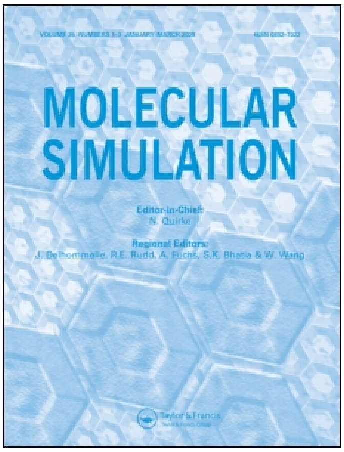

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A New Monte Carlo Method for Direct Calculation of the Critical Size and the Formation Work of a Microdrop

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A NEW MONTE CARLO METHOD FOR DIRECT CALCULATION OF THE CRITICAL SIZE AND THE FORMATION WORK OF A MICRODROP

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New Monte Carlo procedures in open ensembles are proposed. Non-stationary Markov chain procedure in the μpT - ensemble provides a direct estimation for the critical size of a condensation nucleus at given p and T. A stationary procedure in the μpT ensemble with two allowed particle numbers n and $n + 1$ provides the direct way to calculate the chemical potential and Gibbs free energy of a cluster; in the grand canonical (μVT) ensemble the same approach gives μ and the Helmholtz free energy. The same procedures are readily applicable to periodic systems representing bulk phases.

KEY WORDS: Monte Carlo, open ensemble, cluster, chemical potential, critical size.

1. INTRODUCTION

The cluster approach to the description of thermophysical properties of highly imperfect gases [1] supposes division of the phase space into several areas. Each area corresponds to a definite separation of the macrosystem into clusters and consequent determination of leading contributions to the partition function. This procedure depends on the specific determination of a physical cluster and admits a certain arbitrariness. If the only aim is to calculate equilibrium properties the partition function is reduced to an integral over coordinates - configurational integral. In this case the cluster division of the phase space is reduced to division of the configurational space: inclusion of kinetic characteristics into the definition of a cluster adds nothing to the theory. It should be pointed out that the usefulness of the cluster approach considerably depends on the specific way of cluster definition which on one hand should be possibly simple and on the other hand should provide a maximally accurate separation of leading and vanishing contributions to the configurational integral.

The calculation of equilibrium properties of clusters - the formation work and the critical size - is the central problem of the theory of homogenous nucleation. These two quantities are usually associated with the determiniation of the Gibbs free energy (G) dependence on the size of the cluster n.

The traditional MC approach provides no opportunity to calculate the Gibbs potential directly since the dispersion of the formal average over the NpT ensemble of the exponent exp $[\beta(H + pV)]$ ($\beta = 1/kT$, H- Hamiltonian, p- pressure, V- volume, T- temperature) usually deviates.

There exists a number of indirect approaches for calculation of G [8]. One of the methods is the integration of the enthalpy (over the reciprocal temperature) or the volume (over the pressure) which should be preliminary determined in a series of MC runs in the NpT ensemble. Another example is the direct calculation of μ [8] with following summation of μ on the particle number n.

Here we suggest a new MC method for direct calculation of the chemical potential at given pressure p, temperature T and particle number n (stationary method). It is preceded by nonstationary method for direct estimation of the critical size at given p and T.

The results obtained by stationary method are compared with the results of other numerical experiments. Different ways of calculation of G dependent on the definition of a cluster are also discussed.

The comparison of the suggested method with the earlier approaches are presented at the end of this paper.

2. NONSTATIONARY MARKOV-CHAIN METHOD

Let us discuss the method of direct calculation of the critical size. It is known that the chemical potential μ, pressure p and temperature$T$ are the input parameters for the μpT ensemble partition function [1]:

$$\Gamma (\mu, p, T) = \sum_{n=1}^{\infty} \exp ((- G (n, p, T) + \mu n)/kT) \tag{1}$$

For

$$\mu = \lim_{n \to \infty} (G (n, p, T)/n) \tag{2}$$

the contributions of all terms in (1) beginning with sufficiently large n are equal – the system is in "neutral" equilibrium with the respect to n, partition function (1) deviates, $\langle n \rangle = \infty$. The value μ determined by (2) is evidently the chemical potential of the macrosystem at given p and T. It is also clear that for $\mu = \mu^*$, other than (2), there should occur a redistribution of the weights among terms providing an extremal n_0 with $\partial G/\partial n|_{n=n_0} = \mu^*$ (term with maximum or minimum contribution to (1)). In the first case $\partial^2 G/\partial n^2|_{n=n_0} > 0$ and the microsystem with the size $n = n_0$ will be thermodynamically stable. In the second case $\partial^2 G/\partial n^2|_{n=n_0} < 0$ and it would be unstable. In the latter case, if the microsystem under consideration is in the condensed state (a microdrop) and the value of parameter μ^* equals to the chemical potential of the gaseous macrophase at given p and T, then the microsystem is to be regarded as the critical nucleus of the liquid (or solid) phase with the size $n_c = n_0$.

Basis of the method

It should be pointed out at once that we do not consider an equilibrium μpT- ensemble but an ensemble fo finite pieces of nonstationary Markov chains beginning with initial number of particles n_0. The determination of the sign of $\partial^2 G/\partial n^2|_{n=n_c}$ and the calculation of n_c are possible in the frames of the following nonstationary MC μpT- emsemble procedure.

