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Transport coefficients and the spinodal of a fluid

Vladimir G. Baidakov[*]
Institute of Thermal Physics, Ural Branch of the Russian Academy of Sciences, 106, Amundsen Street 106, 620016 Ekaterinburg, Russia

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Based on the results of computer simulation of transport coefficients in a Lennard-Jones fluid, it has been shown that in (p,T) coordinates, lines of constant values of coefficients of self-diffusion D and excess shear viscosity $\Delta\eta$ extended into the region of superheated liquid and supersaturated vapor have an envelope. Each of the ensembles of such lines is divided into two parts by a critical isoline, where the conditions $\varphi = \varphi_c = \text{const}$ $(\varphi = D, \Delta\eta)$ are fulfilled. One part of this ensemble has as an envelope the branch of the spinodal that refers to superheated liquid; the other part has the branch of the spinodal of supersaturated vapor. The critical point of liquid-vapor equilibrium is the cusp of the spinodal, at which the critical isolines have a common tangent line with the spinodal and the binodal. Thus, at the approach to the spinodal, the relations $(\partial D/\partial p)_T \to \infty$ and $(\partial \Delta\eta/\partial p)_T \to \infty$ hold.

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I. INTRODUCTION

A first-order phase transition presupposes the existence of metastable states. In most cases with a deep penetration into a metastable region, the phase stability decreases not only against the discontinuous changes that cause nucleation, but also against small (continuous) changes of state parameters. In this case, the boundary of essential instability (spinodal) is determined by the conditions [1]

$$(\partial p/\partial \upsilon)_T = 0, \quad (\partial T/\partial s)_p = T/c_p = 0, \tag{1}$$

where p is the pressure, υ is the volume, T is the temperature, s is the entropy, and c_p is the isobaric heat capacity. Conditions (1) correspond to the vanishing of the reactions tending to restore the initially homogeneous state of the system regardless of how small the mechanical or thermal perturbations of the initial state are. If the spinodal exists, the region of metastable states is limited at the thermodynamic surface $F(p,T,\upsilon)$ by two curves: the phase-equilibrium line (binodal) and the line of the stability boundary (spinodal).

A spinodal exists in liquid-vapor systems in stratifying liquid and solid solutions. Our discussion concerns the former case.

Conditions (1) are a consequence of thermodynamic stability theory. Thermodynamics makes it possible to judge the character of changes of some thermodynamic quantities at the approach to the spinodal. More complicated is the question of the behavior of the transport coefficients near the spinodal, i.e., of the coefficients of self-diffusion D, shear η, and bulk η_υ viscosities, and the thermal conductivity λ [2,3]. The basic thermodynamic features of a liquid-vapor phase transition with metastable states are reproduced qualitatively correctly by the van der Waals equation of state. In nonequilibrium statistical mechanics, however, there does not exist an analog of the van der Waals equation allowing one a description of the behavior of the transport coefficients, although attempts have been made to describe transport coefficients in a van der Waals fluid [4,5].

The spinodal as the limit between thermodynamically metastable und unstable states is real, but by its nature it is unachievable in quasistatic experiments. It is also unachievable in computer experiments (employing molecular dynamics and Monte Carlo methods). In a fluctuating system—which the metastable system is—this feature is connected with nucleation processes resulting in the formation of inhomogeneous states prior to the approach of the spinodal. In this way, nucleation processes act as a limiting factor for the possible depth of penetration into the region of metastable states. Such problems are not unique to the spinodal curve. A similar situation may be observed upon examining systems of a different nature (for instance, oscillating ones) when there is a boundary of stability of motion or state.

Usually, the boundary of thermodynamic stability is determined asymptotically by data obtained for stable (and slightly metastable) ranges of the phase diagram. The behavior of the system close to and at the stability boundary itself differs from that at a sufficiently large distance from it. It might seem that it is impossible to determine the position of the boundary of stability without knowing the respective laws governing the behavior of the quantities under investigation. However, in almost all cases, the determination of the stability limit by the asymptotic extension of data measured for stable and slightly metastable systems proves to be satisfactory.

Following these considerations, in the present paper the results of molecular-dynamics calculations performed for stable and metastable systems are used to analyze the behavior of self-diffusion and shear-viscosity coefficients at the spinodal of a metastable Lennard-Jones fluid. In Sec. II, the method of determination of the spinodal is described based on the data on transport coefficients, and the values of the transport coefficients at the spinodal are established. Section III, which summarizes the results and conclusions, completes the paper.

