theta)=P(n_B,\Theta),\quad \mu(n_A,\Theta)=\mu(n_B,\Theta)\ . \tag{1}$$

(here P is pressure, μ is the chemical potential, $n=N/V$ is the number density of particles, and $\Theta=k_BT$ is temperature). Having calculated the dependences $P(n)$ and $\mu(n)$ for each of the phases A and B using certain approximations, one can calculate those values of $n_A(\Theta)$ and $n_B(\Theta)$ for which the coexistence conditions (1) are satisfied. The theory is thus based on *comparing* the parameters of different phases. But is such a comparison possible in nature? Indeed, if $n<n_A$ (Fig. 1), there are no nuclei of phase B inside phase A, so that molecules of phase A cannot be exposed to the difference between P_A and P_B or between μ_A and μ_B, and conversely for phase-B molecules, if $n>n_B$, when phase A cannot exist. Certainly, there can exist heterophase fluctuations inside the old phase, the structure of which is similar to the structure of the new phase. However, these virtual nuclei cannot be used to make a comparison because the chemical potential and pressure inside such fluctuations differ significantly from those we have inside the new phase due to the microscopically small size of the nuclei. Remember that the coexistence conditions (1) operate with the volume values of P and μ, corresponding to the macroscopic size of the coexistent phases. At the same time the macroscopic nuclei cannot arise because this process requires enormous energy. For this reason, the comparison procedure of the theory is not adequate to describe what happens in actual experiments. It is natural to hypothesize that *phase transitions in actual experiments are caused by processes of destabilization which take place in each phase, regardless of whether it is in contact with the other phase or not.*

Exactly this concept of stability loss is taken as the basis for the theory of formation of a new phase.[1-3] In this theory it is supposed that when crossing the phase-equilibrium line (say from point n_A^* to point n_A^{**}, Fig. 1) phase A is initially stable and becomes metastable with respect to the heterophase fluctuations. As a result, nuclei of the new phase form in the system; moreover, this process occurs without the presence of the stable second phase. Hence, the process is not directly connected with the equilibrium conditions (1). These criteria determine only a boundary between equilibrium (stable) and metastable states. In the theory of formation of the new phase, the phase-transition curves, as a matter of fact, are

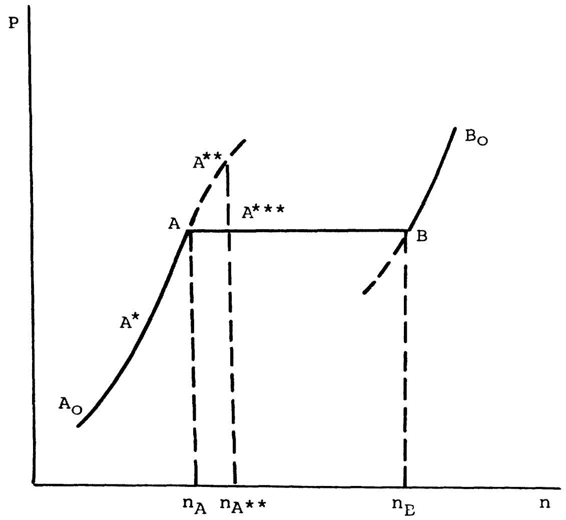

FIG. 1. The type of pressure isotherms $P=P(\rho)$ possible in the phase-transition vicinity.

identified as the curves on which the spatially uniform metastable states vanish. Consequently, in a statistical mechanical analysis of equilibrium systems, phase transitions should be associated with the vanishing of the spatially uniform equilibrium states.

It is well known that calculation of the Gibbs distribution can be reduced to solving an infinite chain of Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) equations for single-particle distribution functions. Therefore, the vanishing of stable states ought at the same time to be described by the vanishing of spatially uniform BBGKY solutions; in the other case the Van Hove theorem would be violated. According to this theorem statistical mechanics does not describe metastable states after passing to the thermodynamic limit (see Sec. III of this paper).

In 1951, Fisher put forward a hypothesis[4] according to which the BBGKY solutions vanish on the phase equilibrium line. However, later on he gave up the idea, and accepted the traditional conception in accordance with which statistical-mechanical equations lose their solutions not on the binodal, that is the liquid-vapor coexistence curve, but on the spinodal which separates weakly unstable metastable states and absolutely unstable states.[5]

The first convincing confirmation of the "loss of the solution" hypothesis was made by Baxter.[6] Applying the Percus-Yevick (PY) equation to the critical point he has found analytically that at subcritical temperatures and critical densities the PY solution becomes a complex one and hence is not well behaved. Thereafter, the curve on which the real PY solutions vanish has been shown to have a parabolic form resembling the binodal. However, more comprehensive investigations showed that $n_{\mathrm{PY}}(\Theta)$ actually is located inside the Monte Carlo binodal which was calculated using the coexistence conditions (1). Moreover, it turned out that the correlation radius on the $n_{\mathrm{PY}}(\Theta)$ curve increases to infinity; this resembles the behavior of the spinodal rather than that of the binodal. That is why the viewpoint is taken that the curve on which the PY solutions vanish should be identified with the spinodal.[7] A less empirical argument however, is that none of the known approximate equations of the theory of liquids has the "loss of solution" property at high densities. That is why there is no description of freezing based on "one-phase" approaches up to now. All this results in the fact that the concept of the "loss of solution" is now almost forgotten; the conventional viewpoint is that only "two-phase" approaches based on the thermodynamic criteria (1) should be used to determine the phase phenomena. This concept is claimed in the review of Baus (1987): "Today it is clear that one-phase approaches cannot locate the two-phase coexistence accurately. The phase transition itself can be located unambiguously only by thermodynamic conditions (1)" (Ref. 8, p. 1129). From this viewpoint it follows that both the Lindemann[9] and Hansen-Verlet[10] rules which allow one to locate the melting point based only on the consideration of the crystal-phase properties, are empirical ones; these rules cannot be grounded theoretically. "These rules are approximate and cannot be used to locate the true thermodynamic coexistence between a liquid and solid; as already stated, such a study does require the simultaneous consideration of both the liquid and solid" (Ref. 8, p. 1130).

