Thermodynamics and the bottom size limit of its applicability

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Abstract. For the description of the size fluctuations the molecular theory on the basis of the lattice-gas model, which unique gives equal-accuracy results in all range of density, and the finite-difference calculation reflecting a discrete structure of substance are used. The bottom limit of the thermodynamics applicability is defined by a size for which at calculations of the thermodynamic functions both the discreteness of a substance and the contributions from spontaneous fluctuations can be ignored. Estimations of the sizes of the two-dimensional and spherical isolated drops and for their internal areas of phases are constructed, less which thermodynamic approaches cannot be applied. It is received that an influence of intermolecular interactions and movements of molecules in dense phases on size fluctuations is as much as possible shown at average density. It keeps estimations for size fluctuations which are most important for small and large densities. The received estimations are focused on a wide spectrum of the small systems arising at formation of a new phase and in high–dispersed systems

Keywords: thermodynamics, molecular theory, lattice gas model, small systems, discreteness of substance, fluctuations, difference calculus

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1. INTRODUCTION
Thermodynamics is a phenomenological science about the most common thermal properties of macroscopic bodies. Thermodynamics considers phenomena caused by the combined action of a large number of constantly moving molecules or other particles of which the bodies that surround us consist, with no models of their motions. In developing the thermodynamic approach, Gibbs (1902) [1] also proposed a statistical way of studying the properties of macroscopic bodies that from the beginning was based on model atomic–molecular representations. This way of solving the problem traces the atomic–molecular mechanism of a phenomenon from the very beginning. As was shown for the first time by Gibbs in the development of statistical mechanics, reducing the size of a system results in an increase in fluctuations. This fundamentally new factor can be assumed only within molecular theories [2].

The statistical approach provides strict substantiation of the law of thermodynamics, and it enables us to determine the limits of their applicability. The foundation of thermodynamics was built upon postulates stemming from experimental measurements of macroscopic
systems, so there were no strict limitations on its applicability in [1].

The problem of the lower boundary of intrinsic linear size $R_t$ of the region in which the thermodynamic approach is applicable, has been many times in the literature data [3-5], and the numerous attempts to search for small bodies restricted in radius $R_t$ were limited to discussing the applicability of the Kelvin equation to drops and bubbles, and the Gibbs–Ostwald–Freundlich equation for the solubility of small bodies.

The lively discussion of different aspects of studying small bodies that has recently arisen is worthy of note [6]. This interest is due to the level of spatial resolution achieved in experimental instruments over the last 15–20 years. A fairly broad spectrum of small systems that belong to so-called micro-reactors (e.g., microcrystals, micelles, colloidal particles, oligomers, and polymer particles) is now being discussed in the literature, along with modifications of micro-reactor systems when their number grows in proportion to a volume unit (e.g., aerosols, aerogels, and porous and nonporous loose bodies with different structures). Processes of the adsorption of substances from vapor and liquid on the surfaces of ultradisperse particles and diffusion inside them are also of interest to researchers.

The presence of fluctuations is the only criterion for using thermodynamic approaches outside of analyzing their consequences, which are described by the Kelvin and Gibbs–Ostwald–Freundlich equations. The magnitude of the contribution from fluctuations therefore determines the lower boundary for using the common equations of classical thermodynamics. The molecular calculations for drops performed in [6] did not, however, solve the problem of the lower boundary of the applicability of thermodynamics.

For the decision of a question about the bottom limit of the sizes of applicability of thermodynamics by means of the analysis of effects of fluctuations, it is necessary to use such molecular-statistical theory which can possible most full would reflect all scopes of thermodynamics. Let’s remind that thermodynamics methods to the same extent concern to different phase and aggregate states of substances, and also their volume and superficial areas [1, 2]. To these requirements now satisfies the discretely-continual description of spatial distribution of molecules on the basis of so-called the lattice-gas model (LGM) [6-8].

In the LGM, a system is partitioned into unit cells with an average size of components (for simplicity, it is assumed that the molecules are comparable in size). The LGM is the only method of statistical physics that is equally applicable to three aggregate states of matter; its current interpretation yields the most accurate description of molecule distributions, compared to the traditional methods developed separately for gases, fluids, and solids [9]. It equal-accuracy describes all densities of substance from zero density, analogue of the rarefied gases, up to unit density (in molar shares) as analogue of dense phases. It allows the given model to consider from identical positions all three types of interfaces between different aggregate states [10]. It provides a discrete description of the spatial distribution of components and a continual description of the particle distribution inside a cell.

For the first time estimations for the bottom limit of applicability of thermodynamics have been received from the analysis of size fluctuations on a surface of liquid drops in vapor with model in work [11] when intermolecular interactions are absent. In this work, we describe the size fluctuations on the interfaces of solid-fluid (vapor and liquid) and when to take into account the interaction between molecules and their moving in the dense phases. A way of construction of size fluctuations to system with strong interaction is shown as well as the estimations for definition of the bottom limit of applicability of thermodynamics are entered.
2. ASSUMING THE DISCRETENESS OF A SUBSTANCE.

