The Energy Characteristics of the Surface of Small Clusters

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Received March 9, 2000

Abstract—The Tolman length \( \delta \) and a similar \( \delta_p \) parameter for the first-order term of the expansion of the cluster surface energy in powers of reciprocal cluster radius were found in the framework of the thermodynamic model of small clusters by calculating their critical size. For simple liquids, both parameters were expressed in terms of the interparticle interaction potential and the number of nearest neighbors. The \( \delta \) values for several substances are reported. The size dependence of the internal energy of argon-like clusters was determined by the method of molecular dynamics. The \( \delta_p \) value obtained by analyzing this dependence was in satisfactory agreement with the estimate obtained for the thermodynamic model. The Tolman length of an argon-like system was found to be \(-0.42 \pm 0.1\) in units of the radius of the molecular cell in the liquid.

INTRODUCTION

The determination of the surface tension of curved surfaces is a traditional problem of thermodynamics and statistical physics \([1, 2]\). One of the most important applications of such studies is to the kinetics of first-order phase transitions \([3–5]\). The rate of the formation of new phase nuclei (clusters for spontaneous bulk condensation, or nucleation, and bubbles for cavitation) is a very sharp function of surface tension, whereas the nuclei themselves are small. Quite a number of qualitative features of nucleation and cavitation therefore cannot be explained without taking into account corrections for the size of nuclei.

As far back as 1949, Tolman used thermodynamic considerations to show that the surface tension of a curved interface \( \tilde{\sigma}(R) \) depended on the radius of curvature \( R \) as \([6]\)

\[
\tilde{\sigma}(R) = \sigma \frac{R}{R + 2 \delta} \equiv \sigma \left( 1 - \frac{2 \delta}{R} \right),
\]

where \( \sigma = \tilde{\sigma}(\infty) \) is the surface tension of a plane boundary and \( \delta \) is the parameter called Tolman length. The \( \delta \) value cannot be determined within the framework of thermodynamics. However, it should clearly be of the order of the thickness of the interphase boundary; that is, of the order of several intermolecular distances.

In spite of a large number of works concerned with curved interphase boundaries, there is no generally accepted view on the problem of their description, largely because systems containing curved boundaries are either finite-size systems or systems in the state of unstable equilibrium (as is known, the formation and decay of such metastable states is the usual mechanism of first-order phase transitions \([1]\)). Generally, thermodynamics is inapplicable to both finite-size systems and nonequilibrium states. For this reason, attempts at thermodynamically describing curved surfaces always contain internal inconsistencies. In essence, precisely these inconsistencies have long (for more than half a century) been the subject of controversy. In particular, the correctness of (1) is questioned. Indeed, the size-dependent surface tension \( \tilde{\sigma}(R) \) in it depends on the position of the imaginary surface that separates phases \([2]\). It follows that \( \tilde{\sigma}(R) \) in (1) is not a physically observable quantity. The approach taken in \([6]\) also contains other inconsistencies. For instance, it is assumed that, far from the interface, the densities and the other thermodynamic characteristics of the phases equal their values in continuous media. This assumption cannot be correct for one of the phases if the radius of curvature is finite, and it is unclear in what region the exact equality \( \tilde{\sigma}(R) = \tilde{\sigma}(\infty)R/(R + 2 \delta) \) is applicable at small \( R \). Indeed, there are indications that this equality is invalid at least when the expansion of \( \tilde{\sigma}(R) \equiv \sigma(1 - 2 \delta/R) \) cannot be truncated at the first-order term in \( 1/R \) \([2]\).

In an alternative approach, only the surface with an infinite radius of curvature \( R \) is considered and the asymptotic behavior of thermodynamic values is studied. In their expansions in powers of \( 1/R \), only those terms are retained that correspond to physically observable quantities \([2]\). This approach also has its weak points, but certain inconsistencies inherent in Tolman’s theory are removed. In particular, if only the first term is retained in the expansion of \( \tilde{\sigma}(R) \) in powers of \( 1/R \), the \( \tilde{\sigma}(R) \) value becomes independent of the selection of the separating surface and is therefore an observable quantity. This approach is used in the present work.

Considering the aforesaid, no wonder that, even for the simplest argon-like system, \( \delta \) values obtained by different methods not only substantially differ in magnitude but also have different signs, in particular, because expressions for calculating \( \delta \) usually have the form of the difference of two values, both of which are
much larger than δ. The δ values are usually obtained based on some a priori assumptions or with the use of the apparatus of statistical physics; often, density functional methods are used. Various analytic methods were also applied to calculate the Tolman length for several systems [7–13]. Microscopic equations for δ were used to determine it in molecular dynamics numerical experiments [2, 14, 15].

Attempts at determining δ in real experiments were made in [16–19]. The data of these work are, however, insufficient to unambiguously determine the magnitude and sign of δ. Indeed, at fairly small \( R \), the influence of surface curvature on \( \delta(R) \) is sufficiently large to be recorded in experiments, Eq. (1), which is used to analyze data, is inapplicable. At large \( R \), at which (1) is an acceptable approximation, the curvature effect is weak and cannot be identified against the background of the errors of measurements.