We cannot agree that the two-phase approach is the only way to solve the phase-transition problem. The first-order phase-transition curve is the curve of loss of stability and at the same time is the coexistence curve. Therefore, both the one-phase and two-phase approaches should be considered to be equivalent.

We show that using an approach that is more accurate than the PY approximate-integral equation,[11] we can predict the evaporation, condensation, and crystallization phenomena.[12–17] Furthermore, we obtain a freezing criterion similar to those of Lindenmann and Hansen-Verlet; this allows us to predict freezing in accordance with the properties of the distribution function of a single liquid phase.

We begin with formulating the exact equations for distribution functions that give a complete description of matter (Sec. II). Then we consider in Secs. III and IV two- and one-phase approaches to the phase transitions as they follow from the exact equations. Subsequent sections treat the results obtained with the approximate equation in terms of the one-phase approach. We consider the processes of crystallization (Sec. V), evaporation (Sec. VI), and condensation (Sec. VII), and we consider phase diagram of simple liquids (Sec. VIII). In conclusion, we briefly discuss the process of crystal melting (Sec. IX).

II. EQUATIONS FOR DISTRIBUTION FUNCTIONS

It was shown that the BBGKY chain can be transformed (with no loss of generality) to a system of two equations[15,16]

$$\Theta^{-1}[\mu-\mu_0(\Theta)]=\ln\rho_1-\int_v \rho_2 C_{12}^{(1)} d(2)\ , \tag{2a}$$

$$h_{12}=C_{12}^{(2)}+\int_v \rho_3 C_{13}^{(2)} h_{23} d(3) \tag{2b}$$

for two unknown distribution functions $\mathcal{G}_{(1)}$ and $\mathcal{G}_{(2)}$, so that all higher-order distribution functions $\mathcal{G}_{(3)}$, $\mathcal{G}_{(4)}$ are thereby eliminated from the BBGKY chain. The following notations are used in (2):

$$\rho_i \equiv \rho(\mathbf{r}_i)=n\,\mathcal{G}_i,\quad \mathcal{G}_i \equiv \mathcal{G}_{(1)}(\mathbf{r}_i)=\exp(\omega_i)\ , \tag{3}$$

$$\begin{aligned}\mathcal{G}_{ij} \equiv \mathcal{G}_{(2)}(\mathbf{r}_i,\mathbf{r}_j) &= \mathcal{G}_i\mathcal{G}_j(1+h_{ij}) \\ &= \mathcal{G}_i\mathcal{G}_j \exp\left[-\frac{\phi_{ij}}{\Theta}+\omega_{ij}\right]\ .\end{aligned} \tag{4}$$

$\omega_i=\omega_{(1)}(\mathbf{r}_i)$, $\omega_{ij}=\omega_{(2)}(\mathbf{r}_i,\mathbf{r}_j)$ are the one-particle and two-particle thermal potentials, $h_{ij}=h(\mathbf{r}_i,\mathbf{r}_j)$ is the total correlation function, $\phi_{ij}=\phi(r_{ij})$ is the two-particle interaction potential, which depends solely on the distance separating the particles, $r_{ij}=|\mathbf{r}_i-\mathbf{r}_j|$,

$$\begin{aligned}C_{ij}^{(1)} &\equiv C^{(1)}(\mathbf{r}_i,\mathbf{r}_j) \\ &= h_{ij}-\omega_{ij}-\tfrac{1}{2}h_{ij}(\omega_{ij}+M_{ij}^{(1)})\ ,\end{aligned} \tag{5}$$

$$C_{ij}^{(2)} \equiv C^{(2)}(\mathbf{r}_i,\mathbf{r}_j) = h_{ij} - \omega_{ij} + M_{ij}^{(2)} = h_{ij} - \gamma_{ij} \ , \qquad (6)$$

are direct correlation functions of first ($C^{(1)}$) and second ($C^{(2)}$) order, $M^{(1)}$ and $M^{(2)}$ are the first- and second-order bridge functionals containing an infinite number of bridge diagrams, each depending only on the product of total functions h_{ij}, and finally, $\mu_0(\Theta)$ is a constant in the chemical potential, whose value is determined by internal degrees of freedom of molecules. The introduction of three interrelated functions $\mathcal{G}_{(2)}$, h, and $\omega_{(2)}$ is caused only by convenience considerations. They are all mutually replaceable once one of them is known; the other two can always be calculated.

The preceding equations contain all of the information that is of interest to us (including that of phase transitions). However, the set of exact equations (2) cannot be used directly to solve the concrete problem, because this set includes bridge functionals $M^{(i)}$, whose values are unknown. Comparison of diagrams contained in functionals $M^{(1)}$ and $M^{(2)}$ allows to assume that [17]

$$M^{(1)} \simeq \tfrac{1}{3} M^{(2)} \ . \qquad (7)$$

On the other hand, the functional $M^{(2)}$ was suggested to have the form[11]

$$M^{(2)} = -\tfrac{1}{2}\omega_{12}^2 \ . \qquad (8)$$

Careful analysis demonstrates that closure (8) provides higher accuracy than such familiar approximations as the HNC and Percus-Yevick approximations.

III. TWO-PHASE APPROACH TO THE PHASE TRANSITION PROBLEM

Consider now the simplest case of vapor-liquid equilibrium. Let a liquid phase occupy the half space $Z<0$ and the vapor phase occupy the space $Z>0$. As Z tends to $\pm\infty$ in (2), we obtain two spatially-homogeneous fluids placed beyond the transition layer whose thickness 2Δ is considered to be finite. As far as inside each of the phases $\mathcal{G}_{(1)}=1$, set of equations (2) is reduced thus to two sets of equations of absolutely the same type

$$\Theta^{-1}(\mu - \mu_0(\Theta)) = \ln n - n \int_v C^{(1)}(r_{12};n,\Theta)\, d(2) \ , \qquad (9a)$$

$$h(r_{12}) = C^{(2)}(r_{12};n_i\Theta) + n \int_v C^{(2)}(r_{13};n,\Theta) h(r_{23})\, d(3) \ . \qquad (9b)$$