Fluctuations are themselves related to the discreteness of the molecular structure of any system, and they are determined by the heat motion of molecules. In order to take into account this demands the use of an appropriate mathematical apparatus. As was mentioned for the first time in [12], it requires that we employ the calculus of finite differences [13] instead of conventional continuous mathematical analysis [13].

Due to the character of molecular theories, a molecule cannot be split into smaller parts; we therefore cannot assume that there is a limit to the infinite splitting of the range in which a derivative is plotted, as is done in ordinary differential calculus [14] when considering the derivatives needed to determine the critical differential calculus [14] when considering the motion of molecules. In order to take into account this demands the use of an appropriate mathematical apparatus. As was mentioned for the quasi-chemical approximation (7, 8), and ε is the parameter of the lateral pair interaction potential, \( N \) is the number of pairs of bonds in the system is denoted as \( M = \frac{\varepsilon M}{2} \).

Let \( J_o \) be the statistical sum of molecules in the gas phase; \( \mu, M, T \) where \( \mu \) is the pressure, \( J_o(k) \) be the statistical sum of \( A \) particles depending on the number \( k \) of neighbors \( A \) of each type in the local environment \( J \) is the mean value of the \( J_o(k) \) or regardless of the effect neighbors \( 7, 8 \) and \( \varepsilon \) is the parameter of the lateral pair interaction potential, \( N \) is the number of pairs of molecules \( ij \) (where \( ij = A, I \)).

When calculating interactions between nearest neighbors only, the expression for statistical sum \( Q \) of a homogeneous system in the quasi-chemical approximation (QCA) has the form

\[
Q = \sum_{N_{ij}, N_{AA}}^{M, M_i} Q_i, \tag{1}
\]

where factor \( Q_i \) is written as [16]

\[
Q_i = \left( C_{M}^{N_i} \right)^{1-z} \left( J_o(k | N_{AA}) \right)^{N_i} \Omega \exp(\beta \varepsilon N_{AA}), \tag{2}
\]

\[
\Omega = M \frac{1}{N_{AA}} \frac{1}{N_{AA}^2} \frac{1}{(N_{AA} - 2)!};
\]

where \( C_{M}^{N_i} = M! [N_{AA}! N_{AA}! (M - N_{AA})! (N_{AA} - 2)!] \) is the number of combinations of \( M \) sites with number of particles \( N_{AA} \) at these sites. Correcting factor is
needed to refine the entropy factor, since the number of independent pairs is overestimated in the QCA [7, 8]. When $\beta k \rightarrow 0$, it yields an accurate solution corresponding to a chaotic distribution of molecules over different types of sites $\tilde{N}_{ij} = zN_iN_j / (2M)$.

Internal collective motions of molecules are considered for each configuration of neighbors $k$, which is denoted as $J_k(k|N_{AA})$. If we introduce expression $J_k = J_k(k|N_{AA})$, and rewrite formulas (1) and (2) as

$$Q = \sum_{N_{AA}=0} (J_k(k|N_{AA}))^v \exp(\beta c N_{AA}) = \sum_{N_{AA}=0} (J_k(k|N_{AA}))^v \exp(\beta c N_{AA})$$

where a term is introduced for effective pair interaction parameter $\varepsilon(N_{AA}) = \varepsilon + \delta \varepsilon(N_{AA})$,

$$\delta \varepsilon(N_{AA}) = \frac{1}{2} \sum_{k=1}^Z \Lambda_k(k) \beta^{-1} \ln(J_k),$$

(4)

here $\Lambda_k(k) = L_k(k) / t_{AA} = C_k^v t_{AA}^{k-1} t_{AA}^{z-k}$.

The lower limit of the sum is $k = 1$, since the summand in (4) is zero at $k = 0$ (because the ratio of statistical sums is unity). Considering the collective character of internal motions thus yields $\varepsilon(N_{AA})$ effective parameter of lateral interaction, which contains the free energy of internal motions and the potential energy of intermolecular interactions. The value $\delta \varepsilon(N_{AA})$ determines the effect the local environment has on pair energy at a given average number of pairs of neighbors $N_{AA}$.

For our analysis of fluctuation contributions, let us consider the probability of system $P(N_A, N_{AA}) = \exp[\beta c N_A]$ being in particular states of a grand canonical ensemble.

