Singular Point of a System of Lennard-Jones Particles at Negative Pressures

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The method of molecular dynamics is used in a system of 2048 Lennard-Jones particles to determine the spinodal of a stretched liquid and crystal and the lines of their phase equilibrium at negative pressures. It is shown that a metastable extension of the melting line does not reach the zero isotherm, and ends on the spinodal of a stretched liquid. The point of termination of metastable liquid-crystal phase equilibrium is the singular point at a thermodynamic surface of states.

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At negative pressures a liquid and a crystal are metastable. Two macroscopic metastable phases, unstable with respect to the formation of a certain third phase in them, may coexist in equilibrium [1]. Thus, the melting line is bound to have an analytic extension beyond the triple point into the region of negative pressures. The depth of such an extension may be limited by the boundaries of thermodynamic stability—the spinodal of a liquid, a crystal, or the zero isotherm.

Modern methods of experiments with shock waves make it possible to conduct an investigation of substance properties at negative pressures to $-(15\text{–}20)$ GPa, and more [2]. A metastable extension of the ice melting line was observed experimentally to -24 MPa [3]. The first attempts at measuring the compressibility of solids [4] and liquids [5] at tensile stresses have been made, but the methods suggested have so far a limited range of applicability. More reliable means of evaluating the substance behavior objectively at high, up to the spinodal, negative pressures are methods of computer simulation (method of Monte Carlo and molecular dynamics) [6–8]. In this Letter the method of molecular dynamics is used to determine thermodynamic properties, the spinodal, melting lines for a simple substance in the region of negative pressures.

The system under study contained 2048 Lennard-Jones particles, with the particle mass $m = 66.336 \times 10^{-27}$ kg, the potential parameters $\sigma = 0.3405$ nm, $\varepsilon/k = 119.8$ K, where k is the Boltzmann constant. Hereafter m, σ, ε are used as parameters of reduction of thermodynamic quantities. Reduced (dimensionless) quantities are marked with an asterisk (*).

Particles were placed in a cubic cell, periodical boundary conditions being imposed on its boundaries. The intermolecular potential was cut at a distance $r_c^* = r_c/\sigma = 6.78$ at densities $\rho^* = \rho\sigma^3 \leq 0.82$. The cutoff radius of the potential was taken to be equal to half the cell length at $\rho^* > 0.82$. The integration step of the classical equations of particle motion was 0.01 ps for a liquid and 0.005 ps for a crystal. Thermodynamic properties (pressure, internal energy, isochoric heat capacity) were calculated in the N, V, E ensemble along 11 isotherms from the interval $T^* = kT/\varepsilon = 0.1\text{–}2.0$.

Calculations always began from a stable region. In liquid simulation a random packing was chosen as the initial configuration of particles in the cell, and in crystal simulation it was a face-centered-cubic lattice. At temperatures $T^* = 0.7\text{–}2.0$ penetration into the metastable region of a liquid was realized by a successive isothermal compression of particles in the cell. The final configuration of particles at every given value of density was initial in calculating a state with a higher density. A balanced irregular packing of particles at $T^* = 0.7$ and $\rho^* = 0.85$ was taken as the initial particle configuration when thermodynamic properties of a liquid were calculated in a region of negative pressures. All the states on the isotherms $T^* = 0.55, 0.4$ have been obtained by an isochoric cooling of this configuration of particles with its subsequent stretch and compression. The characteristic time in which the system reaches equilibrium in a stable region is ~0.5 ns, in a metastable region it is up to 1 ns. The time of averaging for the values being calculated varied from 5 to 10 ns.

The results of calculating the pressure in the liquid phase are presented in Fig. 1(a). The last points on the isotherms on the high-density side determine the maximum supercompression (supercooling) of a liquid in the model. The extreme points on the isotherms $T^* = 0.4, 0.55, 0.7$ of the low-density side show the maximum stretch preceding the liquid boiling up.

The boundary of the thermodynamic stability of a homogeneous phase—spinodal—is determined by the condition $(\partial p/\partial \rho)_T = 0$ [9]. As it follows from Fig. 1(a), an increase in the density (pressure) is accompanied by an increase in the isothermal elasticity of an irregular structure. Thus, to the point of maximum supercooling the liquid phase does not tend to decrease thermodynamic stability against infinitesimal long-wave perturbations of density. It agrees with the statement that there is no spinodal in a supercooled one-component liquid [10]. This fact is also corroborated by density dependences of the internal energy u and the isochoric heat capacity c_v.