A thermodynamic model of arbitrary small-sized clusters that allows their thermodynamic functions to be estimated was constructed in [20–22]. This model does not include the surface tension concept, which, as mentioned, is meaningless for small clusters. Nevertheless, the relation between the expansions of the thermodynamic functions of clusters in powers of \( 1/R \) in this model and in classical thermodynamics is of interest. Through studying this relation, we can, for instance, determine Tolman length δ and a similar \( \delta_E \) value present in the expansion of the internal energy of a cluster. In this work, this is done by comparing the sizes of clusters that are in unstable equilibrium with supersaturated vapor (that is, by comparing the critical sizes of clusters). Further, the method of molecular dynamics is used to determine the dependence of the internal energy of an argon-like cluster on its size in the region where this dependence is appreciable. Treating this dependence in terms of the thermodynamic model of small clusters yields the \( \delta_E \) value. A comparison of the \( \delta_E \) value obtained in this way with its theoretical value [20–22] allows the reliability of theoretical predictions to be checked.

THE CRITICAL SIZE OF CLUSTERS
IN CLASSICAL THERMODYNAMICS

Here, the equation for the critical size will be derived based on classical thermodynamics. Consider a one-component two-phase system formed by a large cluster (drop) that exists in unstable equilibrium with ideal supersaturated vapor. We call this cluster a critical one. The origin will be placed at the center of mass of the cluster surrounded by an imaginary sphere of a large radius (\( \bar{R} \)). In thermodynamics, the notion of equimolar radius \( R_e \equiv \bar{R} \) is introduced; \( R_e \) equals the radius of the cluster, whose density profile has the form of a step function. By definition [1, 2], \( R_e \) satisfies the equation

\[
\frac{4\pi}{3} R^3_{\nu} n_{\nu} + \frac{4\pi}{3} (\bar{R}^3 - R_{\nu}^3) n_{\nu} = G(\bar{R}),
\]

where \( n_{\nu} \) and \( n_{\nu} \) are the densities of the continuous liquid and gas phases, respectively, and \( G(\bar{R}) \) is the total number of molecules within the sphere of radius \( \bar{R} \). The equimolar radius of the cluster will be introduced in the form \( g_c = (R_s/r_l)^3 \), where \( r_l = (3/4\pi n_l)^{1/3} \). Equation (2) can then be rewritten as

\[
g_c = \left(1 - \frac{n_{\nu}}{n_l}\right)^{-1} \left[G(\bar{R}) - \frac{4\pi}{3} n_l \bar{R}^3\right].
\]

The \( g_c \) value equals the number of molecules that we assume to constitute the condensed phase; it is taken that \( R_c, \bar{R} - R_c \to \infty \); that is, deep inside the cluster, the density of the condensed phase is attained, and, far from the cluster, the density equals that of the vapor phase.

By definition [2], surface tension \( \tilde{\sigma} \) is determined by the surface part of the grand canonical potential \( \Omega_s = \Omega - (4\pi/3)R^3 \omega_0 - (4\pi/3)(\bar{R}^3 - R^3) \omega_0 \), where \( \Omega \) is the total potential of the system; \( \omega_0 \) and \( \omega_0 \) are the potentials of unit volumes of the condensed and gas phases, respectively; and \( R \) is the conventional interphase boundary

\[
\tilde{\sigma} = (\tilde{\delta} \Omega / \tilde{\delta} A)_{R, \nu, \mu} = \Omega_s / A.
\]

Here, \( A = 4\pi R^2 \) is the area of the interphase boundary, \( T \) is the temperature, \( V \) is the volume, and \( \mu \) is the chemical potential.

The \( \tilde{\sigma} \) value depends on \( R \) [2]

\[
\frac{\tilde{\sigma}[R]}{\tilde{\sigma}[R_c]} = 1 + \left(\frac{R - R_c}{R_c}\right)^2 R_c + 2 R / 3 R_c,
\]

where square brackets denote the dependence on the position of the conventional interphase boundary, and \( R_c \) corresponds to the surface of tension at which the \( p_l - p_{\nu} = 2 \tilde{\sigma}[R_c]/R_c \) Laplace equation is satisfied exactly (\( p_l \) and \( p_{\nu} \) are the pressures inside and outside the cluster far from its surface).

Let us define the dimensionless Tolman length as

\[
\delta = (R_e - R_c)/r_l
\]

(usual the definition is \( \delta = R_c - R_e \)). It follows from (5) that, at large \( R \), \( \tilde{\delta} \) is independent of \( R \) accurate to terms first-order in the \( \delta r_l/R \) parameter; therefore, \( \tilde{\delta} \) is an observable physical quantity. The asymptotic equation for the size dependence of \( \tilde{\delta} \) has the form

\[
\tilde{\delta}(R_e) = \tilde{\delta}(R_c) = \tilde{\sigma}(\infty)(1 - 2 \delta r_l/R_c) = \sigma(1 - 2 \delta/r_c),
\]
where \( \rho_e = g_e^{1/3} \).