Extreme conditions $\Delta \ln P(N_A, N_{AA}) \Delta N_A = 0$ and $\Delta \ln P(N_A, N_{AA}) \Delta N_{AA} = 0$ yield equations for the local adsorption isotherm that relate the chemical potential of the system ($\mu = \mu_0 + \beta^{-1} \ln(f)$) set by the thermostat with the number of molecules $N_A$, and the relation between pair functions

$$\beta(\mu + \delta \mu) = \frac{1}{2} \ln \left[ \sum_{N_{AA}=0} (J_k(k|N_{AA}))^v \exp(\beta c N_{AA}) \right] + \frac{1}{2} \ln \left[ \frac{(N_{AA} - z)(N_{AA} + z) / z!}{(N_{AA} - z / 2)!^2} \right],$$

(5)

$$\beta \varepsilon(N_{AA}) + \varepsilon_1 = \frac{1}{2} \ln \left[ \frac{N_{AA}(N_{AA} + 1) N_{AA}^{N_{AA} + 1)}{(N_{AA} + z / 2)!^2} \right],$$

(6)

where $\delta \mu = N_A \Delta \varepsilon(N_{AA}) / \Delta N_A$ and $\varepsilon_1 = N_{AA} \Delta \varepsilon(N_{AA}) / \Delta N_{AA}$ are the exact difference derivatives of function (4). Summands $\delta \mu$ and $\varepsilon_1$ determine the influence of effective lateral interaction parameter (4) and size corrections due to the limited size of the system.

Formulas for dispersion matrix elements $\eta_{km} = -(1/2) \Delta X_k \ln P(N_A, N_{AA})$ [2], where $X$ and $Y$ correspond to independent variables $N_A$ and $N_{AA}$, are derived with average values found by solving Eqs. (5) and (6). Knowing $\eta_{km}$, we can obtain corrections $\Delta X_k$ for the degrees of occupancy of different types of sites and their pair probabilities due to fluctuations in the form

$$\Delta X_k = \frac{1}{2} \frac{\partial \ln \text{Det} \Delta X_k}{\partial \ln(\lambda_k)} = \frac{1}{2} \sum_{k=1}^Z \frac{\partial \ln \text{Det} \Delta X_k}{\partial \ln(\lambda_k)} \frac{\partial \lambda_k}{\partial \ln(\lambda_k)},$$

(7)

where $\text{Det}$ is the determinant of a dispersion matrix composed of $\eta_{km}$ elements (its dimensionality $T_D = 2$ is the number of independent variables $N_A$ and $N_{AA}$), and to express the degrees of site occupancy with regard to fluctuations $X_k(\beta) = X_k + \Delta X_k$. In formula (7), we use $\lambda_k = \exp(\beta \mu)$ for $N_A$ and $\lambda_k = \exp(\beta \varepsilon)$ for $N_{AA}$. Equations (5) and (6) are used to calculate derivatives $\partial \ln \text{Det} / \partial X_k$. Derivatives are calculated numerically. Let us write the structure of expressions for dispersion matrix elements $\eta_{km}$ used in Eq. (7),

$$\frac{\Delta^2 \ln P}{\Delta N_A^2} = \frac{\Delta^2 \ln P}{\Delta N_A^2} \bigg|_{j=\text{const}} + \beta \frac{\partial \delta \mu}{\Delta N_A},$$

(8)

$$\frac{\Delta^2 \ln P(N_A, N_{AA})}{\Delta N_{AA}^2} = \frac{\Delta^2 \ln P(N_A, N_{AA})}{\Delta N_{AA}^2} \bigg|_{j=\text{const}} + 2 \beta \frac{\partial \delta \varepsilon}{\Delta N_{AA}} + \beta \frac{\Delta^2 \delta \varepsilon}{\Delta N_{AA}^2},$$

(9)
\[ \frac{\Delta^2 \ln P}{\Delta N_A \Delta N_{AA}} = \frac{\Delta^2 \ln P}{\Delta N_{AA} \Delta N_A} = \frac{\Delta^2 \ln P}{\Delta N_{AA} \Delta N_A} |_{J=\text{const}} + \beta \frac{\Delta \delta \mu}{\Delta N_{AA}}, \]  

where the summands for \( J = \text{const} \) were determined in Eqs. (10)–(13) in [17] and are not repeated here.

### 3. COMPARISON OF CONTINUAL AND DISCRETE CALCULUSES

The general principle of a finding of the lower size limit \( R_t \) of the applicability of thermodynamics is comparison of thermodynamic properties in continual and discrete descriptions to reveal distinctions at the expense of limitation of volume or dimensional effects for small number of particles. On the curved interfaces it is necessary to reveal in addition conformity between continual and discrete descriptions of the area of an interface of phases and internal volume of phases. The absence of any fluctuations is considered in all equations of thermodynamics and continuum mechanics for bulk phases and interfaces. The mathematical apparatus used in thermodynamic equations and to describe the curvature of any local region of an interface [1, 2] is differential geometry operating with continual derivatives of the second order.