In obtaining (9) we have taken into account the fact that the direct correlation functions $C^{(i)}$ decrease very rapidly as r_{12} increases. Therefore, at $|Z| \gg \Delta$ the contribution of the next phase to the integral over volume becomes equal to 0. Now the set of equations (9) can be solved at liquid and vapor densities n_l and n_v independently (note that the value of constant μ_0 is the same both for liquid and vapor and does not depend on Z). Having found correlation functions $\mathcal{G}_{(2)}^v$ and $\mathcal{G}_{(2)}^l$ with the Ornstein-Zernike (OZ) equation (9b) one can calculate μ_v and μ_l values using formula (9a) and pressure P_v and P_l by formula

$$P = n\Theta - \tfrac{1}{6} n^2 \int_0^\infty r \frac{d\phi}{dr} \mathcal{G}_{(2)}(r) 4\pi r^2 dr \ . \qquad (10)$$

In solving (9) at different densities, it is possible to finally find those values of $n_v(\Theta)$ and $n_l(\Theta)$ that change the coexistence conditions (1) into identity. These points are the phase-equilibrium ones. This method of constructing the phase-equilibrium curves is an absolutely general one. Therefore, it can be applied both to liquid-solid and solid-solid transitions. However, in the latter case we meet with difficulties arising because inside the solid the density $n(\mathbf{r})$ is a periodical function of $\mathbf{r}$. Hence n depends on r even at $r \to \infty$ and, therefore, to determine two unknown functions $\mathcal{G}_{(1)}(\mathbf{r})$ and $\mathcal{G}_{(2)}(\mathbf{r}_1,\mathbf{r}_2)$ it is necessary to solve the whole set of equations (2) simultaneously. This is a more difficult task then simply solving the OZ equation (9b), as in the liquid-vapor transition case. To avoid these difficulties, the density-functional method has been proposed.[8,18] In this method two functions $\mathcal{G}_{(1)}(\mathbf{r};n,\Theta)$ and $\mathcal{G}_{(2)}(\mathbf{r}_1,\mathbf{r}_2;n,\Theta)$, each of them depending not only on n and Θ but also on the coordinates of particles $\mathbf{r}_1$ and $\mathbf{r}_2$, are replaced by a single function-free energy $F(n,\Theta)$, which depends now only on n and Θ. One would think that the method yields great advantage because the dependence on distance $\mathbf{r}$ is now removed. However, the situation is not so simple since the dependence of F on density and temperature is not known *a priori* and there is no equation to provide an estimate of F directly. The conventional indirect approach to this problem is to expand the excess free energy $F_{\text{ex}} = F - F_0$ in a functional Taylor's series in density $n(r)$ about the state $n_r(r)$ of a reference system in which F_{ex} is supposed to be known. F_0 is an ideal-gas term. Integrating the series gives[8]

$$F_{\text{ex}}[n] = F_{\text{ex}}[n_r] + \int_v \frac{d\mathbf{r}\,\delta F_{\text{ex}}[n]}{\delta n(\mathbf{r})} \Delta n(\mathbf{r}) + \int_v d\mathbf{r} \int_v d\mathbf{r}' \int_0^1 d\lambda (1-\lambda) \frac{\delta^2 F_{\text{ex}}[n_r + \Delta n]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \Delta n(\mathbf{r}) \Delta n(\mathbf{r}') + \cdots \ , \qquad (11)$$

where $\Delta n = n(r) - n_r(r)$. To use this formula it is necessary to know the under-integration functional derivatives, which are usually determined using different approximations; this is, in essence, equivalent to finding an approximate solution of the set of equations (2). In fact, it has been shown[8] that

$$\delta F(n)/\delta n(\mathbf{r}) = \mu \ , \qquad (12)$$

$$\delta^2 F(n)/\delta n(\mathbf{r}) \delta n(\mathbf{r}') = C^{(2)}(\mathbf{r},\mathbf{r}') \ , \qquad (13)$$

where μ is the chemical potential, $C^{(2)}$ is the second-order direct-correlation function determined with (6).

Strictly speaking, both μ and $C^{(2)}$ can be obtained only by solving (2). However, if a solution is found, then, as shown in the following, there is no need to calculate the free energy: The phase-transition points can be found directly from the set of equations (2).

IV. ONE-PHASE APPROACH TO THE PHASE-TRANSITION PROBLEM

Let us take a cylinder of volume V filled up with vapor and increase the pressure P gradually. As soon as the vapor density reaches its value n_A (Fig. 1), there comes into existence two changes in the system: either it can change into a metastable state that is at the same time a spatially uniform phase or the system separates into two equilibrium phases A^{***} becoming heterogeneous with an average density n_A^{**} equal to that of the metastable phase A^{**}. In actual experiments either of these situations can happen with its appropriate probability. However, in the Gibbs statistics only the latter case is possible. This fact follows from the Van-Hove theorem, according to which for Gibbs systems the derivative $(\partial P/\partial n)_0$ is always either positive or equal to zero.[19] Therefore, the pressure isotherm $P(n)$ has a continuous form A_0ABB_0, as it is shown in Fig. 1. An understanding of the essentials of this result is probably best reached on the basis of the theory of formation of new phase. Indeed, let us divide the whole volume V occupied by the system into elementary cells of volume V_0 that are much greater than the size of the critical nucleus of the new phase. In this case the probability of formation of the critical nucleus in a given cell does not depend on what is happening in the neighboring cells. Hence, the probability p_v that one nucleus forms throughout the system (this allows the system to make the transition from the one-phase metastable state to the two-phase equilibrium state without a barrier) is proportional to the number of elementary cells $v = V/V_0$. Hence, the larger a system is the higher the probability is of the spontaneous transition from the metastable state to equilibrium state. In the limiting case of infinite volume $V \to \infty$ at any small oversaturation (that is at any small probability p_0) the probability of transition $p_v = vp_0$ is always equal to unity. From this it follows that metastable states do not exist in infinite systems at all. Remember now that the Gibbs statistics are built in the thermodynamic limit

$$N, V \to \infty ; \quad n = \frac{N}{V} = \text{const} , \tag{14}$$

which means that the Eqs. (2) are justified only under the conditions (14). Since there are no metastable states in those systems that satisfy conditions (14), then those systems are not described by Eqs. (2).

