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Statistical substantiation of the van der Waals theory of inhomogeneous fluids

V. G. Baidakov,* S. P. Protsenko, G. G. Chernykh, and G. Sh. Boltachev
Institute of Thermal Physics, Urals Branch of the Russian Academy of Sciences, Ekaterinburg GSP-828, Russia

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Computer experiments on simulation of thermodynamic properties and structural characteristics of a Lennard-Jones fluid in one- and two-phase models have been performed for the purpose of checking the base concepts of the van der Waals theory. Calculations have been performed by the method of molecular dynamics at cutoff radii of the intermolecular potential $r_{c,1}=2.6\sigma$ and $r_{c,2}=6.78\sigma$. The phase equilibrium parameters, surface tension, and density distribution have been determined in a two-phase model with a flat liquid-vapor interface. The strong dependence of these properties on the value of r_c is shown. The p,ρ,T properties and correlation functions have been calculated in a homogeneous model for a stable and a metastable fluid. An equation of state for a Lennard-Jones fluid describing stable, metastable, and labile regions has been built. It is shown that at $T \geqslant 1.1$ the properties of a flat interface within the computer experimental error can be described by the van der Waals square-gradient theory with an influence parameter κ independent of the density. Taking into account the density dependence of κ through the second moment of the direct correlation function will deteriorate the agreement of the theory with data of computer simulation. The contribution of terms of a higher order than $(\nabla\rho)^2$ to the Helmholtz free energy of an inhomogeneous system has been considered. It is shown that taking into account terms proportional to $(\nabla\rho)^4$ leaves no way of obtaining agreement between the theory and simulation data, while taking into consideration of terms proportional to $(\nabla\rho)^6$ makes it possible to describe with adequate accuracy all the properties of a flat interface in the temperature range from the triple to the critical point.

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I. INTRODUCTION

In recent years the van der Waals theory [1] and its modifications [2,3] have been widely used for describing nuclei of new phases [4,5], wetting transitions [6], interfaces in the vicinity of critical points [2], and some other surface phenomena [3]. Many authors state in their papers a good qualitative and quantitative agreement between the results of theory and experiment even in regions of state variables where seemingly the conditions of the theory applicability are violated. And although the basic equations of the van der Waals theory can be obtained as some limiting cases of rigorous statistical theories, many of its concepts are yet to be statistically substantiated.

The starting point of the van der Waals theory is the presentation of the local Helmholtz free energy density of inhomogeneous fluid as the sum of two terms — the local free energy density of homogeneous fluid and the term taking into account the presence of inhomogeneity. It is assumed that in the whole range between the densities of liquid and vapor existing in equilibrium the Helmholtz free energy density of homogeneous system $f_0(\rho,T)$ at a fixed temperature is an analytic function of the local density ρ. The term taking into account the presence of inhomogeneity imposes the condition of existence of a certain characteristic length for a fluid medium and in a first approximation is proportional to the square of the density gradient. The coefficient of proportionality at the square of the density gradient (influence parameter κ) is a temperature and density function. Thermodynamic stability requires $\kappa>0$. Otherwise the formation of inhomogeneities would be an energetically profitable process as it would result in a decrease of the Helmholtz free energy. The molecular theory of surface tension relates the influence parameter with the two-body direct correlation function $c(r;\rho,T)$ of a homogeneous fluid [7]. In this case it is assumed that $c(r;\rho,T)$, as well as the Helmholtz free energy density $f_0(\rho,T)$, has been determined in the whole range between the densities of coexisting phases, where a homogeneous system can exist only as a metastable or a labile one.

We shall now highlight the most debatable points of the van der Waals theory. The van der Waals theory postulates the introduction of local thermodynamic quantities describing a certain hypothetical system, which can exist as a homogeneous one in the whole range of the state variables of a fluid phase. The Helmholtz free energy density and the local pressure of such a system at the liquid-vapor interface, as density functions at a fixed temperature, should have the form presented in Fig. 1. The densities of phases coexisting in equilibrium are determined by constructing a common tangent to the function $f_0(\rho;T=\text{const})$ or using the equal area criterion of Maxwell for pressure. In an actual macroscopic system the states between point A and B are metastable and labile. The region of metastable states is separated from the region of lability by a spinodal, which is determined by the following conditions [8]:

$$\left(\frac{\partial p}{\partial \rho}\right)_T=0, \quad \left(\frac{\partial T}{\partial s}\right)_p=0, \tag{1}$$

where s is the entropy.

The conception of homogeneity may be introduced only with respect to a certain linear size l. Thus, the molecular density ρ will be homogeneous on the scale l if the volumes

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*Electronic address: bai@itp.uran.ru

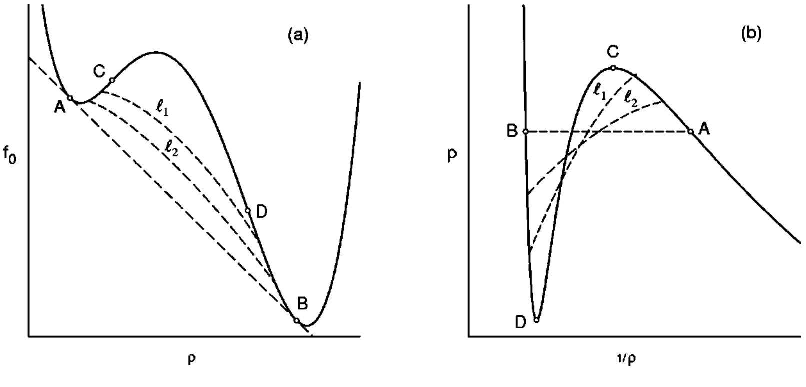

FIG. 1. Helmholtz free energy density (a) and pressure (b) in a homogeneous system at a precritical $(T<T_c)$ isotherm. A, B are binodal points and C, D are spinodal points. Dashed lines schematically show states realized in small systems with linear dimensions l_1 and l_2 $(l_1<l_2)$.

l^3 always contain ρl^3 molecules. The van der Waals theory makes use of a continual approach, therefore, the boundary from below for the scale l is determined by the inequality $l \gg d$, where d is the effective molecular size.

In the stable region, the isolated linear scales are the radius of action of molecular attractive forces R_c and the correlation radius ξ. If $l \gg \xi$, on such a linear scale the molecular system is homogeneous, and the system states are equilibrium and stable. In the metastable region, in addition to R_c and ξ, there appears a new linear scale, the radius of a critical bubble, by which we will understand the radius of the tension surface R_*. If the correlation radius characterizes homophase fluctuations, the radius R_* is connected with heterophase fluctuations. A system whose linear dimension $l \gg \xi$ and R_* can exist as a homogeneous one only for a limited time, whereupon phase separation will take place. The type of functions $f_0(\rho,T)$, $p(\rho,T)$ in this case depends on the value of l, as is schematically shown in Fig. 1 with dashed lines. In the limit $l \to \infty$, the thermodynamic properties of a system become the same as in the absence of restrictions. In Fig. 1, the line AB will correspond to the value l_∞.

In a system with a linear dimension $\xi < l < R_*$ nucleation is suppressed, and on the scale l the system retains homogeneity. As the spinodal is approached, $\xi \to \infty$ and $R_* \to 0$. Here it is impossible to stand out the scale of homogeneity. It is also characteristic of the labile region, where a substance relaxes into a new phase without activation through the stage of spinodal decay [9]. Thus, in the region of a first-order phase transition the condition of homogeneity cannot be formulated so rigorously as outside it. This means that the functions $f_0(\rho,T)$, $p(\rho,T)$ and others cannot be calculated here without imposing additional conditions on the statistical integral.

If we assume that within the limits of the radius of action of attractive forces in the vicinity of a molecule there is the same number of neighboring molecules (mean-field approximation), in such a medium all fluctuations on the scale $l = R_c$ will be suppressed. At $R_c \to \infty$ the condition of homogeneity is formulated on a macroscopic scale, which is equivalent to the absence of any characteristic scale at all. In this case, the properties of the system are described rigorously by the analytic functions $f_0(\rho,T)$, $p(\rho,T)$ presented in Fig. 1 [10].

The next debatable moment of the square-gradient version of the van der Waals theory is the fact that the term taking account of inhomogeneities usually retains only lower spatial derivatives of density. It is admissible if inhomogeneities are weak. As a critical point is approached the interfacial region broadens and the density gradients at the interface decrease. Therefore, in a critical region neglect of derivatives of a higher order than the first ones is justified. *A priori*, this is not evident in the vicinity of a triple point, where the density gradient at the interface is large.

In the general case, the influence parameter (coefficient of proportionality at the square of the density gradient) is a function of the density and temperature and is determined through the second moment of the direct correlation function. Calculation of $\kappa(\rho,T)$ through the direct correlation function of a homogeneous system is connected with a number of fundamental difficulties as the latter, strictly speaking, cannot be determined behind the spinodal, in the labile region.

In the simplest versions of the van der Waals theory the influence parameter κ is a constant determined only by intermolecular forces. In more rigorous modifications of the theory κ depends on T and does not depend on ρ. This case is the most interesting one as at given values of the Helmholtz free energy density $f_0(\rho,T)$ and the planar surface tension one makes it possible to determine the value of κ and calculate the interfacial density distribution. As is shown in Ref. [11], such an approach gives for argon values of the effective thickness of the interface that are in satisfactory agreement with data obtained by ellipsometric study. Besides, this approach makes it possible to determine the dependence of the surface tension of new-phase nuclei on their size [5,12]. Taking into account this dependence in the classical homogeneous nucleation theory improves the agreement between theory and experiment in superheated simple liquids [5,13]. Nevertheless, such a check of the van der Waals theory is only indirect. Experiments based on measuring the interface reflectance with scattering of light, x-rays, and neutrons give information only about the effective thickness of the interface, and not about the interfacial density distribution. Experiments on nucleation also give indirect information about the surface tension of nuclei as to measure its value for bubbles (droplets) of radius 10–100 nm directly by experiment seems to be impossible.

In this paper, the van der Waals theory is checked on a model system of Lennard-Jones particles. The method of molecular dynamics is used in a two-phase system with a flat liquid-vapor interface to calculate the parameters of phase equilibrium, surface tension, interfacial density distribution in the temperature range from the triple point to temperature close to critical one. To determine the Helmholtz free energy density and the direct correlation function for a homogeneous fluid use is made of a one-phase molecular-dynamic model. The temperature dependence of the influence parameter is found in the framework of the van der Waals theory from data on the surface tension, the effective thickness of the interface, and the Helmholtz free energy density. The dependence of κ on ρ and T is also determined by direct calculation of correlation functions in computer experiments.

The paper consists of five sections. Section II formulates the basic ideas of the van der Waals theory. Section III describes the results of calculating the properties of two phase and one-phase molecular systems by the method of molecular dynamics. Section IV is devoted to analysis of the obtained data in the framework of the van der Waals theory. Section V contains conclusions and discussions.