On the equimolecular surface, we can introduce the specific surface energy [1]

\[
\sigma_E = \frac{E_i}{A} = \tilde{\sigma} - T \frac{\partial \tilde{\sigma}}{\partial T},
\]

(8)

where \( E_i = E - (4\pi/3)R_3^3 - (4\pi/3)(R^3 - R^3) \), is the surface part of the total internal energy \( E \) and \( e_i \) and \( e_r \) are the internal energies of unit volumes of the condensed and gas phases, respectively. Substituting (7) into (8) yields

\[
\tilde{\sigma}(g) = \sigma_E (1 - 2\delta_E/\rho_e),
\]

(9)

where

\[
\delta_E = \delta \left(1 - \frac{\sigma}{\sigma_E} T \frac{\partial \log \delta}{\partial T}\right)
\]

(10)

is an analogue of the Tolman length for internal energy, \( \sigma_e = \tilde{\sigma}_E (\infty) \).

The critical cluster radius \( R_c \) is given by the Kelvin equation

\[
R_c = \frac{2\tilde{\sigma}[R_c]}{n_kT\log S} = \frac{p_v}{p_w(T)},
\]

(11)

where \( k \) is the Boltzmann constant, \( S \) is the degree of vapor supersaturation, and \( p_w(T) \) is the saturation pressure over a plane surface. Substituting (6) and (7) into (11) yields the critical size \( g_{cr} \) in the first order with respect to \( g_{\ast}^{1/3} \),

\[
g_{cr} = (R_c/r_1)^3 \equiv g_{\ast} (1 - 3\delta_{g_{\ast}}^{-1/3}),
\]

(12)

\[
g_{\ast}^{1/3} = \frac{8\pi}{3} \frac{\sigma r_1^2}{kT\log S}.
\]

Here, \( g_{\ast} \) is the critical size calculated without taking into account the size dependence of surface tension; this parameter is introduced in the classical theory of nucleation [3–5] and assumed to be large, \( g_{\ast} \gg 1 \).

THE CRITICAL CLUSTER SIZE IN THE GENERALIZED MODEL OF VIRTUAL CHAINS

In the model described in [20–22], a cluster is treated as a nucleus comprising \( g_{\ast}g_0 \) molecules surrounded by a layer of \( g_0 \) surface molecules. The model is based on the virtual chain approximation [22], according to which clusters are fractal-like chains of bound chains of atoms. Similar structures formed in aerosols were studied in [23].

The gas phase is assumed to be an ideal mixture of clusters of various sizes \( g_e \) present in the equilibrium concentrations

\[
n(g_e) = n(1) \exp[-\Delta \Phi(g_e)],
\]

(13)

\[
\Delta \Phi(g_e) = \frac{4\pi\tilde{\sigma}(g_e) r_1^2}{kT} - (g_e - 1) \ln S,
\]

where \( n(1) \) is the concentration of monomers, and the function

\[
\tilde{\sigma}(g_e) = \frac{\sigma}{3g_{e}^{2/3}} [g_{0}(g_{0} - 1)],
\]

(14)

called “effective surface tension,” is introduced for convenience. The number of surface molecules \( (g_0) \) in (14) is given by the equation

\[
g_0 = \frac{3\omega(g_e - g_0)^{2/3} + 3\omega \lambda (g_e - g_0)^{1/3} + \omega \lambda^2}{(z/\omega - 3/4)^{1/2} - 3/2},
\]

(15)

where the \( \omega \) and \( \lambda \) parameters are defined as

\[
\omega = \frac{4\pi}{3} \frac{\sigma r_1^2}{kT \log (K_{0}(n_\infty))}, \quad \lambda = (z/\omega - 3/4)^{1/2} - 3/2,
\]

(16)

\( K_{0}(T) \equiv n^2(1)/n(2) \) is the equilibrium constant of the dimer, \( n_\infty \) is the concentration of monomers in saturated vapor over a plane surface, \( z \) is the number of nearest neighbors in the liquid phase, \( \omega \) is the density ratio between the surface layer and the nucleus of the cluster, and \( \lambda r_{1} \) is the thickness of the surface layer. If intermolecular interaction potential \( u(r) \) is pair and additive,

\[
K_{2}(T) = 2\pi \int_0^{r_{0}} r^2 \exp \left[ -\frac{u(r)}{kT} \right] dr.
\]

(17)

Here, \( r_{0} \) is the criterion of the bound state (see below); in (17), it is the distance at which two molecules are still considered a dimer.