II. SPINODAL AS THE ENVELOPE OF A FAMILY OF LINES OF CONSTANT VALUE OF SELF-DIFFUSION AND THE SHEAR-VISCOSITY COEFFICIENT

Our results of the molecular-dynamics calculations of the self-diffusion coefficient and the coefficient of shear viscosity of a Lennard-Jones fluid in stable and metastable states, upon

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[*] Author to whom all correspondence should be addressed: bai@itp.uran.ru

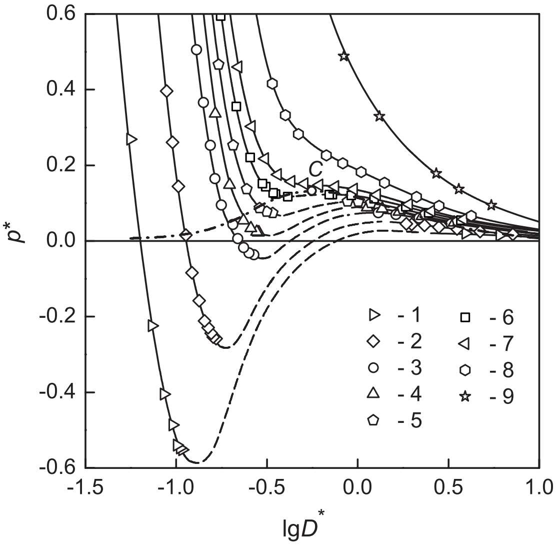

FIG. 1. Pressure as a function of the decimal logarithm of the self-diffusion coefficient along isotherms: $T^* = 0.85$ (1), 1.0 (2), 1.15 (3), 1.2 (4), 1.25 (5), 1.3 (6), 1.35 (7), 1.5 (8), and 2.0 (9). Dashed-dotted line, binodal; C, critical point.

which the present analysis is based, have been presented in Refs. [6–8]. The system under investigation contained 4000 interacting particles with a potential cutoff radius $r_c = 6.78\sigma$. From this point on, σ,ε are parameters of the Lennard-Jones potential. Calculations were made in the ranges of temperatures from $T^* = k_B T/\varepsilon = 0.4$ to 2.0 and densities from $\rho^* = \rho\sigma^3 = 0$ to 1.1. Maximum supersaturations of the gas and liquid phases were limited by homogeneous nucleation.

Figures 1 and 2 illustrate, respectively, the dependence of pressure on the self-diffusion coefficient $D^* = D m^{1/2} \varepsilon^{-1/2}\sigma^{-1}$ and the excess viscosity $\Delta\eta^* = \Delta\eta\sigma^2(m\,\varepsilon)^{-1/2} = \eta^* - \eta^*_T$ at temperatures higher and lower than the temperature at the critical point. Here, η^*_T is the viscosity of the system in the limit of zero density at a temperature T according to the Chapman-Enskog solution of the Boltzmann equation [5], and m is the particle mass. The parameters of the critical point of the system under investigation are $p^*_c = 0.137$, $T^*_c = 1.330$, and $\rho^*_c = 0.311$ [9].

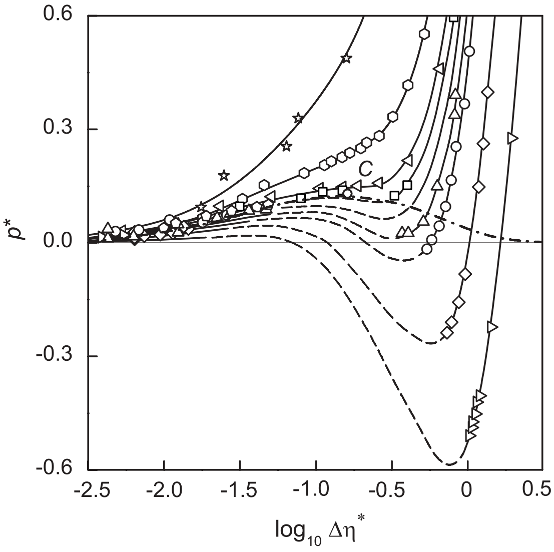

FIG. 2. Pressure as a function of the decimal logarithm of excess viscosity along isotherms (for designations, see Fig. 1).