II. VAN DER WAALS THEORY

The van der Waals theory assumes that in an inhomogeneous system the Helmholtz free energy density at $\vec{r}$ depends on the local density, $\rho(\vec{r})$, and its spatial derivatives of various orders [1]

$$f\{\rho(\vec{r})\}=f_0(\rho)+\kappa_1(\nabla\rho)^2+\kappa_2\Delta\rho+\kappa_3(\nabla\rho)^4+\kappa_4(\nabla\rho)^2\Delta\rho+\kappa_5(\Delta\rho)^2+\kappa_6(\nabla\rho)(\nabla\Delta\rho)+\kappa_7(\Delta\Delta\rho)+\cdots. \tag{2}$$

Here $f_0(\rho)$ is the Helmholtz free energy density of a homogeneous system, $\kappa_1,\ \kappa_2,\ \kappa_3,\ldots$ are coefficients depending in the general case on the temperature and density.

If the inhomogeneities are weak, in expression (2) one can retain only lower spatial derivatives of density. Then for the total free energy of an inhomogeneous system we have

$$F\{\rho(\vec{r})\}=\int[f_0(\rho)+\kappa(\nabla\rho)^2]d\vec{r}. \tag{3}$$

Here integration is performed through the whole volume of a system, which is assumed to be macroscopic, the influence parameter $\kappa=\kappa_1-\partial\kappa_2/\partial\rho$. Equation (3) is the basic one of the van der Waals square-gradient theory.

The influence parameter κ is related to the direct correlation function of a homogeneous fluid $c(r;\rho,T)$ by the following relation [7]:

$$\kappa=\frac{k_BT}{12}\int r^2c(r)d\vec{r}, \tag{4}$$

where k_B is the Boltzmann's constant. In a mean spherical approximation

$$c(r)\sim-\frac{\phi(r)}{k_BT}, \tag{5}$$

where $\phi(r)$ is the intermolecular potential, and Eq. (4) together with Eq. (5) gives the well-known Rayleigh–van der Waals result [2]:

$$\kappa=-\frac{1}{12}\int_{r>d}r^2\phi(r)d\vec{r}. \tag{6}$$

Here integration is limited by the region of action of attracting forces, d is the effective diameter of molecules. In approximation (5) the influence parameter proves to be independent of temperature and density.

This paper investigates properties of a flat liquid-vapor interface. We shall introduce the Cartesian system of coordinates whose z axis is normal to the interface and directs from liquid into vapor. For a grand thermodynamic potential of a two-phase system with allowance for Eq. (3) we have

$$\Omega\{\rho(z)\}=F\{\rho(z)\}-\mu N=A\int_{-\infty}^{\infty}\left[\omega(\rho)+\kappa\left(\frac{d\rho}{dz}\right)^2\right]dz. \tag{7}$$

Here $\omega(\rho)\equiv f_0(\rho)-\mu\rho$, μ is the coexistence chemical potential, N is the number of particles in the system, A is the interface area. We shall be interested in distributions $\rho(z)$, which correspond to the boundary conditions,

$$\rho(z\to-\infty)=\rho_l,\quad \rho(z\to+\infty)=\rho_g,$$
$$d\rho/dz(z\to\pm\infty)=0, \tag{8}$$

where ρ_l, ρ_g are the equilibrium densities of saturated liquid and vapor phases.

By minimizing the functional (7) we obtain the Euler-Lagrange equation for calculating the planar interfacial density profile $\rho(z)$,

$$\frac{d}{dz}\left[\kappa\left(\frac{d\rho}{dz}\right)^2\right]=\frac{d\omega}{dz}. \tag{9}$$

Integrating Eq. (9) with allowance for the boundary conditions (8), we have

$$dz=\left[\frac{\kappa}{\omega-\omega_s}\right]^{1/2}d\rho, \tag{10}$$

where $\omega_s=\omega(\rho_l)=\omega(\rho_g)=-p_s$, p_s is the saturated-vapor pressure.

The surface tension may be calculated by any of the following formulas:

$$\sigma=2\int_{-\infty}^{+\infty}\kappa\left(\frac{d\rho}{dz}\right)^2dz, \tag{11}$$

$$\sigma=2\int_{\rho_g}^{\rho_l}[\kappa(\omega-\omega_s)]^{1/2}d\rho. \tag{12}$$

Formula (12) is the most important one as in the case of κ independent of ρ it makes it possible to determine the influence parameter by data on the surface tension and the Helmholtz free energy density of a homogeneous system (macroscopic characteristics), and then from Eq. (10) to calculate the interfacial density profile (microscopic characteristic).

The van der Waals theory is a local theory. At every point of an inhomogeneous system the state of the medium is fully determined by its local properties. The effect of the surroundings is taken into account only through spatial derivatives of density. A rigorous theory based on introduction of the density functional gives the following expression for the Helmholtz free energy of an inhomogeneous system [7]:

$$F\{\rho(\vec{r})\}=\int\left[f_0^I\{\rho(\vec{r})\}-\frac{\rho(\vec{r})}{2}\int c(\vec{r},\vec{r}\,')\rho(\vec{r}\,')d\vec{r}\,'\right]d\vec{r}, \tag{13}$$

where $f_0^I(\rho)$ is the free energy density of homogeneous fluid in the ideal-gas state, $c(\vec{r},\vec{r}\,';\{\rho\})$ is a two-body direct correlation function of inhomogeneous fluid, it is a functional of the density distribution in a system. Calculation of $F\{\rho(\vec{r})\}$ by Eq. (13) is unrealizable as it requires a knowledge of $c(\vec{r},\vec{r}\,';\{\rho\})$ or, which is equivalent, direct correlation functions of all orders in a homogeneous fluid. To circumvent this difficulty use is made of approximations that make it possible to present the second integral of Eq. (13) as the sum of two terms determined by a two-body direct correlation function of a homogeneous system

$$F\{\rho(\vec{r})\}=\int f_0\{\rho(\vec{r})\}d\vec{r}+\frac{k_BT}{4}\int\int[\rho(\vec{r}\,')-\rho(\vec{r})]^2 \times c(|\vec{r}\,'-\vec{r}|;\overline{\rho})d\vec{r}\,'d\vec{r}, \tag{14}$$

$$f_0\{\rho(\vec{r})\}=f_0^I\{\rho(\vec{r})\}+\frac{k_BT}{2}[\rho(\vec{r})]^2\int c(|\vec{r}\,'-\vec{r}|;\overline{\rho})d\vec{r}\,'. \tag{15}$$

In the formulation of Ebner *et al.* [14] $\overline{\rho}=[\rho(\vec{r})+\rho(\vec{r}\,')]/2$, and $c(|\vec{r}\,'-\vec{r}|;\overline{\rho})$ is interpreted as the direct correlation function of a hypothetical homogeneous medium constrained to have uniform density $\overline{\rho}$. The theory of inhomogeneous fluid based on Eq. (14) is essentially nonlocal. By expanding the integrand in the second term of Eq. (14) and restricting ourselves to the first terms of expansion we obtain the equation of the van der Waals theory (3). Equation (14) is more rigorous than Eq. (3). However, the density functional theory, contrary to the van der Waals theory, gives no way of expressing the quantities involved only through thermodynamic parameters measurable by experiment.

III. MOLECULAR-DYNAMIC SIMULATION

A. Two-phase system

Molecular-dynamic experiments on two-phase models were carried out for determining thermodynamic parameters of coexisting phases, surface tension, and interfacial density profiles. The system under investigation contained $N=4096$ interacting particles. Particles interact through a cutoff Lennard-Jones (LJ) potential

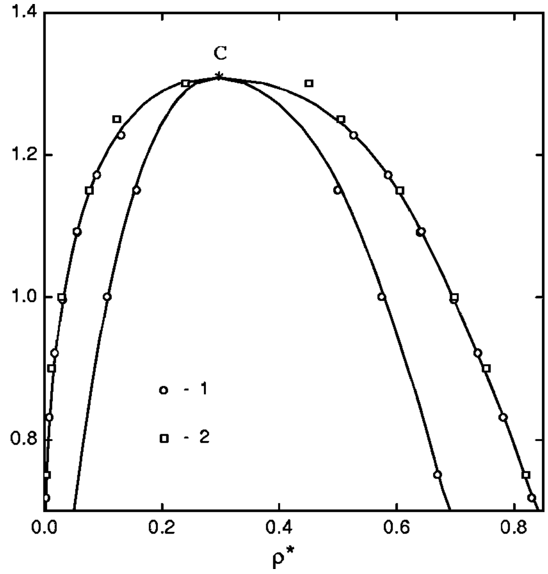

FIG. 2. Binodal (external curve) and spinodal (internal curve) of a LJ fluid. 1, data of this paper; 2, Ref. [16]. Solid lines show calculation by the equation of state (23), *C* is the critical point.

$$\phi(r)=\begin{cases}4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right], & r\leqslant r_c,\\ 0, & r>r_c,\end{cases} \tag{16}$$

where $\varepsilon=1.653\,24\times10^{-21}$ J, $\sigma=0.3405$ nm are the potential parameters, $r_c=6.78\sigma$ is the cutoff radius of the intermolecular potential. Further use is made of nondimensional quantities obtained by division of dimensional parameters r, ρ, T, f, κ, μ, p, by, respectively, σ, σ^{-3}, ε/k_B, ε/σ^3, $\varepsilon\sigma^5$, ε, ε/σ^3 and marked with an asterisk.

The system is enclosed in a rectangular box with periodic boundaries. The reduced box sizes are $L_x^*\times L_y^*\times L_z^*=13.56\times13.56\times58$. A two-phase system was given in the form of a two-sided liquid slab with vapor on either side on it.

The Beeman's algorithm was used to integrate the equations of particle motion [15]. The integration step in time was closed equal to 10^{-14} s. The equilibration took no less than 2×10^5 time steps. The properties of the system were found by averaging over 2×10^6 time steps in the equilibrated system.

Density distributions $\rho(z)$ were obtained by dividing the box into 1160 layers 0.05σ thick, paralled to the plane x,y. The number of particles in the layers was determined at every time step, whereupon time subaverage was performed. Data on the coexisting densities obtained in the range of reduced temperatures $\Delta T^*=0.718$–1.227 are shown in Fig. 2.

The coexistence parameters depended considerably on the value of the cutoff radius of the LJ potential r_c^* and to a lesser degree on the number of particles in the box. The results of investigating such dependences are presented by us in Ref. [17], where it is shown that the uncertainty of thermodynamic quantities connected with the choice of r_c^* does not exceed the error of their determination if $r_c^*\geqslant6.78$.