The critical cluster size is determined by the equality of the fluxes of molecules undergoing condensation on the surface of the cluster and vaporizing from it, \( [d\Delta \Phi(g_e)/dg_e]_{g_e = g_{cr}} = 0 \) [20, 21]. Let us calculate this derivative taking into account (13) and (15). Solving the resulting equation with respect to \( g_{cr} \) yields

\[
g_{cr} = g_e + 3\omega g_e^{2/3} + 3\omega \lambda g_e^{1/3} + \omega \lambda^2,
\]

(18)

\[
g_e = \lambda^3 \left[ (1 + 2\lambda/(g_{\ast}^{1/3} - 2\omega))^{1/2} - 1 \right]^{-3}.
\]

We are interested in the asymptotic behavior of \( g_{cr} \) at a large cluster size. Expanding (18) in powers of \( g_{\ast}^{-1/3} \) yields

\[
g_{cr} = g_{\ast} \left[ 1 - 3\delta_{g_{\ast}}^{-1/3} + \left[ 4(\delta_{g_{\ast}})^3 - \frac{5}{4} \delta_{g_{\ast}} \lambda \right] g_{\ast}^{-1} - \frac{3}{16} \lambda^4 g_{\ast}^{-4/3} \right],
\]

(19)

\[\delta' = \omega - \lambda/2.\]
A comparison of (19) and (12) shows that the Tolman length
\[
\delta = \delta' = \omega - \lambda/2 \quad (20)
\]
coincides with the coefficient of the first term in the expansion of effective surface tension (14) in powers of \( \rho^{-1} \) in [20, 21].

Equation (20) solves the problem formulated above. It expresses the Tolman length in terms of macroscopic and microscopic values known for many substances. Some \( \delta \) values are listed in Table 1. The data on water and mercury are taken from [21], those on cesium, from [20, 24], and on argon, from [25]; the \( \omega \) value for argon was calculated using \( \sigma \) from [26]. For comparison, the table contains the data on an argon-like system with a 12-6 Lennard-Jones interparticle interaction potential (see below). According to Table 1, \(|\delta| < 1\); \( \delta \) can take on both positive and negative values. In conformity with the asymptotic definition of the surface tension of a curved surface used in this work, negative (positive) Tolman length values mean that the surface tension of a cluster increases (decreases) as the size of the cluster becomes smaller.

Note that expansion (19) does not contain terms second-order in \( g_*^{1/3} \), and the coefficient of the third-order term is not too large. This means that the first approximation \( g_{cl} \approx g_* (1 - 3\delta g_*^{-1/3}) \) gives a fairly high accuracy (on the order of several percent) even for comparatively small clusters (\( g_{cl} \geq 100 \)). It follows that the knowledge of the Tolman length is sufficient for estimating the size of nuclei in the theory of nucleation. For cavitation, the first approximation provides even a higher accuracy. The expansion of the potential barrier of the critical cluster has to surmount in powers of \( g_*^{1/3} \), however, contains a second-order term,
\[
\Delta \Phi(g_*) \approx \Phi_\ast \left[ 1 - 6\delta g_*^{-1/3} + \left( \frac{5}{4}\lambda^2 - 12\delta^2 - \frac{2}{2\delta + \lambda} \right) g_*^{-2/3} + \left( \frac{5}{2}\delta \lambda^2 - 8\delta^3 + 2 \right) g_*^{-1} \right]. \quad (21)
\]
Here, \( \Phi_\ast = g_\ast \ln \sqrt{5} \) is the barrier height in the classical theory of nucleation, which is of the order of 40–60 under typical nucleation conditions. As the rate of nucleation is proportional to \( \exp[-\Delta \Phi(g_\ast)] \), the first approximation with respect to \( g_*^{1/3} \) is certainly insufficient for calculating it or the rate of cavitation even if \( g_\ast = 1000 \).

Expansions (19) and (21) show that the thermodynamic functions of a curved surface cannot be represented by expansions in powers of \( \delta(\rho_\ast) \) or \( \delta(\rho_\ast) \), where \( \rho_\ast = R_s/\rho_\ast = \rho - \delta \), because, starting with the second-order term, the coefficients of the expansion also depend on \( \lambda \). This follows from the expansion of effective surface tension (14) in powers of \( 1/\rho_\ast \),
\[
\frac{\widetilde{\sigma}(\rho_\ast)}{\sigma} \equiv 1 - \frac{2\delta}{\rho_\ast} + \frac{6\delta - 3\omega^2 + 2V_e^2}{\rho_\ast^2}. \quad (22)
\]
As distinguished from the Tolman theory [6], in which \( \widetilde{\sigma}(\rho_\ast)/\sigma = \rho_s/(\rho_\ast + 2\delta) \equiv 1 - 2\delta/\rho_\ast + 4\delta^2/\rho_\ast^2 \), the second-order term in (22) depends on both \( \delta \) and \( \omega \).

The expansion of (14) in powers of \( 1/\rho_\ast \),
\[
\frac{\widetilde{\sigma}(\rho_\ast)}{\sigma} \equiv 1 - \frac{2\delta}{\rho_\ast} + \frac{3\omega (2\omega - \omega)}{\rho_\ast^2}. \quad (23)
\]
allows the range of the applicability of approximation (1) to describing all thermodynamic characteristics of a cluster to be determined (this range is narrower than with the critical size). On the assumption that the required accuracy is attained if the third term on the right-hand side of (23) is ten times smaller than the second, we obtain \( \rho_\ast \approx 15\omega [2 - \omega/\delta] \). For an argon-like Lennard-Jones system (Table 1) this gives \( g_\ast \approx 10^9 \).