Now the only thing left is to show that the horizontal part AB on the $P(n)$ isotherm does describe the two-phase state (that is, spatially inhomogeneous) of a system. For this it is easier to use the thermodynamic relations (see Appendix A) which can be obtained from the Gibbs distribution. Since Eqs. (2) follow also from the Gibbs distribution, then there ought to be reciprocation between Eqs. (2) and thermodynamics. Therefore, if thermodynamics predict that the spatially uniform states vanish at densities n_A and n_B where $P_A = P_B$ and $\mu_A = \mu_B$, then the same result ought to follow from Eqs. (2). Hence, our goal is to find points where the one-phase solutions of system (2) vanish. The condition of vanishing of solutions is formulated in an especially simple form for liquid and gases in which the homogeneity condition takes the form $\mathcal{G}_{(1)} = 1$. In the case of a homogeneous system, (2a) degenerates from an equation to the definition of chemical potential, and (2b) reduces to the OZ equation for a single unknown function $\mathcal{G}_{(2)}$. Obviously, condition $\mathcal{G}_{(1)} = 1$ ceases to hold inside the interval $\{n_A, n_B\}$ as there exists a transition layer between two phases where the density is not constant. Consequently, phase-transition points (i.e., points of stability loss) in gases and liquids are the points at which the solution of the OZ equation vanishes. In the case of crystals, the solutions are more complicated, see the following. These statements call for certain elaboration.

First, the OZ equation has numerous solutions, only one of which satisfies all constraints and thus has a physical meaning. When we say that a solution vanishes, we mean that this physically meaningful solution vanishes.

Second, we need to emphasize that the fact that a solution has vanished does not signify at all that thermodynamic functions of the system vanish simultaneously with it in the interval $\{n_A, n_B\}$. As follows from Appendix A, the thermodynamic functions exist but are defined by additive formulas of type (A2).

Third, the vanishing of a solution as such does not yet carry any information on the mechanism of the loss of stability. To identify it, one needs to analyze the behavior of the distribution functions at the points where the solution vanishes. We show that the mechanism is different in different types of phase transitions: on the crystallization curve the system undergoes stability loss at the point of the first minimum of the thermal potential, and on the evaporation curve the asymptotic behavior of distribution function becomes unstable, and so forth.

Fourth, the conditions of phase coexistence (1) is to be completely satisfied at the points at which the solutions vanish, which is consistent with the theorem of uniqueness of solution; there is no need to introduce these conditions into the theory by hand. Of course, this is justified only in case of a perfect theory operating with the exact equations (2) for distribution functions. In an imperfect theory the thermodynamic and "loss of solution" criteria may differ (see, for example, Sec. VIII and Table III). Nevertheless using the "loss of solution" criterion one can obtain some important results at the microscopic level.

Finally, let us consider one of the possible causes of the vanishing of the OZ solution. Substituting (6) into (9b) gives

$$\gamma(r_{12}) = n \int_v [h(r_{13}) - \gamma(r_{13})] h(r_{32}) d(3) . \tag{15}$$

In the Fourier transforms this equation reduces to the quadratic equation for $h(k)$

$$nh^2(\mathbf{k}) - n\gamma(\mathbf{k})h(\mathbf{k}) - \gamma(\mathbf{k}) = 0 . \tag{16}$$

The solution is as follows:

$$h(k)=\frac{1}{2n}\{n\gamma(k)+\sqrt{n\gamma(k)[n\gamma(k)+4]}\}\ . \tag{17}$$

If at certain k values the transform $h(k)$ becomes negative, this means that the $h(k)$ value is complex. Hence, $h(r)$ also becomes complex; this is at variance with the definition of the distribution function $\mathcal{G}_{12}=1+h_{12}$ that requires that $\mathcal{G}_{12}$ is real. Therefore, the points where $\gamma(k)$ becomes equal to zero are the points at which physical solution of the OZ equation vanish. (Of course the problem of whether this way in which the solution vanishes exists in reality is still open).

V. CRYSTALLIZATION OF LIQUIDS

The vanishing of the solution at the phase-transition point is a property of the exact OZ equation in which all the diagrams are taken into account in $M^{(2)}$. However, the exact equation cannot be used in real calculations, it should be closed using any approximation. The approximate equations of the theory of liquids may not possess the properties of "vanishing of solutions" at all or they may possess them partly. Therefore, the validity of the "one-phase" approach in the first place depends on the accuracy of the applied approximate equation. There is only one reliable idea in choosing the approximation: The more accurately the given equation describes the "traditional" parameters of a system (pressure, compressibility and so on), the higher the validity of the equations is to predict the phase-transition lines. That is why we take for this approximation the formula that follows from (8)

$$\tfrac{1}{2}\omega^2(r)+\omega(r)=\gamma(r)\ . \tag{18}$$

The obtained equation can be solved for ω, if we "forget" for a time that γ is in its turn a functional of ω. This gives

$$\omega(r)=-1+\sqrt{1+2\gamma(r)}\ ; \tag{19}$$

the second solution, corresponding to a minus sign in front of the square root, must be dropped because it does not satisfy the condition $\omega\to 0$ as $r\to\infty$. If we denote by $r_{\min}$ that point on the r axis at which $\gamma(r)$ reaches a minimum, it is obvious that this point corresponds to the minimum value $\omega_{\min}=\omega(r_{\min})$. This last quantity is real only if $\gamma_{\min}\geq-\frac{1}{2}$; if $\gamma_{\min}<-\frac{1}{2}$, the thermal potential becomes complex. Therefore, the points of the phase diagram where

$$\gamma_{\min}=-\tfrac{1}{2},\quad \omega_{\min}=-1 \tag{20}$$

are the points where the real solutions of Eq. (18) vanish; only these solutions have a physical meaning. According to the arguments already given, the system must undergo the loss of stability at just these points. Let us test these statements.