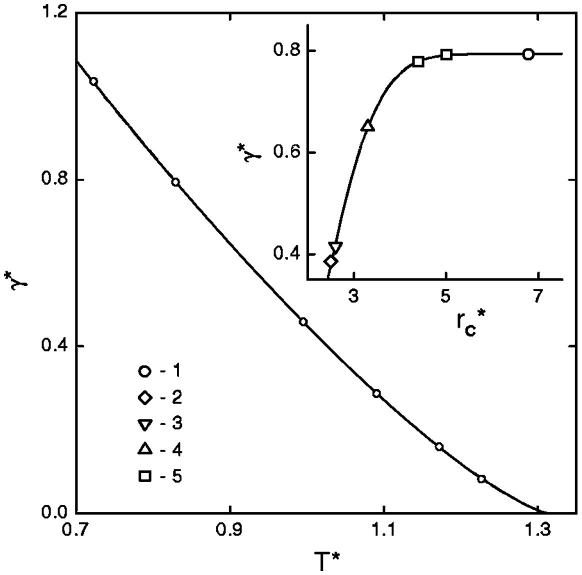

FIG. 3. Surface tension as a function of the temperature. The figure inset shows the dependence of the surface tension on the value of the cutoff radius of the LJ potential at $T^*=0.8268$. 1, data of this paper; 2, Ref. [19]; 3, Ref. [20]; 4, Ref. [21]; 5, Ref. [22].

In the whole investigated temperature range the difference between the coexisting densities within the limits of statistical error of its determination is described by power law of the form

$$\rho_l^* - \rho_g^* \sim (T_c^* - T^*)^{\beta}, \tag{17}$$

where $\beta=0.32$, $T_c^*=1.285$. The critical density obtained by the law of rectilinear diameters is $\rho_c^*=0.315$.

The surface tension was calculated according to its stress definition

$$\gamma = \frac{1}{2}\int_{-\infty}^{\infty} [p_N(z) - p_T(z)]dz, \tag{18}$$

where the factor 1/2 appears due to the presence of two interfaces in the system. The difference of the normal $p_N(z)$ and the transverse $p_T(z)$ components of the pressure tensor was determined by the Kirkwood-Buff expression [18]

$$p_N(z_n) - p_T(z_n) = \frac{1}{2V_s}\left\langle \sum_{i=1}^{N}\sum_{j\neq i} \frac{x_{ij}^2 + y_{ij}^2 - 2z_{ij}^2}{r_{ij}} \times \phi'(r_{ij})\,\delta(z_n - z_i)\right\rangle. \tag{19}$$

Here $\langle \cdots \rangle$ denotes ensemble average of all pairs of particles, of which at least one (i or j) is in a layer 0.05σ thick with a number n ($n=1,\ldots,1160$), V_s is the layer volume.

In Fig. 3, the results of calculating the dependence $\gamma^*(T^*)$ are compared with the results of some other authors [19–22]. The values of γ, as well as of p,ρ,T properties at the phase equilibrium, essentially depend on the cutoff radius of the LJ potential.

The temperature dependence of γ^* is well approximated by the power law

$$\gamma^* \sim (T_c^* - T^*)^{\mu}, \tag{20}$$

where $T_c^*=1.314$, $\mu=1.314$. The value of the critical temperature proves to be somewhat overestimated with respect to its value determined by data on the coexisting densities.

The values of critical parameters in computer simulation depend on the kind of the model, the cutoff radius of the LJ potential, the box size, and some other factors. In the critical region the effects of the finite size of the box may be taken into account in the framework of finite-size scaling analysis. For a LJ fluid such an approach gives asymptotic ($L\to\infty$) values of critical parameters $T_c^*=1.326$, $\rho_c^*=0.316$, $p_c^*=0.111$ [23,24].

B. One-phase system

To determine the Helmholtz free energy density of a homogeneous fluid and the influence parameter by the method of molecular dynamics the p,ρ,T properties and the radial distribution function have been calculated in systems of $N=2048$ and 8788 LJ particles. The box containing the particles was cubic. As in the case of a two-phase model, for integrating equations of particles motion use was made of the Beeman's algorithm [15] with a step in time $\Delta t=10^{-14}$ s. Calculations were made in a microcanonical ensemble at temperatures close to $T^*=0.7$, 1.0, 1.15. The derivative $(\partial p/\partial T)_V$ was determined along with the pressure, temperature, and internal energy. It was used for subsequent pressure correction in a one-phase system to the fixed temperature values mentioned above.

Calculations were started in a stable liquid or vapor region. Transformation into a new state was realized by compression (liquid) or expansion (vapor) of a system by means of scaling of the box boundaries and the coordinates of all the particles from the equilibrium configuration of the previous state. The equilibration of the system at every new density took $(5–15)\times 10^4$ time steps. Thermodynamic and structural characteristics of the system were determined by averaging over $(5–30)\times 10^5$ time steps. Calculations were made at two value of the cutoff radius of the LJ potential, $r_{c1}^*=2.6$ and $r_{c2}^*=6.78$ (6.58 for isotherm $T^*=0.7$). Within the cutoff radius of the potential the pressure was calculated by the formula

$$p = \frac{1}{3V}\left\langle 2\sum_{i=1}^{N}\frac{mv_i^2}{2} - \sum_{i>j} r_{ij}\frac{\partial\phi(r_{ij})}{\partial r_{ij}}\right\rangle. \tag{21}$$

The contribution to the pressure of particles located at a distance $r>r_c$ from the isolated one was taken into account by introduction of a correction Δp_c, which was calculated under the assumption that there were no correlations between particles at distances exceeding r_c,

$$\Delta p_c^* = -\frac{16\pi}{3r_c^{*3}}\rho^{*2}, \tag{22}$$

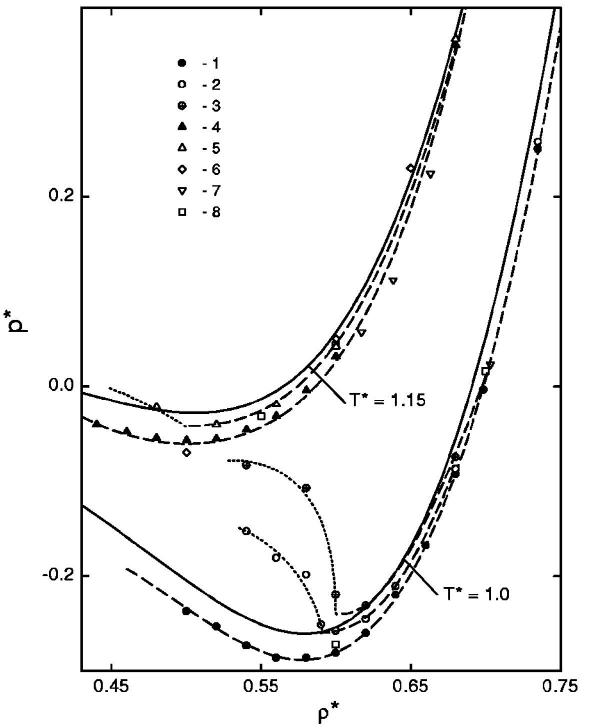

FIG. 4. Pressure as a function of the density at $T^*=1.0$ and $T^*=1.15$ for the liquid phase: 1, 4—our data, $r_c^*=2.6$, $N=2048$; 2, 5—our data, $r_c^*=6.78$, $N=2048$; 3, our data, $r_c^*=6.78$, $N=8788$; 6, Ref. [25]; 7, Ref. [26]; 8, Ref. [27]. Solid lines show the equation of state (23).

thus, the total pressure is the result of summation of Eqs. (21) and (22).

Figures 4 and 5 give the results of calculating the pressure at isotherms $T^*=1.0$ and 1.15 for the liquid (Fig. 4) and the gas (Fig. 5) phases in a stable and a metastable states. In the region of stable states and at small supersaturations data on the pressure obtained in models with different numbers of particles and at different values of the cutoff radius of the potential agree with each other within the limits of statistical error of calculation. Here one can also observe good agreement of our results with data of computer experiments of Hansen and Verlet [25], Adams [26], Johnson *et al.* [27]. In a region of high metastability the value of the pressure in the model essentially depends on the number of particles and the cutoff radius of the potential (Figs. 4 and 5). At $r_c^*=2.6$ isotherms of the total pressure have points of minimum (liquid) and maximum (gas) typical for the van der Waals isotherms. Such a character of dependence of p on ρ points to the retention of the system homogeneity in the density range under investigation. An increase of r_c^* from 2.6 to 6.78 causes the appearance of nonanalyticity in the dependence $p(\rho)$, which is connected with phase separation in the system containing a finite number of particles. After the formation of a critical nucleus a stable aggregate of a new phase is generated here in the form of a bubble in liquid or a droplet in vapor. In such an inhomogeneous system containing a curved interface the pressures inside and outside the nucleus are different. In the calculations presented here this fact is not taken into account. Calculation by Eq. (21) gives some effective (averaged) pressure, which is shown in Figs. 4 and 5 with dotted lines. A decrease in density (increase in volume) in a micro-two-phase system forming during the decay of a homogeneous liquid results in a growth of the effective radius of a stable vapor bubble and an increase in the effective pressure in the whole system. And vice versa, condensation of the gas phase into a droplet decreases the effective pressure in a model.

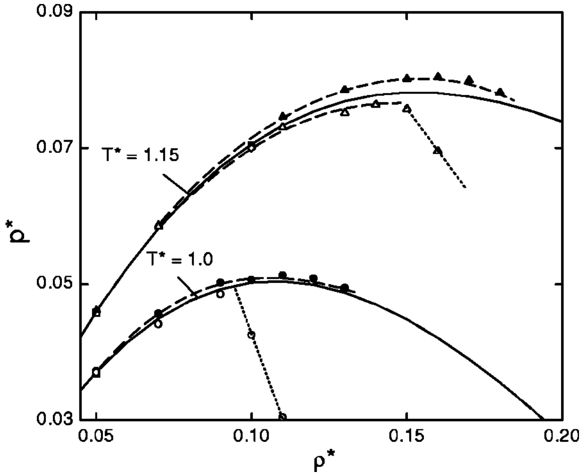

FIG. 5. Pressure as a function of the density at $T^*=1.0$ and $T^*=1.15$ for the the gas phase, details same as for Fig. 4.

The probability of formation of a new phase critical nucleus in the same time interval is higher in a system of a larger size than in a small one. Therefore, phase separation in a system with $N=8788$ particles takes place at lower supersaturations than in a system with $N=2048$ particles. Besides, in a system with $N=8788$ particles before the appearance of a critical nucleus there are more developed heterophase fluctuations, which increase the effective pressure in a liquid at densities close to the point of beginning of phase separation (Fig. 4).