The problem of which parameters of a small body should be compared, bulk or surface, also plays an important role. At a given level of precision in describing the properties of a drop’s volume \( (M > 200) \), the radius of the drop \( R_v \) is much less than radius \( R_s \) when describing its surface properties.

It should be noted that the concept of an interface in thermodynamics applies only to macrosystems. The assumption of interface contributions is important if the surface area \( (A) \) is so developed that the contribution from the surface components in thermodynamic potentials is commensurate with the contribution from volume phases. If the Gibbs potential \( (G) \) is written as \( G = U - TS + PV - \sigma A \), where designations for internal energy \( U \); entropy \( S \); temperature \( T \); pressure \( P \); volume \( V \); and \( \mu_i \) and \( m_i \), representing chemical potential and mass of component \( i \), respectively, were used; and \( \sigma \) is the surface tension \( (ST) \).

For an isolated small body, all components of the thermodynamic potential should be described with equivalent precision. Thermodynamic equations describe both the bulk and surface components from the continuous viewpoint without the assumption of fluctuations. Surface characteristics should be used in comparing the continuous and discrete molecular viewpoints for small bodies. If the volume of small body is chosen as the condition for the precision of description, its surface characteristics will include fluctuation effects, changing the precision of the system’s description. Below we shall consider the relative root-mean-square fluctuations \( \eta \) on the surface of tension and not in within the bulk of a drop. This is necessary in order to have not only a volume but also a surface that does not experience fluctuations, i.e., that meets the requirements of thermodynamics.

For more precise estimates of \( R_p \), let us compare the thermodynamic properties of a certain surface section from the viewpoint of (a) thermodynamics and (b) molecular theory.

(a) From the viewpoint of continuum theory, the considered section represents the elementary minimum area with the use of which the full surface is “covered” (according to Borel’s lemma). We should remember that according to this lemma [14], if full closed gap \([a, b]\) is covered by an infinite system of open gaps (i.e., without including the limiting points of this gap), then a finite subsystem of open gaps that also covers all of full gap \([a, b]\) can always be selected from it. This means that for a continuum of internal points in the finite range considered, some covering that consists of a finite number of internal gaps can always be plotted. For the sake of simplicity, this formulation of Borel’s lemma...
was written for the case of one dimensionality. Its generalization on a two-dimensional surface is performed by literally substituting the concept of “range” for that of “area” and has exactly the same sense. From the viewpoint of thermodynamics, the section under discussion corresponds to macroscopic radii and is planar.

(b) From the viewpoint of a discrete medium, the same section represents the minimum section in which the thermodynamic function and its first and second derivative should be determined (the second derivative is also required to describe the curvature of the surface). According to the approach described above for discrete systems, this section is the local area containing the minimum number of junctions $L = 4\lambda$ in one dimensionality. We have one dimensionality for a circle of a two-dimensional drop and two dimensionalities for a spherical surface.

A comparison of the two methods (a) and (b) for describing the minimum range of the surface yields the answer for the desired drop radius.

4. TWO-DIMENSIONAL DROP
A “surface” of a two-dimensional drop is a circle which is approximated by a correctly inscribed polygon containing $N_s$ number of sides with base length $L = 4\lambda$ (Fig. 1a). Let us denote the precision of the coincidence of the length of the polygon and the circumference of the circle by $\xi$, we can then easily obtain $R_i/\lambda = N_s L$, where $N_s = \pi / (6\xi^{1/2})$ is determined by the precision of $\xi$ in describing of the circumference of the circle by the broken line. From a physical point of view, the precision of $\xi$ determines the number of particles $N_i$ on the dividing surface. The procedure for inscribing the broken line in the circle is quickly found. At $N_i = 4$, we have precision $\xi \sim 10\%$; for $N_i = 6$, precision $\xi \sim 4.5\%$. This corresponds to $R_i = 16$ and $24\lambda$, for which $\eta \sim 1.8$ and $1.2\%$. It is obvious that these values are somewhat rough approximations. As a rule, the precision of calculating the concentration profiles of drops $\{\theta_q\}$ is greater than $\sim 0.1\%$; by raising the accuracy of the correspondence of the number of particles on an expanding surface, we therefore find $N_i = 12$ (precision $\xi \sim 1\%$, $R_i = 48\lambda$, and $\eta = 0.6\%$) and $N_i = 24$ (precision $\xi \sim 0.5\%$, $R_i = 96\lambda$, and $\eta = 0.3\%$). It should be noted that in the latter case, root-mean-square fluctuation $\eta$ is even greater than the precision of calculating the concentration profile.

5. THREE-DIMENSIONAL DROP
For a spherical drop, we must assume the second dimensionality. In this case, $S_0 \sim L_2$ corresponds to the elementary area. Let us approximate the surface of a spherical drop of radius $R$ by the multiplicity of these elementary sections (“mathematical points”). A structure with $z = 6$ having bond length $\lambda$ between cells corresponds to the densest two-dimensional packing of molecules. This structure has an anisotropic area formed by cells within two coordination spheres around a central cell. The maximum diameter of an elementary area with this structure corresponds to a section with length $L$ (Fig. 1b). The minimum size of the section is $2 \times 3^{1/2} L$, resulting in $S_0 = 6 \times 3^{1/2} L^2$.