In calculations of the crystalline-phase properties the initial state on an isotherm is always the state with the highest density. Calculations were made to stretches at which the loss of crystal order of particles in a model

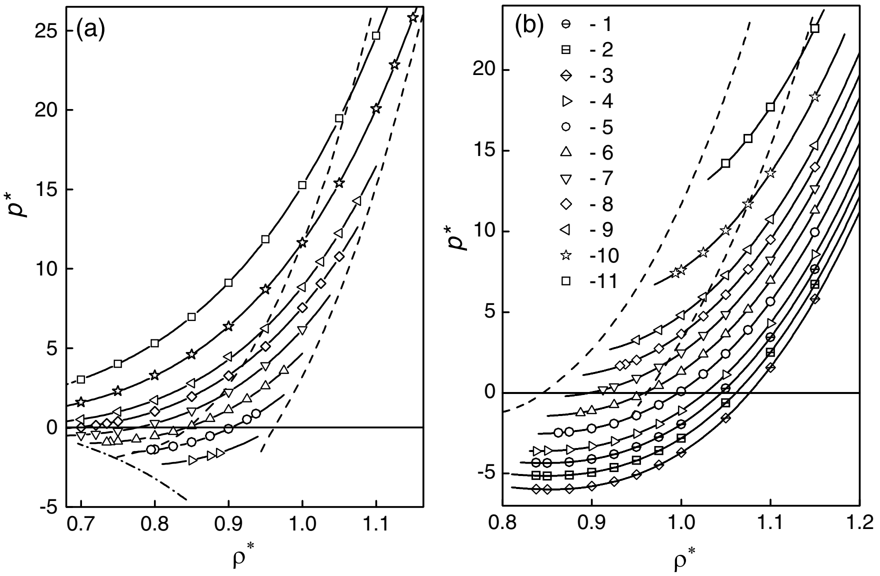

FIG. 1. Isotherms of (a) liquid and (b) crystal: $1 - T^* = 0.1$, $2 - 0.2$, $3 - 0.3$, $4 - 0.4$, $5 - 0.55$, $6 - 0.7$, $7 - 0.85$, $8 - 1.0$, $9 - 1.15$, $10 - 1.5$, $11 - 2.0$. Dashed lines show lines of liquid-crystal phase equilibrium, and a dash-dotted line shows the spinodal of a stretched liquid.

took place. As this point is approached, the thermodynamic stability of the crystalline phase decreases [Fig. 1(b)]. The dependence $p(\rho)$ is in agreement with the notion of the existence of points on isotherms at which the derivative $(\partial p/\partial \rho)_T$ equals 0. As it follows from Fig. 1(b) at high temperatures, the disruption of a crystalline structure is observed well away from the spinodal. With decreasing temperature the value of the derivative $(\partial p/\partial \rho)_T$ at the boundary of spontaneous disorder decreases, and at $T^* \leq 0.4$ the disruption of a crystalline structure occurs at stretches close to spinodal ones. It is in agreement with general notions of the thermoactivation nucleation theory [11].

The p, ρ, T data of the liquid and the crystalline phase of the Lennard-Jones system have been approximated by local equations of state of the type

$$p^* = \sum_{j=0}^{n} \sum_{i=0}^{m} a_{ij} \rho^{*j} T^{*i}. \tag{1}$$

The coefficients of Eq. (1), and also the maximum values of the exponents n and m, were determined by the method of regression analysis. For the liquid phase, $a^l_{01} = 12.727$, $a^l_{02} = -31.7465$, $a^l_{05} = 14.9614$, $a^l_{12} = -18.1082$, $a^l_{13} = 75.0892$, $a^l_{14} = -61.2481$, $a^l_{15} = 19.1732$, $a^l_{21} = 1.804\,06$, $a^l_{22} = -5.711\,91$, $a^l_{32} = 0.641\,04$. For the crystalline phase at practically the same error of description of the p, ρ, T data of a molecular-dynamic experiment, a regression analysis gives a set of equations differing by the character of the extension of isotherms beyond the line of spontaneous disorder. This leads to ambiguity in the approximation of the spinodal of the crystalline phase at high temperatures. We present here one of the equations obtained, which was later used to determine the line of phase equilibrium: $a^{cr}_{00} = -69.8834$, $a^{cr}_{01} = 286.813$, $a^{cr}_{02} = -412.723$, $a^{cr}_{03} = 191.151$, $a^{cr}_{10} = 9.4696$, $a^{cr}_{20} = -31.8944$, $a^{cr}_{21} = 47.2784$, $a^{cr}_{22} = -17.2507$, $a^{cr}_{30} = 71.9482$, $a^{cr}_{31} = -170.891$, $a^{cr}_{32} = 135.637$, $a^{cr}_{33} = -36.0205$.