Somewhat surprising is the appearance of points of minima (maxima) on isothermes $T^*=1.0$ and 1.15 in a model with a cutoff radius of the LJ potential $r_c^*=2.6$. The van der Waals form of isotherms in this case points to the retention of phase homogeneity in the model at least to the density values to which calculation has been made (Figs. 4 and 5). Here, however, one should bear in mind the following circumstance: isotherms with points of minima (liquid) and maxima (gas) appear when a correction for long-range interaction (22) is applied to a pressure calculated in a model with a short-range (cutoff) potential (21). In a model with a cutoff LJ potential (without corrections) isothermal elasticity retains a positive value in the whole density range in which calculation has been made (Fig. 6). A different situation is observed at $T^*=0.7$. Here for the liquid phase at density $\rho^*=0.71$ the pressure in a model with a short-range potential proves to be close to its spinodal value, and a subsequent decrease in density results in the loss of stability of a homogeneous liquid (Fig. 6). As in a model with a large cutoff radius of the potential, the gas phase is isolated in the form

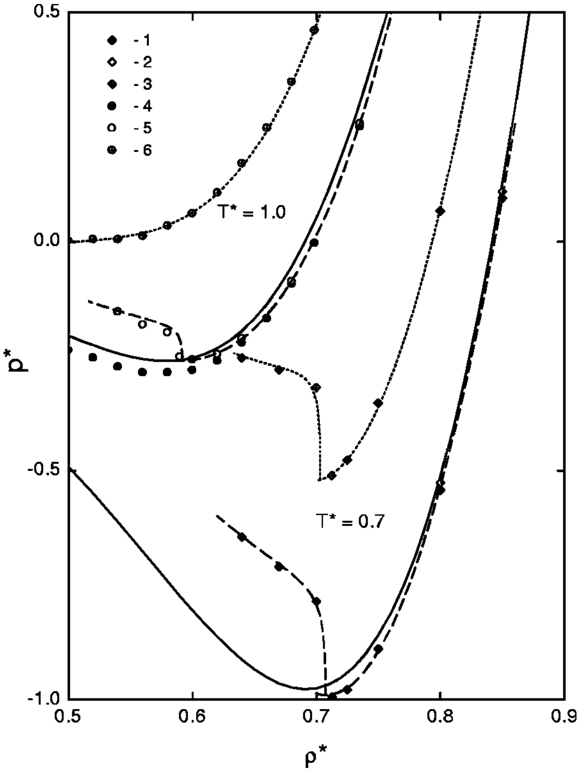

FIG. 6. Isotherms $T^* = 0.7$ and $T^* = 1.0$ with allowance for the contribution to the pressure of particles at a distance $r_c^* > 2.6$ [Eqs. (21), (22)—dark dots] and without its allowance [Eq. (21), marked light dots]: 1, 4—$r_c^* = 2.6$, $N = 2048$; 2, 5—$r_c^* = 6.78$, $N = 2048$; 3, 6—$r_c^* = 2.6$, $N = 2048$. Solid lines show the equation of state (23).

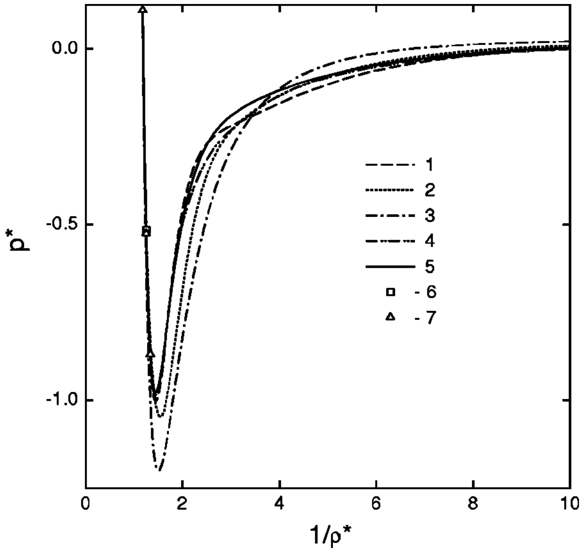

FIG. 7. Isotherm $T^* = 0.7$ by the equations of state from the papers: 1, Ref. [27]; 2, Ref. [28]; 3, Ref. [29]; 4, Ref. [32]; 5, this paper [Eq. (23)]. Data of molecular-dynamic calculations: 6, Ref. [27]; 7, our data.

of a closed cavity, which leads to increasing effective pressure. Thus, pressures obtained with allowance in Eq. (21) for the correction for long-range interaction by formula (22) and absence of phase separation may be considered only as an estimation from below for a homogeneous liquid and an estimation from above for a homogeneous gas phase.

C. Equation of state for the homogeneous fluid

A number of empirical equations of state with free parameters determined by data of the methods of Monte-Carlo and molecular dynamics have been suggested for describing homogeneous phases of the LJ fluid [27–32]. The authors of the papers [27–32] used different analytical forms of presentation of the equation of state. In a region of liquid-vapor phase transition all equations give a form of the dependence $p(\rho)$ similar to that of van der Waals. However, numerical data obtained by these equations in a region of high metastability and a labile region are in essential disagreement with each other (Fig. 7).

When the p,ρ,T data of our molecular-dynamic experiments are adequately described by the equation of state of Mecke *et al.* [32], the values of the critical parameters of this equation ($T_c^* = 1.328$, $\rho_c^* = 0.3107$) differ essentially from those predicted by our data on phase equilibrium and surface tension. Besides, the ρ,T projection of the spinodal liquid branch calculated by the equation of state from the Ref. [32] has a bend in the temperature range $T^* = 1.05$–1.28, in connection with which it cannot be approximated by an equation of the type (17). Feasibility of an equation of the type (17) for the density values at the spinodal is shown in the Refs. [33,34].

All this required a new equation of state for the LJ fluid, which in a mutually coordinated way would describe the data of our molecular-dynamic calculations in one-phase and two-phase models and adequately reproduce the position of the binodal, spinodal, and critical point.

In setting up the equation of state apart from our data we used the results of computer experiments of Johnson and coauthors [27] pertaining to pressures $p^* \leqslant 0.6$ and temperatures $T^* = 0.7$–6. To ensure the correctness of high-temperature $T^* = 7$–35 extensions of isochores and isobars we included in the array of the processed data the results of the papers by Hansen [35] and Ree [29]. To avoid nonphysical oscillations on isotherms at low temperatures into the data array to be formed we introduced the density values on the isotherm 0.7 pertaining to the labile region of a homogeneous fluid and calculated by the equation of state of Mecke *et al.* [32].

The results of calculation of coexisting densities in a two-phase model were included in the initial array with an enlarged weight with respect to the data enumerated above. At given values of ρ_l^*, ρ_g^*, T^* it was necessary to fulfill the conditions of mechanical $p^*(\rho_l^*, T^*) = p^*(\rho_g^*, T^*)$ and chemical $\mu^*(\rho_l^*, T^*) = \mu^*(\rho_g^*, T^*)$ equlibria. The equilibrium pressure in this case was not fixed. Data on the density and pressure on a spinodal approximated from the results of our computer experiment were imparted a weight of 8.

The equation of state is written in the form of pressure expansion in density and temperature

$$p^* = \rho^* T^* \left[1 + \left(\frac{2\pi}{3} \right) B\rho^* + \left(\frac{2\pi}{3} \right)^2 C\rho^{*2} + \sum_{i=3}^{7} \sum_{j=0}^{6} b_{ij} \frac{\rho^{*i}}{(T^*)^{j/2}} \right]. \tag{23}$$

Here the first three terms are a virial equation of state and are included in Eq. (23) for correct description of the gas phase of a LJ fluid. The second B and the third C virial coefficients have been calculated by the following formulas:

$$B = -\frac{3}{4\pi} \int h_0(r_{12}) d\vec{r}_{12}, \tag{24}$$

$$\begin{aligned} C &= -\frac{3}{4\pi^2} \int \int h_0(r_{12}) h_0(r_{23}) h_0(r_{31}) d\vec{r}_{12} d\vec{r}_{23} \\ &= -12 \int_0^\infty r h_0(r) dr \int_0^r r' h_0(r') dr' \\ &\quad \times [\Phi(r+r') - \Phi(r-r')], \end{aligned} \tag{25}$$

where

$$\Phi(r) = \int_0^r h_0(r') r' dr',$$

$$h_0(r) = \exp[-\phi(r)/k_B T] - 1, \tag{26}$$

$h_0(r)$ is the limit of the pair correlation function at $\rho \to 0$.

The results of calculating B and C in the temperature range $0.7 \leqslant T^* \leqslant 35$ have been approximated by the expressions

$$B = \sum_{i=0}^{6} b_i (T^*)^{-i/2}, \tag{27}$$

$$C = \sum_{i=0}^{4} c_i (T^*)^{-i/2} + c_5 [c_6 - (T^*)^{-1/2}]^{-9}, \tag{28}$$

where $b_0 = 0.27165$, $b_1 = 2.8813$, $b_2 = -9.9257$, $b_3 = 11.9895$, $b_4 = -12.8825$, $b_5 = 7.0894$, $b_6 = -1.9618$, $c_0 = 0.11035$, $c_1 = 0.9249$, $c_2 = 1.0342$, $c_3 = -5.6725$, $c_4 = 7.2901$, $c_5 = -137.2732$, $c_6 = 2.5155$. The absolute approximation error of the second virial coefficient does not exceed 0.0002 and third one does not exceed 0.004.

The coefficients b_{ij} of Eq. (23) have been determined by the least-squares fit. By the method of regressive analysis the number of coefficients b_{ij} in the equation has been reduced to 25 without any essential decrease in the accuracy of description of the initial array of p, ρ, T data. The coefficients of the equation of state are given in Table I.

The mean-square deviation in p^* of values obtained in computer experiments from those calculated by Eq. (23) is 0.0123. The values of the critical parameters are as follows: $T_c^* = 1.3084$, $\rho_c^* = 0.2961$, $p_c^* = 0.1262$. The area of validity of the equation of state is limited in pressure by the value of $p^* = 0.5$, in temperature by the range of $T^* = 0.7$–35.