Each planar elementary section can serve as the base for a cone constructed from the center of the sphere. In order to simplify our estimates, let us say that the elementary section has the shape of a circle; the surface of the spherical part of a cone based on this section is then a lathe figure and can be easily determined [14]. Let us denote it by $S_c$. The full number of cones on the surface of a sphere of radius $R$ corresponds to the number of molecules $N_c = 4\pi R^2 / S_c$.
and coincides with the number of sections approximating the sphere. We can introduce the effective radius of the circle, which (having been determined as \( R' = \sqrt{\langle S_0/S \rangle} \)) is equal in area to the section under discussion. Then \( S^*_c = 2\pi R^2\{1 - \{1 - (R' / R)^2\}^{1/2}\}. \) Expanding the expression for \( S^*_c \) under the radical to the second component of smallness, we obtain the relationship between \( \langle S_0 - S \rangle \) and ratio \( (R' / R) \).

Assuming the proportionality of the number of molecules and the area of the planar elementary section, let us require that the difference between the areas of all planar sections and all spherical parts of our inscribed cones satisfy the condition

\[
\frac{\langle S_0 - S \rangle}{\langle S_0 \rangle} < \xi,
\]

where \( \xi \) is the relative accuracy of describing the area of the surface of a drop with radius \( R \), (where \( \xi \sim \xi_s \)). This condition is easily met by increasing the radius of the sphere. The condition of the smallness of density fluctuations at the minimum size boundary for the applicability of thermodynamics can be verified indirectly, in comparison to the \( \eta \) value of the relative root-mean-square fluctuation \[4\] of number of molecules \( N_c \) on the surface of a sphere with radius \( R \). The \( \eta \) value must a priori be less than the possibility of the exact experimental determination of a \( ST \) \( \sigma \).

We thus obtain from condition (11) an expression that relates the size of the diameter of a sphere \( R \) to the accuracy of describing the area of the sphere’s surface \( \xi: R / \lambda = [6 \times 3^{1/2}/(2\pi\xi)]^{1/2} = 1.29 / \xi^{1/2} \), measured in units of cell length \( \lambda \). The following sets of values correspond to this expression: \( \xi_s \sim 0.1\%, \quad R = 41\lambda, \quad \eta \sim 0.7\%; \quad \xi_s \sim 0.05\%, \quad R = 82\lambda, \quad \eta \sim 0.34\%; \) and \( \xi_s \sim 0.01\%, \quad R = 129\lambda, \quad \eta \sim 0.2\% \).

Considering that the precision of calculations using the system of equations in molecular theory \[6\] is no less than \( 10^{-3} \) or \( 0.1\% \), we obtain \( R' / \lambda = 41 \), which evidently satisfies existing experimental procedures \[3-5\]. If we substantially increase the possibilities of an experiment for a more exact determination of the size of the diameter of the sphere, we must lower the value of this criterion to \( \xi = 10^{-4} \); this will expand the radius to \( R' / \lambda = 129 \) and correspond to a value of \( \eta \sim 0.2\% \).

This evaluation correlates well with the results from numerical calculations, mentioned in \[6\]: up to reduced critical temperatures \( \tau = 0.99 \) the width of transition layer \( \kappa \) both for the planar boundary and for drops does not reach the discussed value \( R' / \lambda \). We must therefore consider that a thermodynamic description is not justified for \( R' \sim 41\lambda \). For argon atoms, this corresponds to \( R' \sim 16 \) nm. Assuming that at \( \xi \sim 0.05\% \), we can ignore both the discreteness of a substance and the contributions from fluctuations, thus allowing us to use a thermodynamic description at \( R' > 80 \)–\(100\lambda \) (or \( R' \sim 40 \) nm for argon atoms). The minimum size of drop radius \( R \) from which a thermodynamic description can be used thus assumes values from 16 to 40 nm. These estimates agree with the initial postulates of thermodynamics on the need for rather large amounts of matter in a system.

6. CONCENTRATION DEPENDENCES OF FLUCTUATIONS

Estimates of the relative root-mean-square fluctuation for Poisson distribution \( \eta_p = <N^2>/N = N^{1/2} \) are traditionally used in qualitative discussions of the role of fluctuations \[1, 2\]. Main condition of this distribution is the absence of correlations between molecules. It was constructed for macroscopically small subsystems where any number of molecules can be present, provided that it is small compared to the total number of molecules in the full system from which this subsystem was selected.