In a one-component two-phase system equilibrium takes place with equal temperatures, pressures, and chemical potentials of coexistent phases. The method of molecular dynamics gives no way of calculating directly the chemical potential and the free energy. However, in the framework of this method it is quite easy to determine the values of the internal energy, which is related to the thermal equation of state by the following relation:

$$\left(\frac{\partial u}{\partial \rho}\right)_T = \left(\frac{\partial(\beta p/\rho^2)}{\partial p}\right)_\rho, \tag{2}$$

where $\beta = 1/T$. By integrating (1) and (2) with respect to density we obtain values of u with an accuracy of a certain function of temperature $u_0(T)$ determined from the results of molecular-dynamics calculation of the internal energy. Using the obtained function $u(\rho, T)$ and integrating the Gibbs-Helmholtz equation

$$\left(\frac{\partial(\beta f)}{\partial \beta}\right)_\rho = u, \tag{3}$$

we find the free energy of the liquid and the crystalline phase with an accuracy of $f_0 = \text{const}$. The value of f_0 was determined from data on the parameters of the triple point of the Lennard-Jones system, which were calculated in a special computer experiment. By our data, which are in agreement with the results of Ref. [12], $T^*_t = 0.692$, $p^*_t = 0.0012$, $\rho^*_{t,l} = 0.847$, $\rho^*_{t,cr} = 0.962$.

The results of calculation of the melting line in the region of positive and negative pressures are shown in

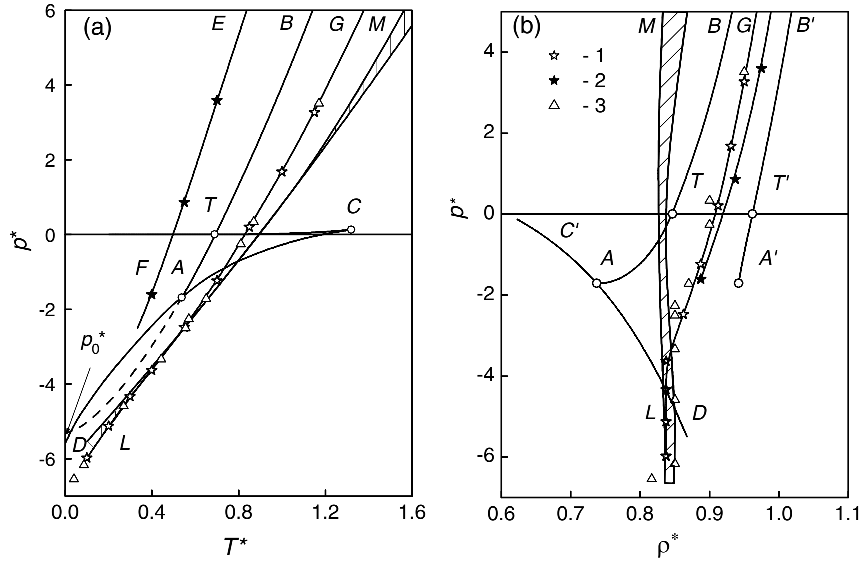

FIG. 2. (a) p, T and (b) p, ρ are projections of lines of phase equilibrium liquid-crystal (BTA and $B'T'A'$), liquid-gas (CT), spinodals of a stretched liquid (CAD and $C'AD$), and a stretched crystal (ML); lines of attainable supercooling of liquid (EF, 1) and superheat of crystal (GL, 2, 3). C is the critical point, T is the triple point, A is the point of meeting of the melting line, and the spinodal, 1, 2—data from this Letter, 3—results from [18].

Figs. 1 and 2. In Figs. 1(a), 2(a), and 2(b) one can see the spinodal $T^* > 0.7$—by the equation of state of the Lennard-Jones fluid from Ref. [13].

As it follows from Fig. 2(a), the melting line in the region of negative pressures "is butted up" against the spinodal of a stretched liquid. It can be shown that at the point of meeting of the metastable extension of the melting line and the spinodal (point A) the following relation holds true:

$$\left(\frac{\partial p}{\partial T}\right)_{m,A} = \frac{\Delta s}{\Delta \nu}\bigg|_A \neq \left(\frac{\partial p}{\partial T}\right)_{sp,A} = \left(\frac{\partial p}{\partial T}\right)_{\rho,A}, \tag{4}$$

where Δs and $\Delta \nu$ are the jumps of entropy and volume on the melting line. For the Lennard-Jones system, $T_A^* = 0.5286$, $p_A^* = -1.7128$, $\rho_{l,A}^* = 0.7374$, $\rho_{cr,A}^* = 0.9423$. The derivatives are $(dp^*/dT^*)_{sp,A} = 4.748$, $(dp^*/dT^*)_{m,A} = 8.480$. From the inequality of slopes of the tangent to the spinodal and the melting line at the point A in the plane p, T follows:

$$\left(\frac{\partial p}{\partial \nu}\right)_{T,A}\left(\frac{\partial \nu}{\partial T}\right)_{m,A} \neq 0. \tag{5}$$