Next, consider the internal energy of the cluster. It is shown in [22] that the mean potential energy \( U(g_* \rangle \), which differs from the internal energy by an insignificant constant of a constant-temperature ensemble, is written exactly like the Gibbs energy,
\[
\begin{aligned}
U(g_\ast) &= 4\pi \sigma g_\ast \int_0^{g_\ast} \int_0^{g_\ast} \left[ \sigma_\ast - g_\ast \right] d\gamma, \\
\sigma_\ast &= \frac{3\omega g_\ast^{2/3} [g_0 - (g_\ast - 1)]},
\end{aligned} \quad (24)
\]
where \( \sigma \) is the mean potential energy of a molecule in a continuous liquid, and the number of surface molecules \( (g_0) \) and the \( \omega_\ast \) parameter are given by
\[
\begin{aligned}
g_0 &= 3\omega_\ast \left( g_\ast - g_0 \right)^{\gamma_\ast} + 3\omega_\ast \lambda_\ast (g_\ast - g_0)^{\gamma_\ast} + \omega_2 \lambda_2, \\
\omega_\ast &= \frac{4\pi}{3} \frac{\sigma_\ast \sigma_\ast^{3/2}}{U(2)-\bar{u}},
\end{aligned} \quad (25)
\]
Here, $\lambda_{E} = (z/\omega_e - 3/4)^{1/2} - 3/2$. For systems with pairwise additive interparticle interactions, the mean potential energy of a dimer is

$$U(2) = \int_{r_0}^{r_b} \left[ u(r) r^2 \exp \left(-\frac{u(r)}{T} \right) \right] dr.$$  \hspace{1cm} (26)

The $g_{0c}$ and $g_{0e}$, $\omega_e$ and $\omega$, and $\lambda$ and $\lambda_{E}$ values have the same physical meaning. They, however, do not coincide because the separation of cluster molecules into internal and surface [20, 21] is conventional and determined by the thermodynamic function under consideration, although they are, as a rule, close to each other.

Assuming that $|e_c| \ll |e|$ for a short-range potential and, therefore,

$$E(g_c) \equiv U(g_c) + (3/2)kTg_e$$  \hspace{1cm} (27)

and using (9), (24), and (25), we obtain

$$\delta_E = \omega_E - \frac{\lambda_{E}}{2} = \delta \left[ 1 - \frac{\sigma}{\sigma_E} T d\ln(\omega - \lambda/2)/dT \right]$$  \hspace{1cm} (28)

for $g \rightarrow \infty$. The $U(g_c)$ value is reliably determined in numerical simulations, which allows $\delta_E$ to be found.

NUMERICAL SIMULATION

The potential energy of clusters in a wide range of their sizes was determined numerically by molecular dynamics simulation of a $(P, T)$ ensemble. The procedure, similar to that used in [22, 27], was as follows. The argon-like system to be modeled was a cluster placed in vapor with fixed concentration and kinetic energy mean values. The system was open; that is, at the boundary of the cell, particles that reached this boundary from the inside were removed, and vapor particles penetrating into the cell were generated. In the absence of a cluster, a Maxwell particle velocity distribution corresponding to given pressure and temperature values was established. In the center of the cell, a cluster was initiated, and the values of interest were recorded during its evolution.

To compare the results of this study with the most recent Tolman length determinations by the method of molecular dynamics, we used the same interparticle interaction potential as in [14],

$$u(r) = \begin{cases} \frac{\nu(r) - \nu(r_0)}{r}, & r \leq r_c \\ 0, & r > r_c, \end{cases}$$  \hspace{1cm} (29)

$$\nu(r) = 4\varepsilon \left( \frac{a_{12}^2}{r^{12}} - \frac{a_{6}^6}{r^6} \right).$$

Here, the cutoff radius is $r_c = 2.5a$, and $\varepsilon$ and $a$ are the depth and the characteristic size of the potential, respectively. Potential (29) is most often employed in studies of argon-like systems, which allowed us to use the literature data on the surface tension of this system. The temperature was set at $0.75\varepsilon/k$ (the same temperature was used in [14]), the cell radius was $R = 16a$, and the concentration of vapor was varied in the range $n_v = (0.008–0.016)\rho^3$.

Under the specified conditions, the critical cluster size was $\approx 10^4$. In simulation experiments, the initial cluster size was 1000; during the evolution, the cluster was completely vaporized. Estimated vapor concentration effects on the potential energy showed that weak effects were only observed for clusters comprising less than 20 particles, probably because of the strongly nonequilibrium character of such clusters. In addition, at very high vapor concentrations, its nonideality manifested itself, and, at very low concentrations, the procedure for thermal cluster stabilization showed poor performance (these effects were discussed in detail in [22, 27]). During simulations, each realization was repeated many times; values of interest were recorded at time intervals of $\tau_0/2$, where $\tau_0 = (a/M/24\varepsilon)^{1/2}$ is the characteristic molecular dynamics time and $M$ is the particle mass.