TABLE I. Exponents and coefficients of Eq. (23).

j	i	b_{ij}	j	i	b_{ij}	j	i	b_{ij}
1	4	−12089.7851	1	5	−22852.7092	1	6	29133.4122
1	7	70064.6030	2	4	78878.1269	2	5	95924.3997
2	6	−229079.316	2	7	−238148.643	3	4	−202813.743
3	5	−108130.890	3	6	535705.401	3	7	306007.586
4	3	1192.26528	4	4	247912.834	4	6	−550260.913
4	7	−179145.690	5	3	−2637.74735	5	4	−141289.814
5	5	52211.5056	5	6	267568.432	5	7	40788.4012
6	3	1450.53860	6	4	29551.8082	6	5	-17802.4658
6	6	−52138.4220						

D. Direct correlation function of a homogeneous fluid

The determining relationship for the direct correlation function of a homogeneous system is the Ornstein-Zernike equation [2], which establishes relation between the function $c(r)$ and the radial distribution function $g(r)$

$$c(r) = h(r) - \rho \int h(r') c(|\vec{r} - \vec{r}'|) d\vec{r}',$$

$$h(r) = g(r) - 1. \tag{29}$$

In physics of liquid state for calculating the radial distribution function use is made of the thermodynamic perturbation theory [36], and also of approximate integral equations, such as the equations of Percus-Yevick (PY) and hypernetted chain approximation (HNC) [37]. The latter follow from the Ornstein-Zernike equation (29) if it is supplemented with approximation relations, which relate the direct correlation function and the radial distribution function:

$$c(r) = \{1 - \exp[\phi(r)/k_B T]\} g(r), \quad \text{PY}, \tag{30}$$

$$c(r) = 1 - g(r) - \ln[g(r)] - \phi(r)/k_B T, \quad \text{HNC}. \tag{31}$$

In the region of liquid-gas phase transition the PY and HNC equations have a region of absence of physical solutions. In the general case the boundary of this region does not coincide with the spinodal line [38]. Thus, the method of integral equations does not make it possible to determine the influence parameter in the whole density range restricted by the coexisting densities.

In the computer experiments the radial distribution function was calculated according to its definition by the formula

$$g(r) = \frac{V}{4\pi r^2 N^2 M} \sum_i^M \sum_j^N \frac{\Delta n_i^{(j)}(r)}{\Delta r}, \tag{32}$$

where $\Delta n_i^{(j)}(r)$ is the number of particles in a spherical layer Δr thick at a distance r from the jth particle when ith calculating $g(r)$, M is the number of calculations of $g(r)$ in the process of integrating the equations of motion.

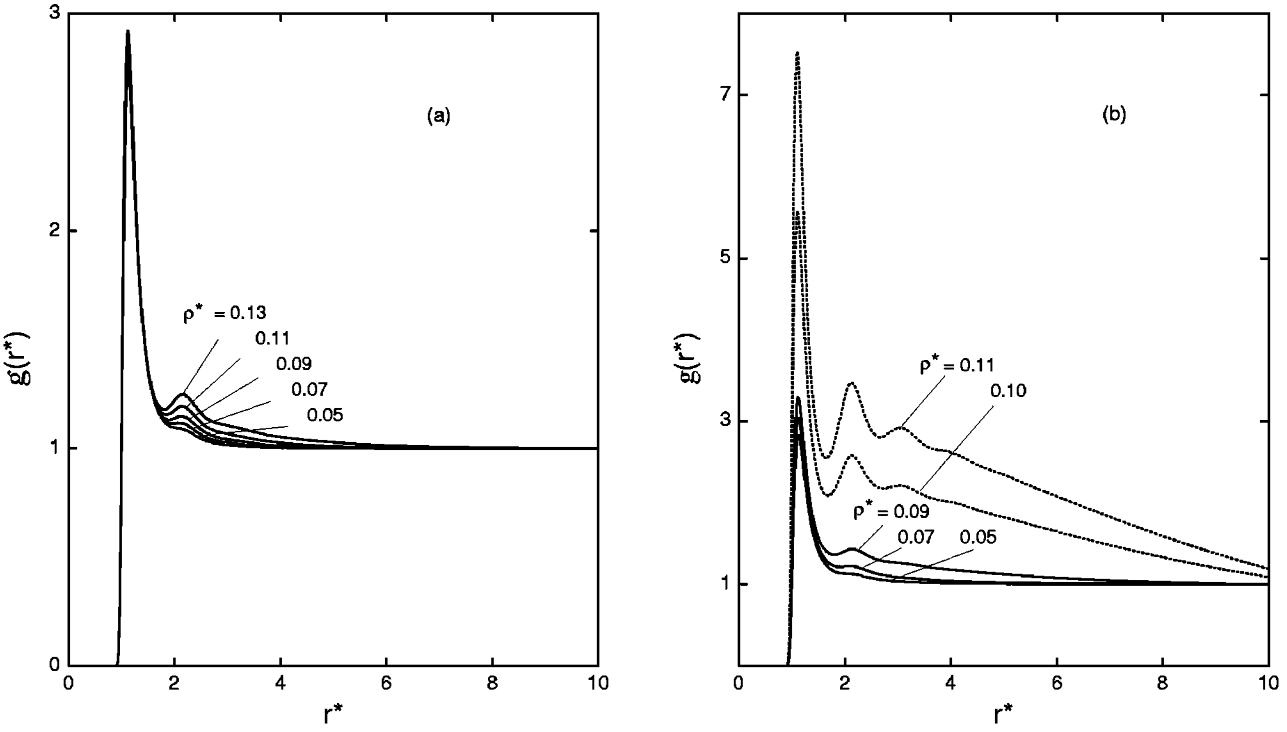

FIG. 8. Radial distribution functions in the gas phase at $T^*=1.0$ in models with a cutoff radius of LJ potential $r_c^*=2.6$ (a) and $r_c^*=6.78$ (b).

In the density range $\rho^*=0.001$–0.18 the radial distribution function was determined at distances that did not exceed 10.0925σ. At densities $\rho^*=0.44$–0.9 calculations of $g(r)$ were made at distances up to $L/2$, which corresponded to $r_{\max}^*=8.3425$–6.9725.

The results of calculating $g(r)$ for the gas phase in models with cutoff radii of the potential $r_{c1}^*=2.6$ and $r_{c2}^*=6.78$ are given in Fig. 8. In the region of stable and homogeneous metastable states these data are in good agreement with each other. An increase in the density of the gas phase results in increasing height of the first peak of $g(r)$ and formation of a second peak. During the decay of a homogeneous metastable state in a model with $r_c^*=6.78$ the radial distribution function of the resulting microheterogeneous structure takes a form qualitatively different from a homogeneous system [Fig. 8(b), dotted lines]: the height of the peaks of $g(r)$ increases considerably, and their number grows, which points to the appearance in the model of domains with an increased particle density. The presence in the system of molecular aggregates with a distinctly different density is also indicated by the fact that oscillation in the radial distribution function takes place not at the lever $g(r)=1$, but at higher levers.

By making Fourier transforms of both parts of Eq. (29) and using the theorem of the convolution we have

$$c(q)=\frac{h(q)}{1+\rho h(q)}, \tag{33}$$

where the Fourier image $\varphi(q)$ of a spherically symmetric function $\varphi(r)$ is

$$\varphi(q)=4\pi\int_0^\infty r^2\varphi(r)\frac{\sin(qr)}{qr}\,dr, \tag{34}$$

and the Fourier preimage

$$\varphi(r)=\frac{1}{2\pi}\int_0^\infty q^2\varphi(q)\frac{\sin(qr)}{qr}\,dq. \tag{35}$$

In calculations of $h(q)$ and $c(q)$ by formulas (34) and (35) integration with respect to r^* was carried out from 0.1 to 10.0925 or to half the box rib and integration with respect to q^* was carried out from 0 to 80. The integration step by the space coordinate $\Delta r^*=0.005$, by the wave number $\Delta q^*=0.001$.

IV. COMPARISON OF THE THEORY WITH DATA OF COMPUTER SIMULATION

A. Temperature dependence of the influence parameter

In the simplest version of the van der Waals theory it is assumed that the influence parameter does not depend on thermodynamic state variables, or is only a function of the temperature. Let us consider how in this case the theory agree with the results of computer simulation of a flat liquid-vapor interface. If the influence parameter κ does not depend on the density, its value may be calculated from Eq. (12) by molecular-dynamic data on the surface tension or from Eq. (10) by data on the effective thickness of the interface. Let us define the effective thickness of the interface L_{10}^{90} as the distance over which the density changes from the value of ρ_{10}

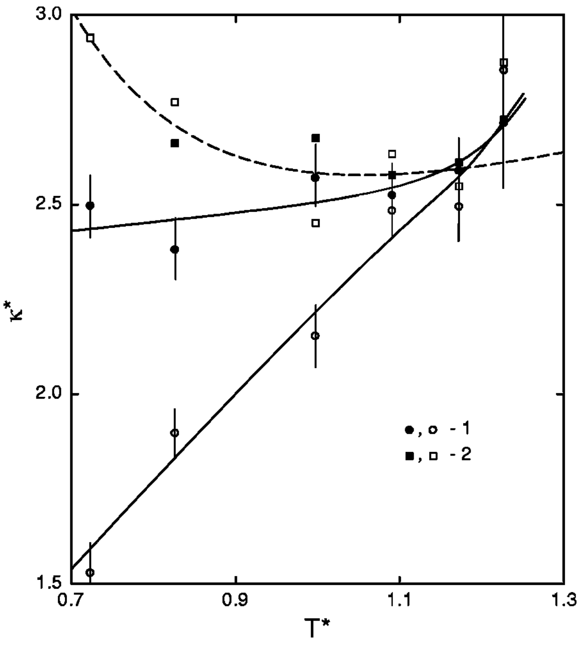

FIG. 9. Influence parameter as a temperature function: 1, in a square-gradient approximation, Eq. (7); 2, with allowance for the higher terms, Eq. (64); dark dots show calculation by data on the surface tension; light dots, calculation by data on the effective interfacial thickness.

$=\rho_g+0.1\Delta\rho$ to $\rho_{90}=\rho_g+0.9\Delta\rho$, where $\Delta\rho=\rho_l-\rho_g$. In the van der Waals square-gradient theory

$$L_{10}^{90}=\int_{\rho_{10}}^{\rho_{90}}\left[\frac{\kappa}{\omega(\rho)-\omega_s}\right]^{1/2}d\rho. \tag{36}$$

The results of calculating the influence parameter by Eqs. (36) and (12) are shown in Fig. 9 with solid lines. At low temperatures the data of these two approaches differ by 40%. As the critical point is approached, the differences descrease, and at $T^*\simeq 1.1$ the values of κ agree within the error of their determination.

If the influence parameter has been calculated through the effective thickness of an interface, the van der Waals square-gradient theory underestimates the surface tension in the region of low temperatures, and in calculations of κ through the surface tension the effective thickness of the interface proves to be overestimated. At a temperature $T^*=0.7$ the discrepancies of the data on L_{10}^{90} and γ are approximately 20%. Thus, the initial equation of the square-gradient theory (7), which does not take into account the density dependence of the influence parameter, makes it impossible within the error of the data of computer experiment to describe the whole complex of properties of a liquid-vapor interface in the whole temperature range from the triple to the critical point. Let us examine how considerable the effect of the density dependence of κ may prove to be.