System of hard spheres. When solving Eq. (18) numerically we have found that the accuracy of finding density $\rho^*=n\sigma^3$ (where σ is the diameter of the sphere) at which the iteration procedure begins to diverge, depends on a procedure used. The higher the accuracy of the procedure used the smaller the difference is between this ρ value and that value obtained using criterion (20). A small excess of ρ over ρ_0 makes the solution of (18) complex only in the small vicinity of $r_{\min}$. Hence, it is difficult to discover this overflow with numerical discrete methods of finding solutions. Taking into account the above mentioned we identified ρ_0 with that of ρ, which corresponds to when the thermal-potential value equals -1 (Fig. 2). This figure also shows the $\omega(r)$ dependence as it follows from the Labik-Malijevsky approximation, the error of which does not exceed 0.5 percent.[20] We have found that $\rho_0=1.02$. On the other hand, a number of works based on the density functional methods present ρ_0 values that lie within the interval $0.94\leq\rho_0\leq0.99$.[21] We cannot judge which of approximations used in the density functional method is more reliable. Note only that the upper limit of these values equals 0.99, which is very close to our value $\rho=1.02$. The difference between both the values is equal to $\approx3\%$ and almost coincides with the 2% error of the Eq. (18) found in accordance with its thermodynamic inconsistency.[11] The value $\rho_0=1.02$ is also close to the point of the loss of mechanical stability $\rho=1.011$ found in a different way.[22] Consider now the Monte Carlo determined value $\rho_0=0.94$,[23,24] which is far from our $\rho_0=1.02$. We think that this discrepancy is most likely due to the way of finding ρ_0 used in.[24] Indeed, the phase-transitions points were determined in Ref. 24 in two stages: first by finding the pressure in the liquid and crystal phases, and then integrating the thermodynamic identity $d\mu=\rho^{-1}dP$ and calculating the chemical potential. The phase equilibrium point was determined via (1). For integrating in dP, it was necessary to find the values of $P(\rho)$ for both phases in the entire density range from $\rho=0$ to the phase-transition density. However, matter cannot exist in the crystal phase at densities below the melting-point value; hence, additional constraints had to be imposed on the systems so as to make the melting of the crystal at low

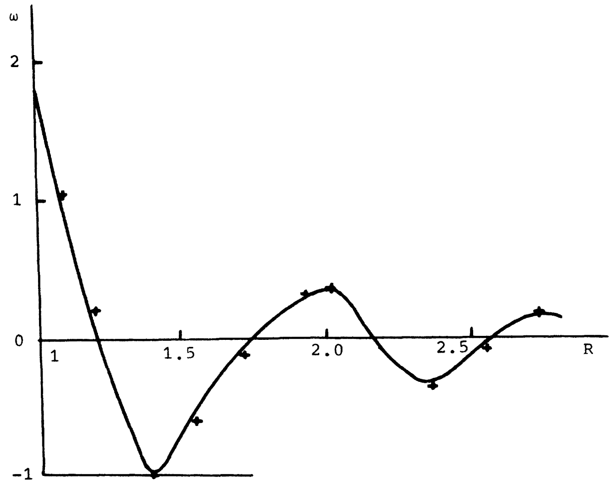

FIG. 2. Thermal potential ω of a system of hard spheres as a function of distance $R=r/\sigma$ at the density value $\rho=n\sigma^3=1.02$. Solid curve, as calculated with (18); crosses, data of Ref. 20.

densities impossible. We know nothing about errors introduced by these constraints. The chemical potential of the liquid phase cannot be determined accurately either. We know that a system of hard spheres with $\rho \geq 0.90$ evinces the so-called "chaos interval" within which the ergodicity of the small system used for the numerical simulation is violated.[25] Taking into account all the above mentioned,[25] we are inclined to consider the value $\rho_0 = 1.00 \pm 0.01$ to be the most probable value of the freezing density.

Lennard-Jones (LJ) liquid. Table I lists the values of density $\rho = n\sigma^3$ and temperature Θ/ε (ε is the energy parameter of the LJ potential) at which the LJ liquid crystallizes. The second line of the table indicates the Monte Carlo (MC) data,[26] and the third line gives the points at which the solutions of equations (18) vanish. We see that (18) and MC simulation give results that very nearly coincide. Table II presents results obtained by density functional methods (second line).[27] The agreement with the points obtained from (18) (third line) is satisfactory being at the same time slightly worse than that at high temperatures.

Unfortunately, we cannot check how accurate the second prediction of the theory is, that is that $\omega_{\min}$ turns into -1 on the crystallization curve, because no such data are reported in the literature. We were able to find data only for the triple point lying at the very "bottom" of the crystallization curve[28] and thus were in a position to calculate the $\omega(r)$ curve. You see that $\omega_{\min}$ at the triple point is exactly equal to -1 (Fig. 3).

Now let us try to understand why none of known approximations, with the exception of (8), describe the process of crystallization. Consider the OZ equation written in the form similar to that of (18),

$$\omega - M^{(2)}[\omega] = \gamma \ . \tag{21}$$

$M^{(2)}[\omega]$ is a functional, which depends on ω. It is evident that in the general case this functional equation determines real ω values only for certain values of γ. In accordance with the above mentioned, the points where ω values become complex are the phase-transition points. In the HNC approximation $M=0$ and (21) reduces to $\omega = \gamma$ for any real γ. In the Labik-Malijevsky approximation the bridge functional $M^{(2)} = M^{(2)}(r)$ and now we have

$$\omega(r) - M^{(2)}(r) = \gamma(r) \ . \tag{22}$$

Hence, (22) can be solved for $\omega(r)$ for any of $\gamma(r)$. The PY equation $\exp[\omega(r)] - 1 = \gamma(r)$ defines complex values of $\omega = \ln(1+\gamma)$ only for $\gamma < -1$. Such high negative values of γ are achieved at densities that are considerably greater than the crystallization density.

TABLE I. Crystallization parameters of the LJ liquid.

Θ/ε	100	10	5	2.74	1.00
ρ_{MC}	2.601	1.50	1.279	1.117	0.90
ρ	2.600	1.53	1.270	1.110	0.82

TABLE II. Crystallization parameters of the LJ liquid.