The surface tension or surface energy can only be determined if we know the position of the equimolar surface (equimolar cluster size). The properties of small clusters cannot, however, be described by continuous phase characteristics such as density. In addition, it follows from definition (3) that, for the $(P, T)$ ensemble under consideration, a change in the number of vapor particles in the cell, which changes $G(\vec{R})$, also changes $g_e$. It follows that the “instantaneous” equimolar radius $R_e$ and size $g_e$ notions are meaningless, and (3) should be understood in the sense of averaging over the ensemble of realizations. But the averaged $g_e$ value cannot be used to describe the dynamics of processes occurring in the system.

The question arises whether we can find such a cluster size definition that would be applicable to small clusters while transforming into $g_e$ in the limit of large clusters. A definition, in particular, applicable to clusters that cannot be approximated by a drop was suggested in [28]; a particle was considered a cluster particle if there existed at least one more cluster particle at a distance not exceeding $r_b$ from the first one. This criterion was augmented by the condition of interparticle interaction potential cutoff at distance $r_b$. In this way, a certain number of cluster particles $(g)$, obviously independent of the number of vapor particles, was put in correspondence to each instantaneous configuration of particles. It was shown in [29] that, if $r_b \sim 2a$, $g$ changes insignificantly under small $r_b$ variations. The definition suggested in [28] was used in works of various authors, in particular, in [22, 27].

The $r_b$ parameter in this definition is determined by the potential cutoff radius, which makes this criterion
is inapplicable to potentials that vanish. We will determine \( r_b \) differently; its value will be selected such that, for \( g \to \infty \), the equality

\[ g_e = g(r_b) \quad (30) \]

is satisfied. The \( g(r_b) \) dependence was studied in numerical simulation experiments conducted as described above. In these experiments, \( g \) and "instantaneous" equimolar size (3) were simultaneously determined at a fixed \( r_b \); for each \( g \), \( g_e \) was found by averaging over the ensemble of realizations. The \( r_b \) value was varied in series of numerical experiments. The simulation results obtained with potential (29) are summarized in Figs. 1–3. Figure 1 shows that, at a sufficiently large \( g \) value \( (g \approx 200) \), the dependences of \( g/g_e \) on \( r_b \) take on the value 1 at \( r_b \approx 1.7a \). These are also inflection points at which the tangents to the corresponding curves are virtually parallel to the abscissa axis. For this reason, equality (30) is satisfied with accuracy of about 1% for the \( r_b \) values in the range 1.5–1.9, and the equimolar size is virtually indistinguishable from the size according to Stillinger [28]. For smaller clusters, the dependence on \( r_b \) becomes noticeable, but even for them, \( g/g_e \to 1 \) in the \( r_b \) range specified above.

In the same series of experiments, the radial distribution function \( f(r) = \frac{4\pi a^2}{N} \left( \frac{dN}{dr} \right) \) for particles in the center of a large cluster was determined; here, \( N \) is the number of particles at a distance not exceeding \( r \) from the center of mass (Fig. 2). The first \( f(r) \) minimum is observed at \( r_{\text{min}} = 1.6a \), which approximately corresponds to the middle of the distance between the first (at \( r = 2^{10/6}a \)) and second (at \( r = 2^{7/6}a \)) \( f(r) \) maxima. The radial distribution function in the center of the cluster is close to that in a continuous liquid starting with \( g > 100 \). Note that \( r_{\text{min}} \) is close to the \( r_b \) value obtained above. This result can be explained by the nearly equal mean distances between a particle and its nearest neighbors both close to and far from the cluster surface. For a plane interphase boundary, this case was discussed in [30].

In this work, we used the \( r_b = 1.65a \) criterion, for which the \( g_e(g) \) dependence was determined in simulation experiments (Fig. 3). The difference between \( g_e \) and \( g \) decreases as \( g \) increases [in the range 300 \( \leq g \leq 1000 \)], the mean relative deviation is very small, \( \langle g - g_e \rangle/g = -1.7 \times 10^{-5} \). At small \( g \), the difference between \( g_e \) and \( g \) is noticeable, probably because the equimolar size notion then becomes meaningless and because small clusters exist in a state which is farther from equilibrium than that of large clusters.

It follows that there is such a range of \( r_b \) parameter values at which the equimolar size of a cluster comprising several hundred atoms coincides with the Stillinger radius. The definition of \( g \) then satisfies asymptotic condition (30) formulated above and can be used to determine the mean potential energy of clusters. According to (27), the energy of a unit surface area is [22]

\[ \tilde{U}_e(g) = \frac{1}{(36\pi)^{1/3}} \left( \frac{n_1}{g} \right)^{2/3} [U(g) - (g - 1)\bar{u}]. \quad (31) \]

The \( U(g) \) values were determined in numerical simulation experiments by many times repeating cluster
vaporization and averaging over the ensemble of realizations for each $g$ value.