B. Density dependence of the influence parameter

According to statistical determination (4), the influence parameter κ in the van der Waals gradient expansion (3) is proportional to the second moment of the direct correlation function. Thus, the density dependence of κ is a direct consequence of the dependence $c(r;\rho)$. Expression (4) can be rewritten through the pair-correlation function. By integrating Eq. (29) with respect to $d\vec{r}$, and also the result of multiplication of Eq. (29) by r^2, and combining the obtained expressions we have

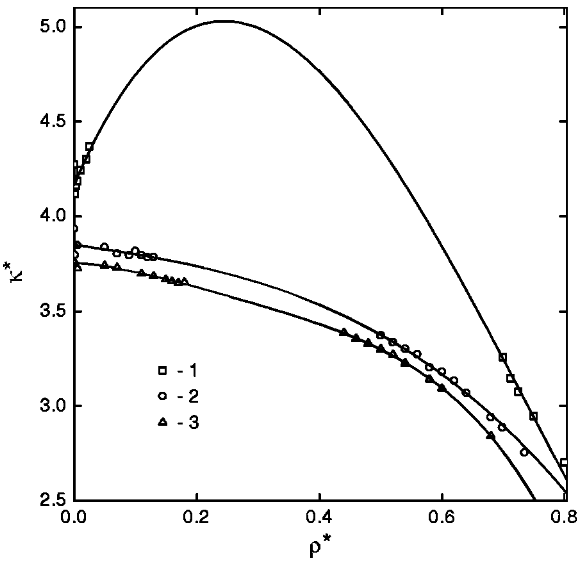

FIG. 10. Influence parameter as a density function at isotherms: $T^*=0.7$ for 1, 1.0 for 2, 1.15 for 3.

$$\int c(r)r^2d\vec{r}=\frac{\int h(r)r^2d\vec{r}}{\left[1+\rho\int h(r)d\vec{r}\right]^2}. \tag{37}$$

The integrals in Eqs. (4) and (37) prove to be very sensitive to long-range parts of correlation functions. As the pair correlation function $h(r)$ has a longer range of action than the direct correlation function $c(r)$, and its asymptotic behavior far from the critical point is less determined, Relation (4) has some advantages over Eq. (37) in calculating κ, at least at high fluid densities.

We have calculated $c(r)$ by data on $h(r)$ using Fourier transforms (33)–(35) of Eq. (29). Since the integrals of Eqs. (34) and (35) were determined on the finite intervals of q and r, the obtained values of $c(r)$ had a considerable error within the limits $r\rightarrow 0$ and $r\rightarrow\infty$. At distances $r>r_{\max}$, where $r_{\max}=10.0925\sigma$ for gas and $L/2$ for liquid, we approximated the function $c(r)$ by expression (5). In this case the correction $\Delta\kappa$ to the influence parameter was calculated by the following formula:

$$\Delta\kappa=\frac{4\pi}{3}\frac{1}{r_{\max}^*}. \tag{38}$$

Figure 10 shows the result of calculating the influence parameter in a model with a cutoff radius of the LJ potential $r_c^*=2.6$ at three isotherms. Althrough the value of κ may

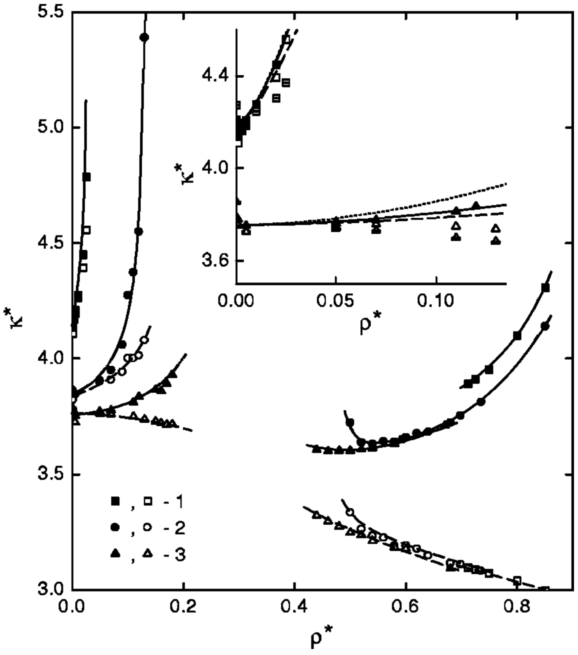

FIG. 11. Influence parameter calculated with the use of PY (light dots) and HNC (dark dots) approximations at isotherms: 1 for $T^*=0.7$, 2 for 1.0, 3 for 1.15. The figure inset shows the dependence $\kappa^*(\rho^*)$ at low densities. Marked light dots, calculation by data of molecular dynamics on $c(r)$; solid line, calculation by Eq. (39) when $\kappa^{(2)}$ is determined with allowance for all the cluster integrals; dotted line, the same when $\kappa^{(2)}$ is determined in HNC approximation, dash-dotted line, the same when $\kappa^{(2)}$ is determined in PY approximation.

have a considerable error (up to 12%), we are sure that they reproduce the temperature and the density dependence of the influence parameter given by formula (4) qualitatively correctly.

The density dependence of κ was earlier determined in the framework of a modified van der Waals model by McCoy *et al.* [39] and Cornelisse *et al.* [38] by data on the direct correlation function obtained by numerical integration of the Ornstein-Zernike equation in PY and HNC approximations. We calculated $\kappa(\rho,T)$ by the radial distribution function of computer experiment using relations (30), (31) (Fig. 11). The results of such calculation differ from the results of directs simulation first of all by an abrupt increase of the parameter κ on the side of the gas phase with deeper penetration into the metastable region. It is most pronounced for HNC approximation (31). This result is in good qualitative and quantitative agreement with the paper by Cornelisse *et al.* [38]. The tendency for the divergence of $\kappa(\rho)$ in the Ref. [38] manifested itself as the boundary of the region of absence of solutions to integral equations was approached. Correlation functions were determined up to distances $r^*_{\max}=51.175$, and as the authors [38] noted, an increase in this distance did not influence the character of the dependence $\kappa(\rho)$ on the side of the gas phase.

On the side of the liquid phase approximations of Eqs. (30) and (31) with the use in them of the results of molecular-dynamics calculations of $g(r)$ give qualitatively different density dependence of the influence parameter. If in an approximation of Eq. (30) $\kappa(\rho)$ is a decreasing density function, which agrees with the results of direct molecular-dynamic calculation (Fig. 10) and the numerical solution of Eq. (29) [38], in an approximation of Eq. (31) it is an increasing density function. The latter also agrees qualitatively with the results of the Ref. [38], but there the tendency for the increase of κ with increasing density is less pronounced. In a rigorous solution of Eq. (29) in an approximation of Eq. (31) the parameter κ increases abruptly at the approach to the boundary of the region of absence of solutions for the HNC equation, which is not observed in our calculations. The latter may be connected with the small value of $r_{\max}$ to which the function $g(r)$ was calculated. The authors [38] point out that the tendency for the divergence of κ for the liquid phase in a HNC approximation manifests itself if the cutoff radius $r^*_{\max}$ of the pair correlation function is equal to 51.175 and disappears with a descrease in $r^*_{\max}$ to 6.375. Approximations of Eqs. (30) and (31) for the liquid phase give a much weaker temperature dependence of κ than for the gas phase, and for Eq. (31) it is practically absent.

In the range of low densities the influence parameter and the pair correlation function may be presented in the form of power series of density

$$\kappa(\rho)=\kappa^{(0)}+\kappa^{(1)}\rho+\kappa^{(2)}\rho^2+\cdots, \tag{39}$$

$$h(r;\rho)=h^{(0)}(r)+h^{(1)}(r)\rho+h^{(2)}(r)\rho^2+\cdots. \tag{40}$$

For the expansion coefficients of $\kappa(\rho)$ from Eqs. (4) and (37) we have

$$\kappa^{(0)}(\rho)=(k_BT/12)H_{02}, \tag{41}$$

$$\kappa^{(1)}=(k_BT/12)(H_{12}-2H_{00}H_{02}), \tag{42}$$

$$\kappa^{(2)}=(k_BT/12)(H_{22}-2H_{12}H_{00}+3H_{02}H_{00}^2-2H_{02}H_{10}), \tag{43}$$

where

$$H_{00}=\int h_0(r)d\vec{r},\quad H_{02}=\int h_0(r)r^2d\vec{r},$$

$$H_{10}=\int h_1(r)d\vec{r},\quad H_{12}=\int h_1(r)r^2d\vec{r},$$

$$H_{20}=\int h_2(r)d\vec{r},\quad H_{22}=\int h_2(r)r^2d\vec{r}. \tag{44}$$

The expansion coefficients of the pair correlation function $h(r)$ are expressed in terms of cluster integrals [40]. The first term of a series (40) is given by formula (26) and determines the value and the temperature dependence of the influence parameter at $\rho\to 0$.

The integrals of Eq. (44) were calculated with a step $\Delta r^*=0.01$ to $r^*_m=40$. The contribution of the range $r^*>r^*_m$ was determined analytically with expansion into a series of the $\exp[-\phi(r)/k_BT]$ and allowance for the first nonzero term. The coefficient $\kappa^{(0)}$ is a weakly decreasing temperature function. In the investigated temperature range $T^* = 0.7–1.15$ it changes by less than 15%. The coefficient $\kappa^{(1)}$ also decreases with increasing temperature, but much more abruptly than $\kappa^{(0)}$. At $T > 1.2$ it takes negative values. A direct calculation of the cluster integrals determining the coefficient h_2 is a complicated problem. The poor convergence of some of the cluster integrals at $r \to \infty$ gives rise to a great error in calculations of $\kappa^{(2)}$. Three of the four cluster integrals included in the coefficient h_2 make up the HNC approximation. The fourth cluster integral, which is not determined by PY and HNC approximations, converges quite rapidly and can be calculated with a good accuracy. This makes it possible to determine the deviation of the value of the coefficient $\kappa^{(2)}$ from the coefficient $\kappa^{(2)}_{HNC}$ obtained in HNC approximation. The coefficient $\kappa^{(2)}$, as well as $\kappa^{(0)}$ and $\kappa^{(1)}$ is a decreasing temperature function. The change of the sign of $\kappa^{(2)}$ from positive to negative takes place in the region of the critical temperature.

The inset of Fig. 11 presents the dependence $\kappa(\rho)$ at isotherms $T^* = 0.7$ and 1.15 in the region of low densities. An increase in the density is accompanied by an increase in the influence parameter, a rise of the temperature decreasing the rate of the increase of κ. The results of Eq. (39) are in good agreement both with the data of computer simulation and with the data of PY and HNC approximations, which become accurate in the limit $\rho \to 0$.