Θ/ε	3.2	3.0	2.5	2.0	1.5	1.0
ρ_{df}	1.226	1.198	1.135	1.069	0.991	0.882
ρ	1.186	1.153	1.070	0.986	0.903	0.820

VI. EVAPORATION OF A LIQUID

We have demonstrated that the loss of stability during crystallization is caused by processes that occur in the vicinity of the first minimum of the thermal potential. Consider now a different mechanism caused by the destruction of the asymptotes of the distribution function. It can be readily shown (see Appendix B) that as $r \rightarrow \infty$, the OZ equation can be written in the form

$$\frac{d\psi}{dr} = 2\pi\rho \int_0^\infty C^{(2)}(\tau)\tau[\psi(r+\tau) - \psi(r-\tau)]d\tau \ , \tag{23}$$

where $\psi = r\omega(r)$. This equation determines the universal asymptotic behavior of the thermal potential, which obviously has the form

$$\psi(r) = Ae^{-\alpha r}, \quad \omega(r) = \frac{A^{e^{-\alpha r}}}{r}; \quad A = \text{const} \ , \tag{24}$$

where α is found from the transcendental equation

$$1 = 4\pi\rho \int_0^\infty C^{(2)}(\tau) \frac{sh(\alpha\tau)}{\alpha\tau} \tau^2 d\tau \ . \tag{25}$$

As a rule, the asymptotic behavior cannot be found by conventional methods of numerical solution of the OZ equation under constraints (24) and (25), because the precision of the available procedure is unsatisfactory. At the same time, the direct function in (25), which according to (6) and (8), equals $C^{(2)} = h - \omega - \frac{1}{2}\omega^2$, decreases fairly steeply; it can be readily found by substituting into $C^{(2)}$

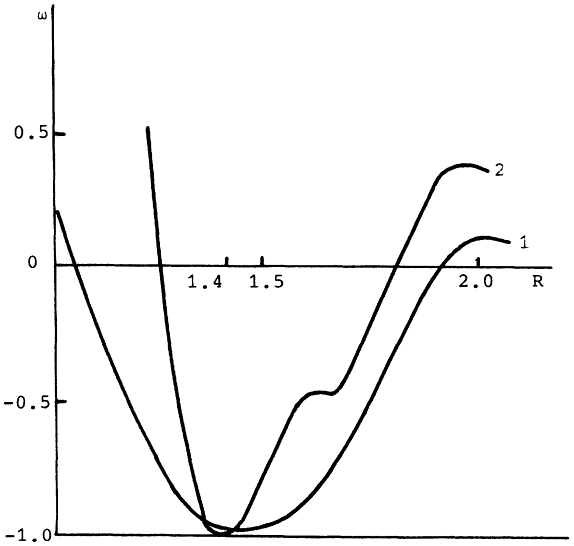

FIG. 3. Thermal potential ω as a function of distance R. Curve 1: triple point of a LJ liquid (by data of Ref. 25). Curve 2: fluid of a hard sphere at the melting point (Ref. 31).

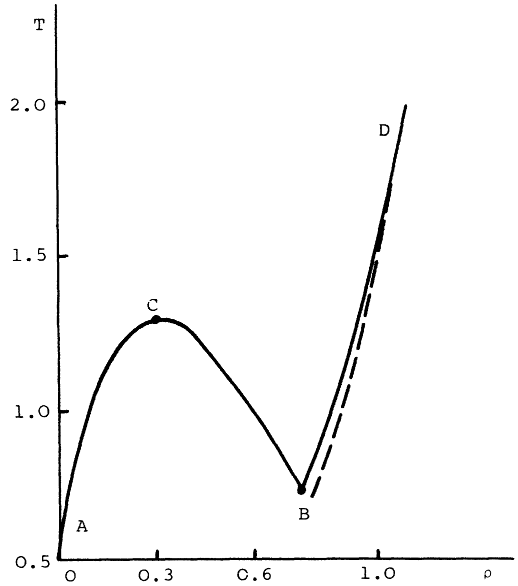

FIG. 4. General curve on which solution to (18) vanish. *C*—critical point, *B*—triple point; dashed curve—MC data.

the values of ω that are found by solving (18). Integrating then the integral in (25), we can find the value of α that turns this equation into identity. It is thus found that no α satisfying (25) exists in the region to the left of the curve CB in Fig. 4, while the corresponding values of α are easily found to the right of this curve. Therefore, from (18) it follows that the stability on the evaporation curve is broken down owing to the destruction of asymptotic behavior (24). On the curve CB, α vanishes [this corresponds to $\gamma(k)\rightarrow 0$ at $k=0$; see (17)], which is certainly an artifact since this is possible only at the critical point *C*, not on the entire curve CB. Actually, this is not the only indication that the approximation (18) is hardly satisfactory at low temperatures and high densities. Thus the pressure of the liquid *P* becomes negative in the vicinity of the curve CB; the phase-equilibrium curves are displaced relative to the MC data; etc. In this case, however, this is not really important. The principal feature is that (18) provides a qualitatively correct description of evaporation.

VII. VAPOR CONDENSATION

The stability-loss mechanism again changes at the vapor-condensation AC (Fig. 4). Note that in this case all numerical-solution methods (we make use of several here) yield the same values of density "upon vanishing." One can, therefore, think that the condensation curve found by these methods is fairly reliable. Furthermore, all methods point in an unambiguous way to the same stability-loss mechanism. The fact is that the zero approximation that we chose in constructing the iterative procedure was always the $\omega(\rho^*)$ value found for the density $\rho^*=\rho-\Delta\rho$. The quantity $\Delta\rho$ was taken to equal 0.02; that is, it was very low and thus ensured sufficiently fast convergence of the iterative procedure that was typically uniform in *r*. On the condensation curve, however,

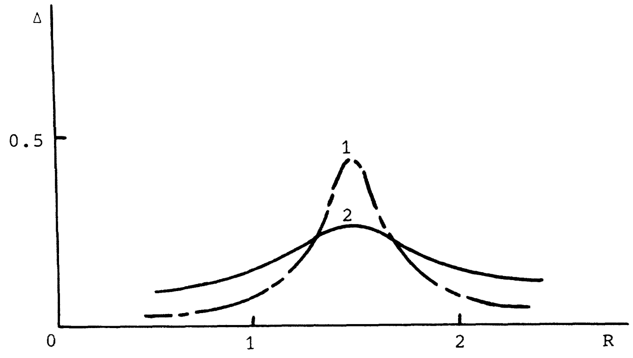

FIG. 5. Divergence of the iterative procedure on the vapor condensation curve.

iterations began to diverge, and the divergence was nonuniform in *r*: the differences $\Delta^{(k)}=\omega^{(k+1)}-\omega^{(k)}$ (k is the number of the iteration) first began to increase only close to the first minimum of the function $\omega(r_{\min})$ while far from this minimum they continued to converge (Fig. 5). Then the divergence region gradually widened and finally covered the entire axis *r*. This type of divergence indicates that the system loses stability at the first minimum of thermal potential $\omega_{\min}$. The coordinate of this minimum, $r_{\min}$, on the condensation curve was always the same ($r_{\min}=1.48\sigma$). The absolute value of $\omega_{\min}$, however, depends strongly on temperature. The asymptotic behavior of the distribution function on the condensation curve was stable because the values of α in (25) deviated appreciably from zero.