The value \( \eta \), an analog to the \( \eta_p \) numbers calculated for the number of molecules \( N \) found in the system of a small compact body (but not as isolated molecules), was used above for drops in analyzing \( \xi \) and \( \xi_s \) with variation of \( M \). Let us discuss the correspondence between
the \( \eta \) and \( \eta_p \) values for small bodies. We thus consider how root-mean-square fluctuation \( \eta \) changes for a homogeneous system containing \( M \) centers in the equilibrium filling of a monolayer on the dividing surface.

Fig. 2 gives the concentration dependences of function \( D \), which are directly related to \( \eta \) as \( D = -2\eta \) \[15\] in dependence on the size of range \( M \) and the number of molecules \( N \) in this range \( (N_v = M - N)\):

\[
D = -\frac{1}{4} \ln \left[ \frac{N(N-1)N_v(N_v-1)}{(N+1)(N+2)(N_v+1)(N_v+2)} \right].
\]

This equation was obtained by means of symmetrical difference derivatives. The dependences of \( D \) on \( \theta = N/M \) for homogeneous system \( M = 10^m \) at various \( m \) are given in Fig. 2. The relationship to \( \eta_p \) values is derived from the \( N = \theta M \) equation. The maximum values of \( D \) are related to the range of high and low degrees of filling \( \theta \). In the range of medium fillings, the \( \eta \) value is considerably lower.

Fluctuations for a low number of molecules in small systems behave as they do in macroscopic systems; i.e., they rise dramatically with a decrease in \( N \). This allowing us to use value \( \eta \) instead of \( \eta_p \) for a normal Poisson distribution. With an increase in density (where \( N \sim M \)), the same rise in fluctuations is observed for small systems as for low numbers of molecules. This is due to the presence of vacancies; as in real liquids, we should then observe fluctuations in the ranges of discharges identical to fluctuations in the number of low-density molecules, and the formation of bubbles in the liquid corresponds to the inversion of phases.

For \( M = 10^4 \), differences from zero values for 2 to 3% density arise in the range of high and low fillings. Later, when \( M \) falls to \( 10^3 \), the range of differences in \( D \) from the zero value expands to 20%. At even lower values of \( M \), value \( D \) differs from macroscopic over the range of densities starting at \( M = 500–600 \). The curves for \( M = 10 \) show the maximum differences for the dispersion for small sections.

In order to ignore density fluctuations completely, \( D \) must be reduced over the range of \( \theta \). With a rise in \( M \), the dispersion value falls dramatically. For \( M = 10^5 \), dispersion remains close to zero over the range of densities; i.e., this size can be considered the counterpart of \( R_p \). For the expanding surface of a drop, this \( M \) corresponds to radius \( R/\lambda \sim 46 \). This value is close to the estimate obtained earlier, \( R/\lambda = 41 \) at \( \xi = 0.1\% \), which corresponds to \( \eta \sim 0.7\% \).

Our calculations confirm the universal character of the obtained estimates. They are based on the discrete nature of a substance, but are not related to the details of molecular distribution and do not depend on the temperature. Near the critical point, however, special consideration is required.

7. SURFACE OF A SOLID

The structure of flat faces of a small solid body is similar to structure to a flat macro-lattice, therefore comparison continual and discrete descriptions is spent on values of thermodynamic functions. These functions can be counted within the limits of the macroscopical description through differential derivative of thermodynamic potentials or in frameworks of finite differences calculations with the symmetric derivatives for defining equilibrium distribution functions. Their difference illustrates a distinction between small bodies in which taking into account of fluctuations, and macroscopical bodies for which fluctuations are absent, is not enough important.
Woolf’s theorem [4], supplementing Gibb’s conditions of equilibrium balance for a solid body, leads to existence of a surface of a crystal in the form of a set of faces of different orientation. It gives the value $ST$ for each orientation of interfaces. Distributions of macroscopical faces on orientations were considered in works [2]. The basic conclusion of these works consists that at equilibrium the number of such different faces corresponds only to small values of indexes of Müller (increase in an index of Müller essentially raises values $ST$).

Therefore it is natural to consider that for small crystals to an equilibrium condition answers such sizes for which there is necessary to take into account of edge contributions [4]. As a whole the problem of the analysis of fluctuations on small crystals is reduced to consideration of finite number of faces and their edge areas, i.e. the surface of a solid body is considered as non-uniform, consisting of the different limited flat faces.

The microscopic theory of such systems was considered in works [6, 15]. The taking into account of fluctuations for non-uniform ideal systems presents the summation of contributions of any characteristics on separate faces. All the results obtained above are therefore easily generalized by the summation with weights $F_q$ and replacement of total coverages $\theta$ by local coverages $\theta_q = N_q / M_q$ related to sites of type $q$, $1 \leq q \leq t$, where $t$ is the number of site types.