As is evident from Figs. 1 and 2, the character of the pressure dependence of the transport coefficient in both cases is similar to the pressure dependence of volume (density) along the van der Waals isotherms. Along the isotherms, one can assume the presence of points where the derivative $(\partial p/\partial\varphi)_T = 0$, and a point where the derivative $(\partial^2 p/\partial\varphi^2)_T = 0$ also takes a zero value. From here on, we always assume $\varphi = D$, $\Delta\eta$. The question then is as follows: Does the line $(\partial p/\partial\varphi)_T = 0$ correspond to the spinodal, where, in accordance with (1), $(\partial p/\partial\upsilon)_T = 0$ holds?

The determination of the points of minimum of the isotherms in the p,φ coordinates is connected with a large error, therefore we proceed as follows. Let the function F relate the thermodynamic parameters p,T to the transport coefficient φ in the region of stable, metastable, and labile states. In three-dimensional p,T,φ space, the equation

$$F(p,T,\varphi) = 0 \tag{2}$$

corresponds to a certain surface, which is considered to be smooth. We will choose as a parameter the transport coefficient φ. Then, the condition

$$F_\varphi = \frac{\partial F}{\partial \varphi} = 0, \tag{3}$$

together with (2), determines the envelope of a one-parameter family of planar curves in p,T variables. From here on, we employ the following simplified notations for the partial derivatives: $F_p = \partial F/\partial p$, $F_T = \partial F/\partial T$, $F_{\varphi\varphi} = \partial^2 F/\partial\varphi^2$, and $F_{\varphi\varphi\varphi} = \partial^3 F/\partial\varphi^3$. The additional conditions [10]

$$|F_p| + |F_T| \neq 0, \quad F_{\varphi\varphi} \neq 0, \quad \frac{\partial(F,F_\varphi)}{\partial(p,T)} \neq 0 \tag{4}$$

supply us with sufficient evidence that the envelope of (2) and (3) is a simple regular curve, and each of the curves of the family $\varphi = \text{const}$ is in contact with the envelope at a single point. If, in addition, at a certain point of the region of determination of the ensemble of curves φ along with (2) and (3) the condition

$$F_{\varphi\varphi} = 0, \;\; F_{\varphi\varphi\varphi} \neq 0 \tag{5}$$

is valid, then the point mentioned serves as the cusp of the envelope. Inequalities (4) are consistent with the results of molecular-dynamics calculations of the coefficients of self-diffusion [6,7] and shear viscosity [8].

For a simple one-component liquid, Skripov [1] has shown that in p,T variables, the spinodal is the envelope of the ensemble of isochores and curves of constant entropy extended into the region of metastable states. The property of the envelope is most visually expressed by the condition

$$\left.\frac{dp}{dT}\right|_{sp} = \left(\frac{\partial p}{\partial T}\right)_\upsilon . \tag{6}$$

The fact that the spinodal is the envelope for a number of isolines is widely used in approximating the spinodal based on experimental data [11–14].

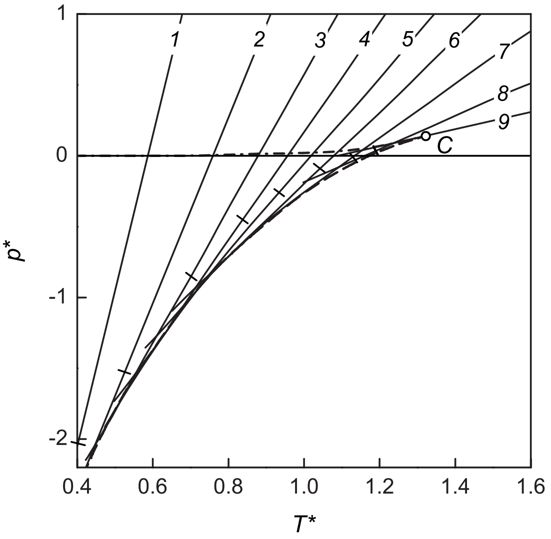

FIG. 3. Lines of constant excess viscosity: $\log_{10} \Delta\eta^* = 0.8$ (1), 0.4 (2), 0.2 (3), 0.1 (4), 0 (5), 0.1 (6), 0.4 (7), 0.6 (8), and 0.78 (9). Dashed line, spinodal of superheated liquid; dashed-dotted line, binodal; C, critical point. Areas where actual data of molecular-dynamics calculations end and their extrapolation begins are separated by strokes on lines, $\log_{10} \Delta\eta^* = \text{const}$.