VIII. PHASE DIAGRAM OF LJ LIQUID

The complete curve on which the solutions to (18) vanish for the LJ liquid is plotted in Fig. 4 in the coordinates ρ versus $T^*=\Theta/\varepsilon$. Obviously, it is qualitatively similar to the phase-equilibrium curve of real liquids: the vapor-condensation curve AC that increases with increasing ρ is replaced at the critical point *C* with a falling curve *CB* of evaporation of the liquid, while the evaporation curve is replaced at the point *B* by an almost vertical line of crystallization, *BD*. At the same time, the complete quantitative agreement with experimental data has not been achieved. Thus the MC data[23] give the critical-point coordinates $\rho_c=0.34\pm0.02$, $T_c^*=1.34\pm0.02$, while (18) yields $\rho_c=0.30\pm0.02$, $T_c^*=1.30\pm0.02$. For the triple point, MC data[23] yield $\rho_B=0.86$ (according to Refs. 27 and 29 $\rho_B=0.818$), $T_B^*=0.67$, while (18) gives $\rho_B=0.67$, $T^*=0.65$. The fit is not as good as one would like to find. On the other hand, it is sufficiently good for not rejecting it as spurious.

We have seen that each of three curves (condensation, evaporation, and crystallization) is characterized by its particular mechanism for which the solution vanishes. How does one pass from one to the other at the critical and triple points? More or less reliably it can be imagined only in case of the triple point. Two mechanisms are at work in this case: the system loses the stability both at the first minimum of the thermal potential and at large distances. It is possible that the situation is the same at the critical point, however, we suggest that this problem is worthy of further investigation.

We have mentioned on several occasions that phase-equilibrium curves $\rho(\Theta)$ determined on the basis of the equality of pressures and chemical potentials must coincide with the curves found from the condition of stability loss. However, this is true only in the rigorous theory based on solving the exact OZ equation (15). Any concrete theory is approximate so that the results obtained via various approximations [e.g., in the framework of the density functional method and upon the vanishing of solution of (18)] need not exactly coincide with one another. For this reason, conditions (1) need not be exactly satisfied in the theory in which the phase-coexistence curves are found from the condition in which the solution to the approximate equation (18) vanishes. Of course, if the approximation used is sufficiently successful, the values of P and μ found on the phase-coexistence curve must be nearly the same in the two phases. Yet another difficulty exists. Any approximate OZ equation is not completely consistent thermodynamically.[30] This means that we arrive at different results depending on the method of calculating P and μ. Hence we can compare only the values of either P_A and P_B or μ_A and μ_B that are calculated by a given method. Even this limitation does not give a waterproof guarantee because the same method may give one error in phase A and a different error in phase B. Nevertheless it may be interesting to compare P and μ values thus obtained for two phases to make a conclusion about the thermodynamic consistency of the theory under consideration. Table III gives the chemical potentials μ and pressure P obtained by formulas (9a) and (10) at points at which the solutions vanish. When $\Theta/\varepsilon \geq 1$ the conditions (1) are fulfilled. However, as we already have said, the accuracy of Eq. (18) falls with the temperature decrease that causes the pressure to become negative and the conditions (1) to be violated. At the same time, curve 2 (Fig. 6) obtained from the coexistence conditions (1) deviate from the curve in which the solution vanishes. Thus, at low-temperature Eq. (18) predicts two different curves of phase coexistence. It is evident that by using different formulas to calculate μ and P we arrive at different phase-equilibrium curves. Which of them should be considered as most correct? As a rule, the curve in which the solutions vanish is identified as spinodal, that is the curve of mechanical-stability loss, while the curve of equality of μ and P is considered to be binodal, that is the true phase transition. It is difficult, however, to agree with this viewpoint since in this case the range inside curves 1 and 2 should be identified as a metastable range.

TABLE III. Pressure P and chemical potential along line of vanishing of solution.

		$P\sigma^3/\Theta$		$(\mu-\mu_0)/\Theta$	
Θ/ε	n_l/n_v	Vapor	Liquid	Vapor	Liquid
1.2	2.67	0.0731	0.0738	−2.97	−3.02
1.1	4.09	0.058	0.026	−3.20	−3.61
1.0	6.50	0.045	−0.034	−3.39	−4.35

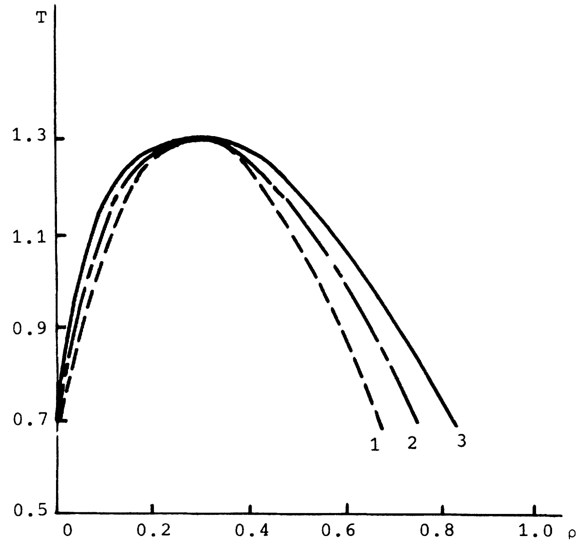

FIG. 6. Liquid-vapor coexistence. (1) Curve of vanishing of solution to Eq. (18). (2) Curve on which the conditions (1) are satisfied. (3) MC coexistence curve for a LJ liquid.