The local second derivative for relative root-mean-square fluctuation on the face $q$ with taking into account the lateral interactions in the mean field approximation and the size effects, is defined according (8) as

$$\Delta^2 \ln P_q(N_q,M_q) = \Delta N_q^2 \left[ \frac{\partial^2 \langle \xi_q^2 \rangle}{\partial \theta^2} + 2 \frac{\partial \langle \xi_q \rangle}{\partial \theta} \frac{\partial \langle \xi_q \rangle}{\partial \theta} + \frac{\partial^2 \langle \xi_q \rangle}{\partial \theta^2} \right].$$

An analysis of the equation (12) shows that (1) Maximum local size density fluctuations exist at $\theta_q \to 0$ and $\theta_q \to 1$. At $\theta_q \sim 1/2$, we have maximum density fluctuations not related to size effects, for macroscopic systems too. (2) An important role in $\eta$ is played by the $M_q / M_p$ ratio. (3) The macro-fluctuations of density on a non-uniform surface oscillate; the maximum number of oscillations equals the number of site types $t$, which provides a possibility in principle of estimating them experimentally [15, 18].

8. LATERAL INTERACTIONS AND NON-UNIFORM SURFACE

A consideration of fluctuation effects will be limited by the simplest case of the adsorption of one substance on different single crystal faces. Let us consider lateral interactions in the mean field approximation. The $\varepsilon_{qq}$ parameters then depend on the type of the face $q$, $1 \leq q \leq t$ [15], but each face is considered separately. This allows the equation for local partition functions $Q_q(N_q,M_q,T)$ for faces of type $q$ in Eq. (3) to be rewritten as

$$Q_q(N_q,M_q,T) = \hat{\nu} \hat{\mu} \hat{\lambda} \left( \begin{array}{c} q \cr q \end{array} \right) \left( \begin{array}{c} q \cr q \end{array} \right) (\theta_q^4 - 2 \theta_q^2) / 2,$$

where $\bar{\varepsilon}_{qq} = \varepsilon_{qq} + \delta \varepsilon_{qq}(\theta_q^4)$,

$$\delta \varepsilon_{qq}(\theta_q^4) = 2 \sum_{k=1}^t C_k \theta_q^{4-k}(\theta_q^{2k})^{-k} \beta^{-1} \ln(J_k(q)).$$

The local second derivative for relative root-mean-square fluctuation on the face $q$ with taking into account the lateral interactions in the mean field approximation and the size effects, is defined according (8) as

$$\Delta^2 \ln P_q(N_q,M_q) = \Delta N_q^2 \left[ \frac{\partial^2 \langle \xi_q^2 \rangle}{\partial \theta^2} + 2 \frac{\partial \langle \xi_q \rangle}{\partial \theta} \frac{\partial \langle \xi_q \rangle}{\partial \theta} + \frac{\partial^2 \langle \xi_q \rangle}{\partial \theta^2} \right].$$

Thus the equation (12) shows that (1) Maximum local size density fluctuations exist at $\theta_q \to 0$ and $\theta_q \to 1$. At $\theta_q \sim 1/2$, we have maximum density fluctuations not related to size effects, for macroscopic systems too. (2) An important role in $\eta$ is played by the $M_q / M_p$ ratio. (3) The macro-fluctuations of density on a non-uniform surface oscillate; the maximum number of oscillations equals the number of site types $t$, which provides a possibility in principle of estimating them experimentally [15, 18].
It follows from this equation that, in the absence of correlations between adsorbed molecules, the contributions of size effects constructed above (the ideal model) retain their form. However, the presence of contributions of lateral interactions in these equations can substantially change solutions to them compared with solutions to the equations given for the ideal model. By way of example, let us see how changes in the first order with respect to \( M^{-1} \) the fluctuation correction

\[
\Delta \theta_q = \theta_q - \theta_q^p \quad (\text{here } \hat{\epsilon}_{qq} = \tilde{\epsilon}_{qq} + 0.5 \partial \ln(\theta_q)) \]

\[
\Delta \theta_q = \frac{(1 - 2\theta_q)}{2M_q[1 - \beta \hat{\epsilon}_{qq} z_{qq} \theta_q (1 - \theta_q)]^2}. \tag{13}
\]

The differences in fillings decrease as the size of the face increases. The Eq. (13) gives this correction with isolating the fluctuations in the denominator. This curve separates the metastable region and the region of thermodynamic instability of stratifying molecules. The correction value in region \( q \) depends on the character of intermolecular interactions.

If \( \hat{\epsilon}_{qq} < 0 \), which corresponds to ordering of chemisorbed molecules, the denominator increases with respect to the denominator for an ideal system as the lateral interaction contribution \( |\beta \hat{\epsilon}_{qq} z_{qq}| \) grows, and the influence of lateral interactions coincides with the influence of an increase in the face size.