RESULTS AND DISCUSSION

The procedure was repeated until the values determined by data processing (see below) ceased to vary by more than 1% when the number of realizations was doubled (it was found that the assumption $|e_i| \ll |e_j|$ did not introduce a noticeable additional error). At the parameter values specified above and $n_r = 0.009$, 40 realizations were necessary in which the total cluster evolution time was of the order of $10^3 \tau_0$. Simultaneously, the $\bar{n} = 4.737\varepsilon$ and $n_r = 0.76$ values were found. These values were used to calculate the energy of unit surface areas (open circles in Fig. 4). Further, this energy was estimated by (24)–(26), and a numerical procedure was used for selecting such $\sigma_k$ and $z$ values at which the sum of the squares of the differences between the $\tilde{\sigma}_k(g)$ values calculated by (24)–(26) and obtained in numerical experiments was minimum. The calculation results are summarized in Table 2 and shown in Fig. 4.

It has been mentioned above that attempts at determining $\delta$ in experiments encounter serious difficulties. This, in full measure, also refers to numerical experiments under consideration. Indeed, according to Table 2, $\delta_k < 0$; that is, $\sigma_k(g)$ has a maximum (at $g \approx 10^{-10}$).

At the maximum, $\tilde{\sigma}_k(g)$ exceeds $\sigma_k$ by only several percent, which prevents $\delta_k$ from being determined with high accuracy in the region of very large $g$ values. At small $g$, the effect of surface curvature is substantial, but there are systematic discrepancies between calculations by (24)–(26) and numerical data in the range of $g$ values $6 \leq g \leq 30$, which also decreases the accuracy of determining $\delta_k$. These discrepancies arise because of the model assumption that, at $g \leq z$, clusters have a minimum number of bonds $1$, whereas, at $g > z$, this number increases in a jump, which leads to Eq. (24). In reality, the state of small clusters is a superposition of states with different numbers of bonds, and the fraction of states with a large number of bonds smoothly increases as $g$ grows [22]. Accordingly, $U(z) < (z - 1)/2$, and $U(2)$ can be considered the third model parameter rather than calculated by (26).

If the effects described above played the key role in determining $\delta_k$, the parameters found for different intervals of $g$ variations and at different $U(2)$ values would certainly be different. Table 2, however, shows that there is no such difference. In different $g$ intervals and when $U(2)$ is varied more than one and a half times, $\delta_k$ has the same sign and changes less than two times. Note that the curves constructed for parameter values taken from different rows of Table 2 virtually coincide. It follows that (24) fairly accurately describes the size dependence of the energy of clusters. According to Table 2, $\tilde{\sigma}_k = 1.913a^2/\varepsilon$, $z = 12.34$, and $\delta_k = -0.17 \pm 0.07$. Note that the mean number of particles within a sphere of radius $r_{min}$ equal to the distance to the first radial distribution function minimum (the number of nearest neighbors) equals 12.4 according to the simulation data, which is very close to the $z$ value cited above.

Compare the numerical calculation results with the estimates based on the thermodynamic model of small clusters [20–22]. The data on $\sigma$, $n_{law}$, and their temperature dependences will be borrowed from [14] (they insignificantly differ from those of the other modern investigations). We find $\omega = 0.773$ from (16) and (17). For $\sigma_k = 1.913a^2/\varepsilon$, Eqs. (16), (20), and (28) yield $\delta = -0.390$, $\delta_k = -0.106$, $(\varepsilon/k)\delta_e/dT = -1.51$ at $z = 11.90$ and $\delta = -0.447$, $\delta_k = -0.159$, $(\varepsilon/k)\delta_e/dT = -1.53$ at $z = 12.59$. Note that the $\delta_k$ values obtained in numerical experiments and estimated analytically satisfactorily agree with each other for the minimum and maximum $z$ values at $U(2) = 0.586\varepsilon$ (Table 2). This leads us to conclude that $\delta = -0.42 \pm 0.1$ for the argon-like system under consideration, although the systematic error may exceed 0.1.

It is well known that such properties of argon-like systems as surface tension and saturation pressure are very sensitive to the cutoff parameter ($r_c$) of the interparticle interaction potential (e.g., see [31]). The thermodynamic properties of the system with $r_c = 2.5a$ used in this work are far from the properties of real argon. The $\delta(r_c)$ dependence is an interesting object of study, but the closeness of $\delta$ for the Lennard-Jones system and
argon (Table 1) implies that this dependence can hardly be strong.