However, as we know, the metastable states cannot be described in terms of the equilibrium statistical mechanics. Hence, the BBGKY chain of equations as well as system (2) has no solution which corresponds to the metastable states. Of course, application of the approximate equation (18) instead of the exact OZ equation (15) can cause a displacement of the phase equilibrium curve on the n-Θ plane or involve new types of solution vanishing. However, what is certain is that an equilibrium equation cannot be converted into a kinetic one. On the other hand, the metastable states are related to their lifetime and therefore should be described just by a kinetic equation.

From the above mentioned, it is now evident that the discrepancy of curves 1 and 2 (Fig. 6) is due to the ordinary thermodynamic inconsistency of the theory. When calculating μ and P (as well as other thermodynamic function) we introduce not only an error stipulated by the original approximation of the bridge functional M, but some additional errors. The letter may be due to different causes. Indeed, for example, the sign of factor

$$r d\phi(r)/dr \exp[-\phi(r)/\Theta]$$

in the integral (10) changes to the opposite one at $r=1.13\sigma$ and as a result the positive and negative parts of the integral become approximately equal. Hence, the pressure P calculated by the virial equation results from a small difference of two large values and may become erroneous.[23] Therefore, curve 2 obtained with the equalities $\mu_1=\mu_v$ and $P_1=P_v$ is less reliable than curve 1 obtained directly from (8). Consequently, in the framework of the approximation used, the curves in which the solution vanishes present more reliable information about the first-order phase transitions. It should be kept in mind, however, that since the theory is based on approximate equation, all the results are rather qualitative than quantitative. Nevertheless, we feel that a one-phase approach based on an equation that is more accurate than Eq. (18) can describe the vapor-liquid coexistence quantitatively.

IX. MELTING OF CRYSTALS

Equations (2) are an exact equivalent of the Gibbs distribution, hence, these equations must describe not only liquid and gases but crystals as well. The one-particle distribution function, however, is not constant in crystals, being a periodic function of the coordinate r. Therefore, in the case of crystals we cannot consider just one OZ equation. The complete system of Eqs. (2) must be solved simultaneously (unfortunately, we cannot do it yet). Correspondingly, the stability loss of the crystal must be determined from the condition in which the solution to the total system of Eqs. (2) vanishes. Only an analysis of this solution can reliably establish details of how this happens. Nevertheless, we feel justified already to hypothesize that one of the mechanisms for which the solution vanishes is again caused by the impossibility of solving Eq. (2a) in real variables for the ω function [in the case of crystals, (2b) is formally written exactly as the OZ Eq. (15)]. If this hypothesis is valid, the solution to (2) must vanish on the melting curve at $\omega_{\min}=-1$. We were able to find in the literature only the MC data[31] on the two-particle distribution function of a system of hard spheres for the density close to that of the melting point. The corresponding curve is also plotted in Fig. 3. We see that for all practical purposes $\omega_{\min}$ is equal to -1, thus confirming the suggested hypothesis.

APPENDIX A

Although the statement that the system is a two-phase system if $\partial P/\partial\rho=0$ is repeated in nearly every textbook, we never saw it proved in the literature. Let us fill this void.

Integrating $dF=-pdV$, we obtain

$$F(n)=F(n_A)-P(V-V_A^0)\ ,$$

where $V_A^0=N/n_A$, $V_B^0=N/n_B$ are the volumes of the system in the states A and B, respectively. Setting $V=V_B^0$, we obtain

$$P=[F(n_A)-F(n_B)]/(V_B^0-V_A^0)\ .$$

Substituting this expression into $F(n)$ and converting to the free-energy density $\phi=F(n)/V$, we obtain

$$\phi(n)=\frac{\phi_A-\phi_B}{n_A-n_B}n+\frac{n_A\phi_B-n_B\phi_A}{n_A-n_B}\ . \tag{A1}$$

We introduce a parameter ν via the expression $n=\nu n_A+(1-\nu)n_B$, where n is matter density averaged over the whole system. Now (A1) can be rewritten in the form

$$\phi(n)=\nu\phi_A+(1-\nu)\phi_B\ . \tag{A2}$$

To clarify the physical meaning of the parameter ν, we derive this formula in a different manner. Assume that the system consists of two phases, that is, of two homogeneous subsystems occupying volumes V_A and V_B and composed of N_A and N_B particles, respectively. Since $V=V_A+V_B$ and $N=N_A+N_B$, the average density is

$$n=\frac{N}{V}=\frac{N_A+N_B}{V}=\frac{N_A}{V_A}\frac{V_A}{V}+\frac{N_B}{V_B}\frac{V_B}{V}$$
$$=\nu n_A+(1-\nu)n_B\ .$$

Likewise, we can derive an expression for the free-energy density. Comparing it with (A2), we find that $\nu=V_A/V$ is the fraction of the total volume V occupied by the phase A.

APPENDIX B

Write the OZ equation in the form

$$\omega(r)-M^{(2)}(r)=\frac{2\pi\rho}{r}\int_0^\infty C^{(2)}(x)x\,dx\int_{|r-x|}^{r+x}h(y)y\,dy\ . \tag{B1}$$

After multiplying (B1) by r and differentiating it with respect to r, we obtain

$$\begin{aligned}\frac{d}{dr}\{r[\omega(r)+M^{(2)}(r)]\}&\\ =2\pi\rho\int_0^\infty C^{(2)}(x)h(r+x)(r+x)x\,dx&\\ -2\pi\rho\int_0^r C^{(2)}(x)xh(r-x)(r-x)dx&\\ -2\pi\rho\int_r^\infty C^{(2)}(x)xh(r-x)(x-r)dx\ .&\end{aligned} \tag{B2}$$

Since $M^{(2)}$ and $C^{(2)}$ are rapidly decreasing functions of r, then as $r\rightarrow\infty$, (B2) reduces to (22) because in this case $h\rightarrow\omega$ and the integral from r to ∞ approaches zero.

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