To use the obtained data for $\kappa(\rho)$ in the van der Waals theory it is necessary to extrapolate them through the density range where the influence parameter has not been determined. We have no physical models that could give substantiation for such extrapolation. Therefore, we have approximated the dependence $\kappa(\rho)$ by polynomials with minimal exponents. The results of such approximation are shown in Fig. 10 with solid lines. From a comparison of Figs. 9 and 10 it follows that one cannot expect improvement in the description of a flat interface by the van der Waals square-gradient theory using in it expression (4) for the influence parameter as the value of κ in this case proves to be 30–40 % higher than it is required to reproduce data for the surface tension and the effective interfacial thickness. When the data for $\kappa(\rho)$ presented in Fig. 10 are substituted into expressions (12), (36), the value of the surface tension proves to be overestimated by ~16%, and the effective thickness by ~25% ($T^* = 1.0$). With decreasing temperature the discrepancies increase and they decrease as the critical point is approached.

An expression for the Helmholtz free energy of the kind (3) is postulated in the classical theory of critical phenomena [41]. This theory is formulated in a mean-field approximation, the square-gradient term takes into account the presence of long-wave fluctuations. The coefficient at the square of the density gradient κ, an absolute analog of the influence parameter in the van der Waals theory, is connected with the correlation radius ξ and the isothermal compressibility $K_T = (\partial\rho/\partial p)_T/\rho$ by the following relation:

$$\xi^2 = \kappa\rho^2 K_T. \tag{45}$$

Thomas and Schmidt [42] expressed the correlation radius through a certain characteristic length l, which in a first approximation has to be a function only of the temperature

$$\xi^2 = \frac{l^2}{10}(\rho k_B T K_T - 1). \tag{46}$$

Substitution of Eq. (46) into Eq. (45) gives

$$\kappa(\rho,T) = \frac{l^2}{10}\left(\frac{k_B T}{\rho} - \frac{1}{\rho^2 K_T}\right). \tag{47}$$

The temperature dependence $l(T)$ may be determined from data on the interfacial effective thickness or the surface tension as it was done in Sec. IV A. The parameter κ in this case is a decreasing density function. At temperatures $T^* \leqslant 1.15$ it becomes negative in the range of densities corresponding to liquid-vapor equilibrium existence. Thus, relation (47) cannot be used in the van der Waals theory at low temperatures, as is assumed in Ref. [38]. Its action is limited only by the nearest vicinity of the critical point.

The results obtained on the description of properties of a liquid-vapor interface by the van der Waals square-gradient theory with allowance for the density dependence of the influence parameter cannot be corrected by choosing any other approximation dependence for the function $\kappa(\rho)$, different from that presented in Fig. 10. At high temperature Eq. (3) gives good results even without allowance for the density dependence of κ. Therefore, the question arises as to the validity of its use at low temperatures.

C. Allowance for terms of a higher order than $(\nabla\rho)^2$ in the Helmholtz free energy

At $T^* < 1.0$, the effective thickness of an interface is smaller than 4–5 molecular diameters, and the question of retention in the expansion (2) only of lower spatial derivatives becomes debatable. According to Eq. (2) the contribution to the Helmholtz free energy of an inhomogeneous system of terms following $(\nabla\rho)^2$ may be written as follows:

$$\Delta F_2\{\rho(\vec{r})\} = \int [k_3(\nabla\rho)^4 + k_4(\nabla\rho)^2\Delta\rho + k_5(\Delta\rho)^2 + k_6(\nabla\rho)(\nabla\Delta\rho) + k_7(\Delta\Delta\rho)]d\vec{r}. \tag{48}$$

Applying the divergence theorem [43] and neglecting the surface contributions of the system boundaries we have

$$\int u(\rho)(\Delta\Delta\rho)d\vec{r} = -\int \left(\frac{du(\rho)}{d\rho}\right)(\nabla\rho)(\nabla\Delta\rho)d\vec{r}, \tag{49}$$

$$\int u(\rho)(\nabla\rho)^2(\Delta\rho)d\vec{r} = -\frac{1}{3}\int \left(\frac{du(\rho)}{d\rho}\right)(\nabla\rho)^4 d\vec{r}, \tag{50}$$

$$\int u(\rho)(\Delta\rho)^2 d\vec{r} = -\int \left(\frac{du(\rho)}{d\rho}\right)(\nabla\rho)^2(\Delta\rho)d\vec{r} + \int u(\rho)(\nabla\rho)(\nabla\Delta\rho)d\vec{r}. \qquad (51)$$

Relations (49)–(51) make it possible to eliminate from Eq. (48) three of its five terms. By retaining in Eq. (48) the terms proportional to $(\nabla\rho)^4$ and $(\nabla\rho)^2$ for an excess grand potential of a two-phase system with a flat interface $\Omega_s = \Omega - \Omega_l - \Omega_g$ with allowance for Eq. (7) we obtain

$$\Omega_s\{\rho(z)\} = A\int_{-\infty}^{\infty}\left[\Delta\omega(\rho) + \kappa\left(\frac{d\rho}{dz}\right)^2 + \lambda\left(\frac{d\rho}{dz}\right)^4 + \beta\left(\frac{d^2\rho}{dz^2}\right)^2\right]dz, \qquad (52)$$

where

$$\lambda = k_3 - \frac{1}{3}\left(\frac{\partial k_4}{\partial\rho} + \frac{\partial^2 k_6}{\partial\rho^2} - \frac{\partial^3 k_7}{\partial\rho^3}\right), \qquad (53)$$

$$\beta = k_5 + k_6 - \frac{\partial k_7}{\partial\rho}. \qquad (54)$$

Let us evaluate the effects of the $\lambda(d\rho/dz)^4$ and $\beta(d^2\rho/dz^2)^2$ terms to the properties of a flat interface assuming that the influence parameters λ and β do not depend on the density. If we assume that $\lambda = 0$ minimization of the functional in Eq. (52) will lead to the Euler equation

$$2\kappa\frac{d^2\rho}{dz^2} - 2\beta\frac{d^4\rho}{dz^4} = \frac{\partial\omega}{\partial\rho} = \mu - \mu_0. \qquad (55)$$

Within the limits of Eq. (8) we may write

$$2\kappa\frac{d^2\chi}{dz^2} - 2\beta\frac{d^4\chi}{dz^4} = \chi\left(\frac{\partial\mu}{\partial\rho}\right)_{\rho=\rho_{l,g}}, \qquad (56)$$

where $\chi = \rho - \rho_{l,g}$. For functions of the kind $\chi(z) = \chi_0\exp(-\alpha z)$ we obtain

$$\alpha^2 = \frac{\kappa}{2\beta}\left\{1 - \left[1 - \frac{2\beta}{\kappa^2}\left(\frac{\partial\mu}{\partial\rho}\right)_{\rho_{l,g}}\right]^{1/2}\right\}. \qquad (57)$$

The absence of oscillations on the density profile means the reality of α. The conditions of reality of α imposes limitation on the maximum admissible value of the coefficient β, namely,

$$0 \leqslant \beta \leqslant \frac{\kappa^2}{2}\left(\frac{\partial\mu}{\partial\rho}\right)^{-1}_{\rho=\rho_{l,g}}. \qquad (58)$$

The derivative $(\partial\mu/\partial\rho)_{\rho=\rho_{l,g}}$ has a large value on the side of the gas phase, therefore, the upper boundary of the coefficient β,

$$\beta_{\max} = \frac{\kappa^2}{2}\left(\frac{\partial\mu}{\partial\rho}\right)^{-1}_{\rho=\rho_g}. \qquad (59)$$

In an approximation $\lambda = 0$ the surface tension is determined by the expression

$$\gamma = \frac{\Omega_s}{A} = \int\left[\Delta\omega + \kappa\left(\frac{d\rho}{dz}\right)^2 + \beta\left(\frac{d^2\rho}{dz^2}\right)^2\right]dz. \qquad (60)$$

If we determine κ through the interfacial effective thickness (36) and assume $\beta = \beta_{\max}$, the contribution to the surface tension of the last component (60) does not exceed 0.15% in the vicinity of the triple point and 1.5% at the highest temperature calculated here.

The situation changes qualitatively with allowance in Eq. (52) for the $\lambda(d\rho/dz)^4$ term. In this case there are no limitations on the value of λ connected with the correctness of the behavior of $\rho(z)$ within the limits of $z \to \pm\infty$. At $\beta = 0$ minimization of the functional in Eq. (52) gives the Euler equation

$$2\kappa\frac{d^2\rho}{dz^2} + 12\lambda\frac{d^2\rho}{dz^2}\left(\frac{d\rho}{dz}\right)^2 = \mu - \mu_0. \qquad (61)$$

Multiplying by $d\rho/dz$ and integrating gives

$$\kappa\left(\frac{d\rho}{dz}\right)^2 + 3\lambda\left(\frac{d\rho}{dz}\right)^4 = \Delta\omega. \qquad (62)$$

Now, turning again to the data of computer simulation, we have two unknowns κ, λ and two equation for these unknowns, Eqs. (12) and (36), which seemingly makes it possible to determine κ and λ in a coordinated manner. However, as is shown by a numerical analysis of Eqs. (52), (62), (12), (36), in such a formulation the problem has no solution. If κ has been determined through the interfacial effective thickness on condition that $\lambda = 0$, the values of the surface tension obtained in this case prove to be lower than in molecular-dynamic calculation. At $L_{10}^{90} = \text{const}$ the surface tension will increase with decreasing λ (i.e., $\lambda < 0$) and increasing κ. However at a sufficiently high, to the modulus, value of λ there appears a region of absence of solutions to Eq. (62), i.e., there appear discontinuities on the density profiles. The latter means that for a correct description of the interfacial properties in the region of low temperatures it is also necessary to maintain in the expansion of (2) the terms of the third order of infinitesimality.