Since at the point of meeting of the spinodal and the melting line $(dp/d\nu)_T = 0$, the inequality (5) and the condition $(dp/dT)_{m,A} > (dp/dT)_{sp,A}$ will be true if $(dT/d\nu)_{m,A} = 0$ and $(d^2T/d\nu^2)_{m,A} \neq 0$. In this case point A in the planes T, $\nu = 1/\rho$ and p, ν is the point of minimum of the liquid branch of the line of crystal-liquid phase equilibrium (Fig. 3). Thus the point of cessation of crystal-liquid phase equilibrium is a certain singular point at the thermodynamic surface of states of a one-component system. In the asymptotic vicinity of this point for the liquid phase $\rho - \rho_A \sim (T - T_A)^{\beta}$, where $\beta = 0.5$.

The melting curve both at positive and at negative pressures is described to a high accuracy by the Simon equation:

$$p_m^* = p_0^*[(T^*/T_0^*) - 1], \tag{6}$$

where $p_0^* = -5.328$, $T_0^* = 0.693$, $c = 1.509$.

In Fig. 2(a) a dashed line shows the extension of the melting line beyond point A according to Eq. (6). At $T \to 0$ the values of the limiting pressure $p_0^* = p_m^*(0)$ on the melting line in the approximation of the Simon equation

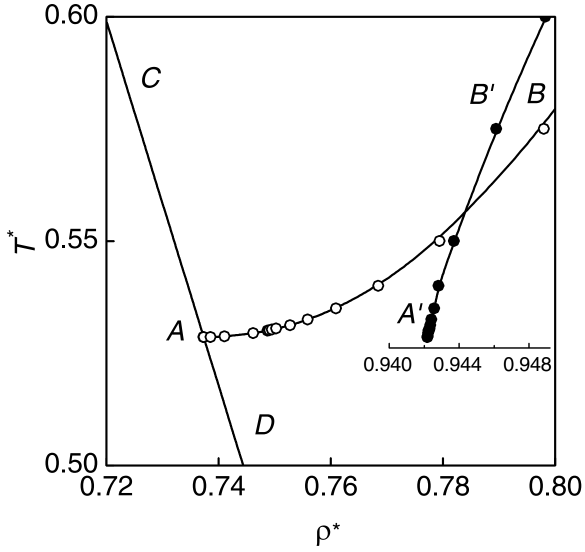

FIG. 3. T, ρ projection of the spinodal (CD) and the line of liquid-crystal equilibrium (AB, $A'B'$).

and the limiting pressure $p^*_{sp,l}(0)$ on the liquid spinodal are close to each other. Though the extrapolation of the melting line beyond the spinodal has no physical meaning, the correlation between the values of p^*_0 and $p^*_{sp,l}(0)$ is of great importance in establishing the thermodynamic similarity of substances in crystal-liquid and liquid-vapor phase transition [1]. The possibility of cessation of metastable equilibrium in a liquid-crystal system on the spinodal of a stretched liquid was mentioned in [1] and discussed in [14].

The spinodal of the superheated Lennard-Jones crystal constructed with the use of a family of local equations of state is shown in Figs. 2(a) and 2(b) as a shaded zone. The width of this zone determines the error of the spinodal approximation. The error increases with increasing temperature. In the plane p, T the crystalline-phase spinodal at low temperatures passes somewhat lower than the spinodal of a stretched liquid phase.

If it is granted that the disruption of metastable states in a model proceeds by the nucleation mechanism (see [15]), the nucleation rate at the final points of isotherms of a supercompressed liquid and a stretched crystal may be evaluated from the relation $J = (V\bar{\tau})^{-1}$, where V is the volume of the metastable phase, and $\bar{\tau}$ is the mean time of expectation of the first viable nucleus. For the conditions of the molecular-dynamic experiment conducted $V \simeq 10^{-20}$ cm^{-3}, $\bar{\tau} \simeq 10$ ns (the time by which the averaging of the calculated parameters was made). Then $J \simeq 10^{27}$ cm^{-3} s^{-1}. Figure 2(a) shows the boundaries of the attainable supercooling of a liquid and superheat of a crystal in the Lennard-Jones system, which correspond to this nucleation rate. For the liquid and the crystalline phase the data presented here agree well with the results of Refs. [16–18]. With decreasing temperature the boundary of the attainable superheat for a crystal approaches the spinodal.

Thus, the computer experiment performed has shown that in the limit $T \longrightarrow 0$ the metastable extension of the melting line does not reach the isotherm $T = 0$, and at a nonzero temperature ends on the spinodal of a stretched liquid. In the low-temperature limit the spinodals of a stretched liquid and crystal approach each other and at $T = 0$ have similar values of pressure and density.

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