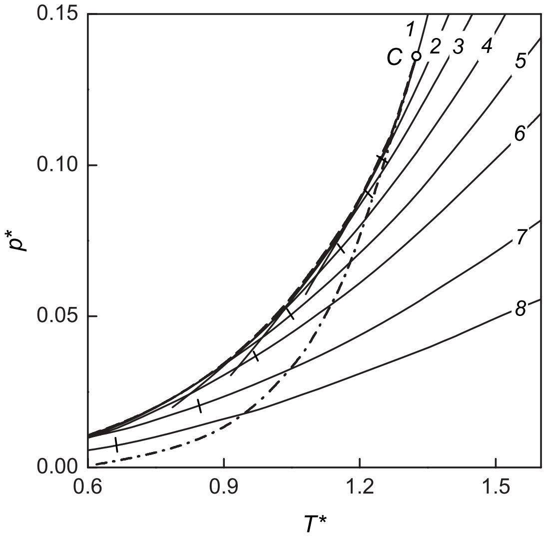

FIG. 4. Lines of constant value of the self-diffusion coefficient: $\log_{10} D^* = -0.2$ (1), 0 (2), 0.1 (3), 0.2 (4), 0.3 (5), 0.4 (6), 0.6 (7), and 0.8 (8). Dashed line, spinodal of superheated vapor; dashed-dotted line, binodal; C, critical point. Areas where actual data of molecular-dynamics calculations end and their extrapolation begins are separated by strokes on lines, $\log_{10} D^* = \text{const}$.

Figure 3 shows in p,T variables the spinodal of a superheated (stretched) Lennard-Jones liquid. The spinodal has been constructed by the results of molecular-dynamics calculations of the p,ρ,T properties of a Lennard-Jones fluid [9]. In the same way, lines of constant excess viscosity have been constructed based on the data of [8]. For the liquid phase, these lines are close to straight lines both in the stable and metastable regions. By extrapolating them graphically to the spinodal, we obtain an envelope, which, within the error of such a procedure, coincides with the spinodal of a stretched liquid. The spinodal of a stretched liquid is enveloped only by the isolines $\Delta\eta^* = \text{const}$ for which $\Delta\eta^* > \Delta\eta_c^* \simeq 0.165$. The isolines with $\Delta\eta^* < \Delta\eta_c^*$ form another envelope, which coincides with the spinodal of supersaturated vapor. Both branches of the spinodal close up at the critical point to form on the p,T plane the cusp of the envelope. The spinodal branches are convex toward each other. The sign of curvature of the gas branch coincides with that of the binodal, and the curvature of the liquid branch of the spinodal is of the opposite sign.

The isolines $D^* = \text{const}$ and $\Delta\eta^* = \text{const}$ in the gas phase, as distinct from the liquid one, are not rectilinear. For the self-diffusion coefficient this is illustrated in Fig. 4, which shows in p,T coordinates the spinodal of supersaturated vapor (data of Ref. [9]). At the critical point, $D_c^* \simeq 0.572$. It should be mentioned that the relative error of molecular-dynamics calculations of transport coefficients in the gas phase and the critical region is much higher than that for a liquid.

An approach to the critical point is connected with an increase of spatial correlations between the positions of different particles, which in its turn results in an increasing length of characteristic relaxation times. This complicates computer simulation of state parameters in this region and leads to "the smoothing" of critical peculiarities. It is known [15] that in the case of shear viscosity this feature is weak, and close to the critical point of liquid-gas equilibrium, the asymptotic region, in which the shear viscosity is described by the laws of dynamic scaling, is practically unachievable. For the self-diffusion coefficient, there have been no unambiguous results to date as to the presence or absence of this peculiarity in the critical region [16].

Figure 5 presents the temperature dependence of the self-diffusion and shear-viscosity coefficients of a Lennard-Jones fluid on the spinodal and the binodal. An isothermal penetration into the region of metastable liquid is connected