If there is attraction of molecules and \( \hat{\epsilon}_{qq} > 0 \), the denominator decreases as \( \beta \hat{\epsilon}_{qq} z_{qq} \) grows, and the influence of lateral interactions is opposite to that of an increase in the face size. As the current local density value \( \theta_q \) on the given face \( q \) approaches the spinodal curve, the character of correction behavior depends on the ratio between \( M_q \) and the term in square brackets.

We see that the denominator as a function of density decreases very rapidly (by the quadratic law). For this reason, at any fixed \( M_q \) value, there exists a density at which correction (13) sharply increases. A more exact description of the phase behavior of molecules in small systems requires the use of more exact approximations than the molecular field approximation.

9. DISCUSSION
A comparison of the received size \( R_t \) with dimensional dependence \( ST[6] \) leads to following two consequences:

1) In thermodynamics it is means the bottom limit of the sizes size \( R \to 0 \), therefore it means that \( R_t \) is this limit below which the thermodynamics cannot be used.

2) The size \( R_t \) is less than the general range of change of drops in a nano-sized range (to 100 nanometers). So, the large area of this range can be described the thermodynamic equations, but under condition of the account of dimensional dependence of values \( ST \sigma(R) \). For this area of the sizes replacement \( \sigma(R) \) on a condition \( \sigma(R) = s_{bulk} \) is incorrect.

However, a macroscopic assembly of small systems has a negligibly small contribution from fluctuations and obeys the usual equations for the average values of molecular distributions.

Internal ranges of phases. For macroscopic bulk phases, continuum and discrete descriptions of the narrow range of the three-dimensional lattice around a selected junction can be compared and, repeating the procedure used above for surface properties, we obtain estimates for and in the bulk phase that are completely analogous to \( R_{t1} \) and \( R_{t2} \) values if we ignore the state of the surface. Limiting ourselves to continuum relationships \( R_{t1}^v = (3R_{t1}^2)^{1/3} \) (and analogously for \( R_{t2}^v \)), we obtain the radii of internal ranges:

\( R_{t1}^v = 17\lambda \) and \( R_{t2}^v = 29\lambda \). This connection was obtained from equality of size of fluctuating substance in different subsystems in a phase and interface area.

Thus, owing to the specificity size fluctuations are shown in limiting areas on density values \( \theta \to 0 \) and \( \theta \to 1 \). In intermediate area of values \( \theta \) contributions of dimensional fluctuations are small and in many situations they can be neglected. Especially it is strongly appreciable in the field of average values \( \theta \) at which the contributions...
connected with intermolecular interactions and internal movements of molecules are most considerably shown. On the contrary, in limiting areas to density values \( \theta \to 0 \) and \( \theta \to 1 \) effects from influence of intermolecular interactions and internal movements of molecules are shown rather weakly and they can be neglected.

This specificity allows to draw a conclusion that the constructed estimations for ideal models remain mainly true and for non-ideal models, except for cases answering to change of a phase condition of substance - for example, in close on condition parameters to area of coexistence of phases.

10. CONCLUSION

The molecular-statistical approach to definition of the bottom limit of the characteristic linear size of area to which the thermodynamics is applicable is formulated. Natural restriction on use of thermodynamic approaches is the discrete structure of substance at atomic-molecular level. For the description of the size fluctuations the molecular theory on the basis of the lattice-gas model, which unique gives equal-accuracy results in all range of density, and the finite-difference calculation reflecting a discrete structure of substance, are used. Influence of intermolecular interactions and movements of molecules in dense phases on dimensional fluctuations is considered. Their basic influence is shown in the field of average fillings.

We have established the existence of the lower size boundary at which thermodynamic descriptions are possible, reflecting the absence of spontaneous heat fluctuations on the expanding surface of a drop. The drop size was quantitatively determined to be \( R'_{\text{v}}/\lambda < 41 \), for which the use of thermodynamic equations is not possible, and \( R'_{\text{v}}/\lambda \sim 80–100 \) for which use of the equations of thermodynamics is strictly proved. The limitation on the bottom limit of the applicability of thermodynamics means that \( R'_{\text{v}}/\lambda < 41 \) must be considered the lower thermodynamic limit corresponding to condition \( R \to 0 \). Restrictions on the sizes of areas in internal local volumes of macro-phases \( (R'_{\text{v}}/\lambda > 29) \) and on conditions of introduction of amendments on the account of fluctuation of density in macro-phases \( (R'_{\text{v}}/\lambda < 17) \) are received. The received estimations are focused on a wide spectrum of the small systems arising at formation of a new phase and in high-dispersed systems.

The molecular theory can be applied to calculation of size fluctuations of many real systems - it has the same generality, as well as model-free thermodynamics, because of the possibility of the account of the basic physical factors (intermolecular interactions, heterogeneity at atomic-molecular level, the account oscillatory and translation moving of molecules), and it allows to supervise the constructed estimations.

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