Applying the divergence theorem and the neglect of the surface contribution of the system boundaries make it possible to exclude in the expression $F\{\rho(r)\}$ seven terms of the third order of infinitesimality out of eleven and write for the excess grand potential of a two-phase system

$$\Omega_s\{\rho(z)\}=A\int_{-\infty}^{+\infty}\left[\Delta\omega(\rho)+\kappa\left(\frac{d\rho}{dz}\right)^2+\lambda\left(\frac{d\rho}{dz}\right)^4+\beta\left(\frac{d^2\rho}{dz^2}\right)^2+\phi_0\left(\frac{d\rho}{dz}\right)^6+\phi_1\left(\frac{d\rho}{dz}\right)^2\left(\frac{d^2\rho}{dz^2}\right)^2+\phi_2\left(\frac{d^2\rho}{dz^2}\right)^3+\phi_3\left(\frac{d^3\rho}{dz^3}\right)^2\right]dz. \tag{63}$$

As has been shown above, the $\beta(d^2\rho/dz^2)^2$ term gives a small contribution to the value of Ω_s and in a first approximation may be omitted. The $\phi_1(d\rho/dz)^2(d^2\rho/dz^2)^2$, $\phi_2(d^2\rho/dz^2)^3$, and $\phi_3(d^3\rho/dz^3)^2$ terms in the general case are not small as compared with other items of expression (63). Nevertheless, for further analysis we choose an approximation that postulates the following kind of the excess grand potential

$$\Omega_s\{\rho(z)\}=A\int_{-\infty}^{+\infty}\left[\Delta\omega(\rho)+\kappa\left(\frac{d\rho}{dz}\right)^2+\lambda\left(\frac{d\rho}{dz}\right)^4+\phi_0\left(\frac{d\rho}{dz}\right)^6\right]dz. \tag{64}$$

The Euler equation in this case can be expressed,

$$\kappa\left(\frac{d\rho}{dz}\right)^2+3\lambda\left(\frac{d\rho}{dz}\right)^4+5\phi_0\left(\frac{d\rho}{dz}\right)^6=\Delta\omega. \tag{65}$$

A system will be stable with respect to the appearance of density inhomogeneity if the sum of the last three items in the integrand of Eq. (64) is a monotonically increasing function of $(d\rho/dz)^2$. For weak inhomogeneities this condition leads to the requirement of $\kappa>0$. At high density gradients it will suffice to require $\lambda>0$, $\phi_0>0$. However, the condition of stability will also be fulfilled at negative value of λ if

$$\phi_0>\frac{\lambda^2}{3\kappa}. \tag{66}$$

More rigorous requirements for the value of the parameter ϕ_0 at $\lambda<0$ are imposed by Eq. (65). For the $\rho(z)$ to be a continuous function the dependence of $\Delta\omega$ on $(d\rho/dz)^2$ has to be monotonic. The latter is reduced to the requirement

$$\phi_0>\phi_{\min}=\frac{3\lambda^2}{5\kappa}. \tag{67}$$

In fulfilling the condition (67) Eq. (65) has a unique solution with respect to $(d\rho/dz)^2$.

Integration of Eq. (65) gives a density profile $\rho(z)$, by which the surface tension is calculated and the effective thickness of the interface L_{10}^{90} is determined. When such calculations were performed, at the first stage the coefficient ϕ_0 was taken to be equal to its minimum value (67). By the results of computer experiments on γ and L_{10}^{90} for $T^*=0.7234$ the following values were obtained: $\kappa^*=2.857$ and $\lambda^*=-1.241\kappa^*$. Then, taking the ratios λ^*/κ^* and ϕ_0^*/κ^* as being independent of temperature, we determined at other temperatures the values of κ_γ^* by data on γ and the values κ_L by data on L_{10}^{90}. The increase of parameter ϕ_0 results in reduction of a mean-square deviation of values κ_γ^* from κ_L^*. The value of $\phi_0=1.1\phi_{\min}$ is optimum (Fig. 9). In this case the temperature dependence of κ^* in range $0.7<T^*<1.25$ may be presented by the following expression:

$$\kappa^*=4.282-3.6/T^*+1.9/T^{*2}, \tag{68}$$

with $\lambda^*=-1.499\kappa^*$.

With such a choice of parameters for Eq. (64) it describes data on the surface tension and the interfacial effective thickness within the statistical error of computer experiment in the whole investigated temperature range.

Figure 12 presents deviations of the calculated density profiles from hyperbolic tangent

$$\rho(z)=\frac{\rho_l+\rho_g}{2}-\frac{\rho_l-\rho_g}{2}\tanh\left(\frac{z}{L_{10}^{90}}\ln(9)\right). \tag{69}$$

Equation (64) makes it possible to achieve satisfactory agreement with the results of computer experiment both at high and at low temperatures. Equation (7) with an influence parameter that is only a function of temperature agrees with the results of computer simulation only at $T^*>1.0$.

V. DISCUSSIONS AND CONCLUSIONS

The basic equation of the van der Waals square-gradient theory, which describes a flat interface (7), contains two determining parameters, the Helmholtz free energy density $f_0[\rho(z),T]$ of a hypothetical homogeneous medium and the influence parameter at the square of the density gradient.

We have determined $f_0(\rho,T)$ by approximating the results of molecular-dynamic calculations of the p,ρ,T properties of a LJ fluid by an equation of state whose form is in agreement with the mean-field theory. Equations of such a type are also used for describing metastable states in actual systems [44].

The influence parameter is determined by the second moment of the direct correlation function, which for homogeneous states of a LJ fluid has been obtained by molecular-dynamic data on the radial distribution function. Although the second moment $c(r)$ in computer experiment is determined with a considerable error, we are sure that the temperature and the density dependences of κ obtained in this case are correct. The latter is supported by good agreement between the results of rigorous analytic calculations of κ at a low density and the results of computer experiment, and also between the results of computer experiment and numerical solutions of PY and HNC integral equations at high densities. Both for $f_0(\rho,T)$ and for $\kappa(\rho,T)$ there is a density range where these functions cannot be determined by computer experiments. For lack of a model that would make it possible to interpolate the values of the function $\kappa(\rho,T)$ through the

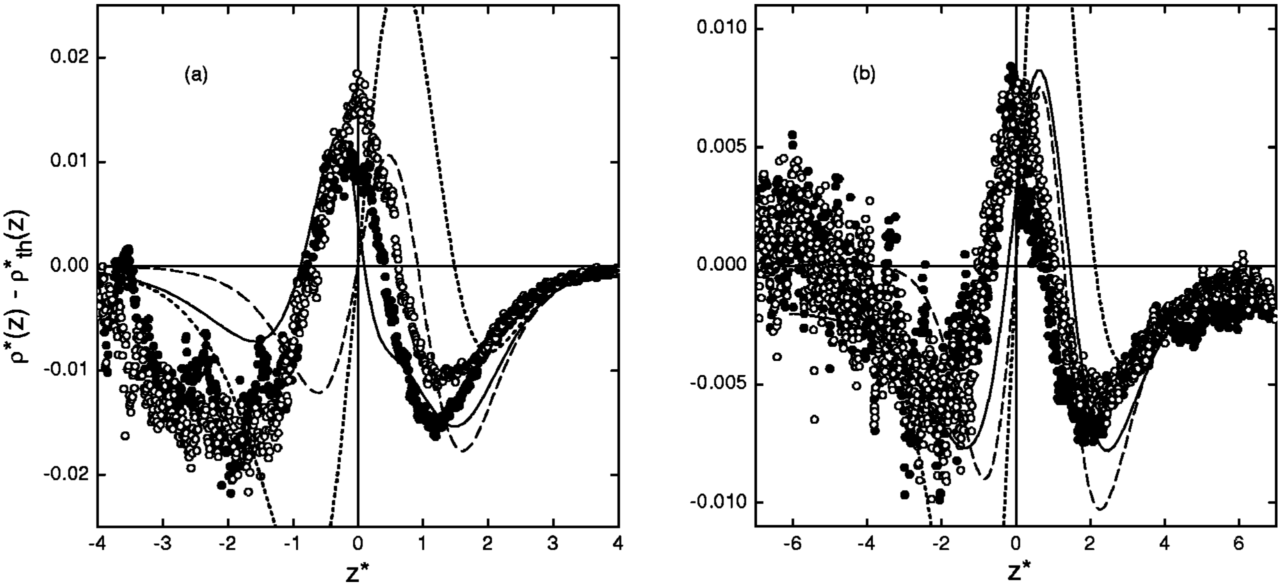

FIG. 12. Deviations of the density profiles calculated by different models from the hyperbolic tangent (69). Dark and light dots shows the results of calculation for two interface of a molecular-dynamic model; dotted line, calculation by Eq. (10) when the influence parameter is determined from data on the surface tension; dashed line, the same when κ is determined from data on the effective interfacial thickness; solid line, calculation by Eq. (65) with the parameters κ, β, ϕ_0 presented in the text; a, $T^*=0.8268$; b, $T^*=0.9975$.

uncertainty range we used a simple polynomial approximation. The surface tension and the interfacial effective thickness calculated in this case by the van der Waals square-gradient theory proved to be considerably overestimated as compared with the results of computer experiment. In the region of the triple point deviations were equal to 30% for the surface tension and $\sim$35% for the effective thickness. As we approach the critical point, the discrepancies decrease, but even at the highest calculated temperature they exceed the error of the computer simulation data. We connect such a discrepancy not with some fundamental drawbacks of the van der Waals theory, i.e., Eq. (3), but with formula (4) for the influence parameter.

In the original van der Waals theory [1] the influence parameter κ is density independent. In this case it is quite easy to obtain its value from Eqs. (12) or (36) by the results of molecular-dynamic calculations of γ and L_{10}^{90} [on condition that the type of the function $f_0(\rho,T)$ is determined]. This approach gives compatible results on κ at $T^*>1.0$. Such a goodness of fit is not observed in the region of the triple point. The significant point of the van der Waals theory with a parameter κ depending only on temperature is the fact that at high temperatures it reproduces qualitatively and quantitatively correctly the subtle structure of the density profile revealed in computer experiment.

Taking into account the terms of the second order of infinitesimality in the expansion of the Helmholtz free energy density (2) with density-independent influence parameters does not make it possible to improve the description of properties of a flat interface. With allowance for the terms of the third order of infinitesimality there appear a large number of unrestricted variables, and the problem of describing properties of a flat interface in the framework of an extended van der Waals theory has no longer an unambiguous solution. We have found such a solution in the framework of a model representation of the Helmholtz free energy of an inhomogeneous fluid (64), which contains only different powers of $(\nabla\rho)$. It has been assumed that the influence parameter κ at $(\nabla\rho)^2$ is a temperature function, whereas the ratios of influence parameters at $(\nabla\rho)^4$ and $(\nabla\rho)^6$ to κ do not depend on thermodynamic state variables.

In this case agreement has been achieved between the van der Waals theory and the results of computer experiment for all the properties of a flat interface and in the whole temperature range from the triple to the critical point.

We have seen (Sec. I) that the van der Waals theory can be substantiated only on condition that certain limitations are imposed on fluctuations. A simple, but natural means of discussing fluctuations at an interface consists in the assumption [45] that there is a spectrum of capillary waves superposed on the internal (without fluctuations) density profile. Capillary-wave fluctuations lead to a transverse radius of correlation and an interfacial thickness diverging in the limit of a vanishing gravity field [45]. As among the fluctuations that are fully suppressed in a mean-field approximation there prove to be capillary waves too, the question arises about the allowance for the fluctuation component in the van der Waals theory. Here there are different viewpoints [46–48]. According to Evans [48], capillary-wave fluctuations are contained in the van der Waals theory, thus, the density profiles and the surface tension obtained in the framework of this theory do not require introduction of capillary-wave corrections for fluctuations of an interface. Attempts to distinguish the capillary-wave contribution for L_{10}^{90} and γ in molecular-dynamic experiments [49] have not given an unambiguous result as yet.

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