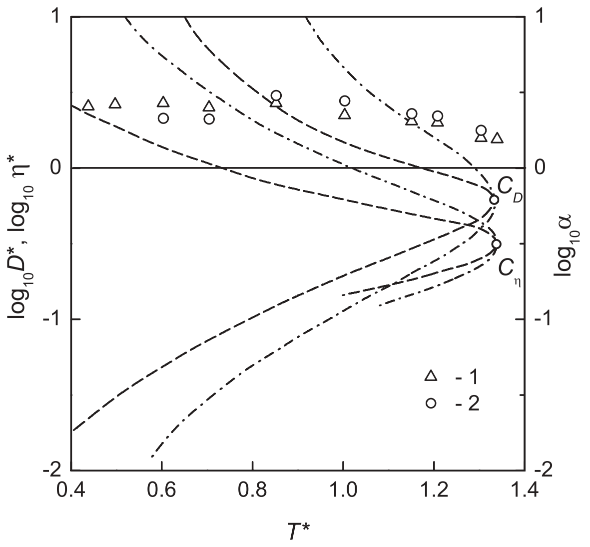

FIG. 5. Coefficients of self-diffusion (D^*) and shear viscosity (η^*) on the spinodal (dashed lines) and binodal (dashed-dotted lines) of a Lennard-Jones fluid. Dots show values of $\log_{10} \alpha$ on the spinodal of a superheated liquid (1) and the liquid branch of the binodal (2). C_D and C_η are the critical point on the temperature dependence of coefficients of self-diffusion and the shear viscosity, respectively.

with a decrease in shear viscosity and an increase in the self-diffusion coefficient. The coefficients of self-diffusion and shear viscosity are related by the Stokes-Einstein relation

$$D = \frac{k_B T}{\alpha \pi \eta R}, \tag{7}$$

where α is a constant and R is the hydrodynamic radius of a diffusing particle. The value of α depends on R and may vary from 4 to 6 [17].

If for a Lennard-Jones fluid we assume that $R = \sigma/2$, then the parameter α on the spinodal of a superheated liquid and on the liquid branch of the binodal varies only slightly with temperature and is equal to 2.25 ± 0.25. The dots in Fig. 5 show the values of $\lg \alpha$ for the spinodal and the binodal. The fact that $\alpha < 3$ indicates that the effective diameter of a diffusing particle in a Lennard-Jones fluid is smaller than σ.

III. CONCLUSION

A metastable state is a state of partial equilibrium. It is assumed in the description of such equilibrium states that a one-component system in a metastable, as well as in a stable, state is determined by the assignment of two thermodynamic state variables. Under changes of the thermodynamic parameters, a rearrangement of the configurations of the particles in the system takes places going over from one equilibrium distribution to another. Such a process requires the time τ (relaxation time). If changes of the external state parameters take place at characteristic times exceeding τ, a metastable system passes through a sequence of quasiequilibrium states, in which it is in equilibrium in any respect except for the eventual formation of new-phase nuclei.

The dynamic behavior is determined by transport coefficients. Transport coefficients limit the growth rate of new-phase nuclei and the kinetics of spinodal decomposition during the transition across the spinodal and in labile states. A substance brought into a labile state, where $(\partial p/\partial \upsilon)_T > 0$, rapidly loses its spatial homogeneity. This initial stage of the decay of an unstable homogeneous system is known as spinodal decomposition [18]. In a one-component system, the rate of decay is limited by the heat exchange between the expanding and compressing volume elements [19]. This process is controlled by thermal diffusivity $a = \lambda/\rho c_p$, where ρ is the density. A transition across the spinodal is accompanied by the change of sign of the heat capacity c_p ($c_p \to \pm\infty$), which is formally equivalent to the change of sign of the time in the heat conduction equation and leads to solutions with exponentially increasing temperature differences. In such a way, the thermal diffusivity on the spinodal becomes equal to zero, the thermal conductivity coefficient being a finite or a diverging (but more slowly than c_p) quantity. The self-diffusion coefficient must also have a finite value on the spinodal. In the case of the spinodal decomposition of two-component systems, the interdiffusion coefficient takes a zero value on the spinodal and is negative in the unstable region [18].

Thus, the investigation performed here shows that on the spinodal curves of superheated liquid and supersaturated vapor, the self-diffusion and shear viscosity coefficients have finite values. The isotherms $p(D)$ and $p(\Delta\eta)$ contain points at which the derivatives $(\partial p/\partial D)_T$ and $(\partial p/\partial \Delta\eta)_T$ assume zero values. From the well-known relation connecting the partial derivatives

$$\left(\frac{\partial \varphi}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_\varphi \left(\frac{\partial p}{\partial \varphi}\right)_T = -1 \tag{8}$$

and the value of the derivative $(\partial T/\partial p)_\varphi$ established by us, it follows that at points where $(\partial p/\partial \varphi)_T = 0$, the derivatives $(\partial T/\partial D)_p$ and $(\partial T/\partial \Delta\eta)_p$ are also equal to zero. In p,T coordinates, these points form lines which coincide with the branches of liquid and vapor spinodal curves. The point of contact of the two branches of the spinodal—the critical point—is the cusp of the envelope of a family of lines of constant value of the self-diffusion and shear viscosity coefficients.

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