Compare the results of this work with the literature data. In [14, 15], the method of molecular dynamics was used. In [14], a fairly rough estimate, $\delta = -0.42 \pm 1.3$ at $T = 0.9e/k$, was obtained. This estimate does not determine the sign of $\delta$ [here and throughout, the literature data are recalculated to dimensionless parameters according to definition (6)]. In this work, the number of particles in clusters was varied from 2299 to 12138. This is much smaller that the above estimate ($10^5$) of the number of particles at which approximation (1), which was used in analyzing the results obtained in [14], is applicable. This explains the large uncertainty value in [14]. In [15], a plane layer of a liquid was studied. The $\delta$ value obtained in [15] differs in magnitude and sign from our estimate: $\delta = 0.24 \pm 0.06$ at $T = 0.75e/k$ ($\delta = 0.28 \pm 0.04$ at $T = 0.9e/k$). Note that the temperature dependence of $\sigma$ obtained in [15] leads to the $\sigma_1 = 1.91$ value, which virtually coincides with our result. Work [15] does not contain estimates for a minimum liquid layer thickness, which is necessary for obtaining reliable results. The use of insufficiently thin layers might cause a substantial systematic error.

In [13], the mean field theory was used to develop a theory that allowed the Tolman length to be calculated. For a potential somewhat different from (29), the authors obtained $\delta = -0.294$, which is close to the value reported in this work.

In [8–10], a curved surface of an argon-like system was studied by the density functional method, and the potential also somewhat differed from (29). This gave $\delta \cong -0.38$, which coincides with our result in sign and is close to it in magnitude.

Consider some results for other substances. In [11], the van der Waals–Kahn–Hillard theory was used, and a small negative $\delta$ value was obtained for nonane. In

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**Table 2.** Parameters ensuring the best description of the effective surface energy of clusters

<table>
<thead>
<tr>
<th>$g$</th>
<th>$U/(2)\varepsilon$</th>
<th>$\omega_E$</th>
<th>$\sigma_E a^2/\varepsilon$</th>
<th>$-\delta_E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 ... 900</td>
<td>0.586</td>
<td>11.90</td>
<td>0.904</td>
<td>1.936</td>
</tr>
<tr>
<td>100 ... 300</td>
<td>0.586</td>
<td>12.86</td>
<td>0.875</td>
<td>1.873</td>
</tr>
<tr>
<td>300 ... 700</td>
<td>0.586</td>
<td>12.16</td>
<td>0.897</td>
<td>1.921</td>
</tr>
<tr>
<td>500 ... 900</td>
<td>0.586</td>
<td>12.59</td>
<td>0.887</td>
<td>1.898</td>
</tr>
<tr>
<td>200 ... 900</td>
<td>0.402</td>
<td>11.26</td>
<td>0.854</td>
<td>1.910</td>
</tr>
<tr>
<td>200 ... 900</td>
<td>0.587</td>
<td>12.49</td>
<td>0.889</td>
<td>1.903</td>
</tr>
<tr>
<td>200 ... 900</td>
<td>0.670</td>
<td>13.12</td>
<td>0.906</td>
<td>1.900</td>
</tr>
</tbody>
</table>
[12], a theory of the surface layer based on the van der Waals theory was developed. The author obtained \( \delta = -0.62 \) for water, which coincides with our result in sign but exceeds it in magnitude. Note that the data on the rates of nucleation in supersaturated water vapor are satisfactorily described by the classical theory without corrections for the size of clusters (see the references in [21]), which is evidence that \( \delta \) is small in magnitude. Note also that the strict inequality \( \delta < 0 \) was obtained in [12]; this inequality contradicts our data on mercury (Table 1) and the experimental data on an anomalously high rate of nucleation in mercury vapor [32]. These data can qualitatively be explained if \( \delta(R) < \sigma \); that is, if \( \delta > 0 \). If the theory developed in [12] is only valid for some limited class of substances, the scope of its applicability is unclear. The small number of literature data prevents us from answering the question whether mercury is an exception or nonnegative \( \delta \) values are typical of liquid metals.

The energy characteristics of alkali metal drops were studied in [7] by the density functional method. The authors obtained \( \delta = 0.086 \) for cesium at the triple point. This value and that given in Table 1 are indistinguishable from zero within the errors of calculations. The experimental data [33] also indicate that \( \delta \equiv 0 \).

The method for calculating the Tolman length that we used is fairly universal and can be of help in calculations of the rate of cavitation in superheated liquids. As is known, the radius of a critical bubble under usual conditions equals the radius of a drop comprising \( 10^3 - 10^4 \) molecules. For this reason, only the first term of the expansion of \( \sigma \) in powers of \( 1/R \) can be retained for bubbles as distinguished from critical drops in vapor–liquid transitions. As the curvature of the surface of bubbles is negative, Eq. (1) for bubbles becomes

\[
\frac{\Delta \sigma}{R} \equiv \sigma(1 + 2\delta/R).
\]

The use of the exact Tolman equation \( \Delta \sigma(R) = \sigma R/(R - \delta) \) or a similar equation containing the higher terms of the expansion in powers of \( \delta/R \) can then cause a noticeable decrease in the accuracy of calculations.

ACKNOWLEDGMENTS

This work was supported in part by the Russian Foundation for Basic Research, project no. 99-02-16094.

REFERENCES