Consider the NpT-ensemble of the microstates with probabilities w_i. Suppose that an ensemble of Markov trajectories of fixed length corresponds to each of these microstate. Each trajectory of the ensemble begins with the microstate i and develops in the microstate space of μpT-ensemble (the change of configuration, volume and number of particles) with the transition probabilities w_{ij}, satisfying conventional detailed balance conditions

$$\frac{w_{kl}}{w_{lk}} = \exp\left(\beta((U_k - U_l) + p(V_k - V_l) - \mu (n_k - n_l))\right) \Lambda^{3(n_k - n_l)} \frac{n_k!}{n_l!} \qquad (3)$$

where Λ is the de Broglie wavelength. One of possible realisations of such chains is described in the Appendix. Each of the trajectories, passing through the microstates $i, k, l. \ldots u, v$ has the probability $w_i \cdot w_{ik} \cdot w_{kl} \cdot \ldots \cdot w_{uv}$. Let us introduce the absorbing states with $n = n_{\max}$ and $n = n_{\min}$ with zero transition probabilities to leave them. All the trajectories could be distributed among classes: each class contains all the trajectories with equal particle numbers $n_i, n_k, n_l \ldots n_u, n_v$ but with arbitrary particle configurations and volumes. The probability of realisation of any trajectory of a given class equals to the sum of probabilities of all the specific trajectories of this class. The initial probability distribution in the configurational and volume space is the equilibrium distribution of the NpT-ensemble. The transition probabilities (3) also provide the conservation of the equilibrium distribution function of the NpT - emsemble on each MC step. Therefore an equilibrium NpT-distribution is being conserved. So the steps with birth or elimination of particles transfer the system from one NpT equilibrium distribution to another.

Let $W(n,m)$ be the probability of transition from the state with the particle number n to the state with the particle number m irrespectively to the values of other parameters (configuration and volume, see (3)), it can be expressed as follows:

$$W(n,m) = {\sum_{ij}}' \exp(-\beta (U_i - p V_i))\, w_{ij}/(\exp(-\beta G(n)) \cdot \Lambda^{3n} \cdot n!) \qquad (4)$$

The Prime at the sum (4) denotes that summation is being carried out under condition: over i - at constant particle number n and over j - at constant particle number m. The transition probabilities $W(n,m)$ direct the evolution of the total trajectory of the given class - the trajectory in the cluster size space. It is easy to notice that for w_{ij} satisfying the detailed balance condition (3), (4) is reduced to:

$$W(n,m)/W(m,n) = \exp(\beta (G(n) - G(m) - \mu (n - m))) \qquad (5)$$

It follows from (5) that trajectories crossing the critical size (the maximum of $G(n) - \mu n$) have low probabilities. If all the trajectories starting at n_0 finish only at $n_{\min}$ or only at $n_{\max}$ then n_c lies correspondingly to the right or to the left of n_0.

If the dependence of $\exp(-G(n, p, T)/kT)$ on n is sufficiently strong then it would be enough to account only for square terms in the expansion of $G(n, p, T)$ over n. While calculating the nucleation rate, it becomes possible to estimate the critical size as the centre of the interval of initial numbers n_0 where in a finite portion of Markov trajectories both the extinction of a cluster or its overfilling take place. The same consideration is valid if we vary the input parameter μ instead of n_0. If it is still necessary to account for higher terms in $G(n)$ expansion it becomes unreasonable to seek the critical size - the nucleation rate depends on the whole profile of $G(n)$; however such a situation should be considered as an exotic case.

Numerical approbation

Figure 1 shows the results of generation of nonstationary Markov chains in μpT-ensemble for argon atoms. A "macrostep" includes one attempt to decrease and one

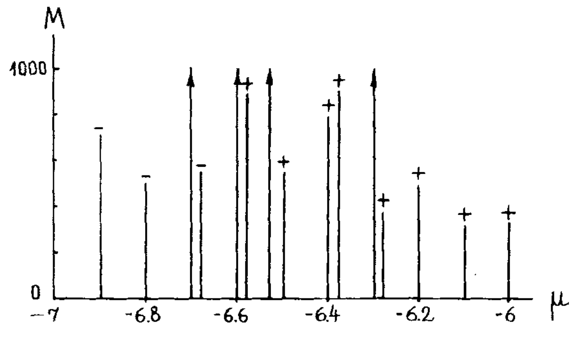

Figure 1 The lengths of nonstationary Markov chains in μpT ensemble at $p = 0.002$, $T = 0.51$, initial number of particles $n_0 = 27$, for different μ.

attempt to increase the number of particles by 1, ten attempts to move particles and forty attempts to vary the volume (spherical cell). The initial configurations were obtained by equilibration of the system in the ensemble with fixed number of particles (NpT-ensemble). Lengths of non-stationary pieces of Markov chains finishing at the absorbing states are represented. The cases in which the system "disintegrated" ($n = n_{\min} = 1$) or the particle number reached $n_{\max} = 2n_0$ are designated correspondingly by " – ' and " + " (all the results here and further are represented in dimensionless system of units with Planck constant h, Boltzman constant k, the Lennard-Jones parameters σ and ε being equal to 1). The system either desintegrated or overfilled during several hundreds of macrosteps depending on given μ.

For the intermediate values $\mu = -6.5 \pm 0.2$ a nonstable equilibrium is observed corresponding to the critical size $n_c = 27$ for $p = 2.10^{-3}$ and $T = 0.51$ (Figure 1). Out of this interval the system proves to be very unstable. It is not difficult in principle to improve the estimated accuracy by getting larger statistics over the initial states. Instead of seeking μ for the given critical n_0 it is possible to determine the critical size for the given $\mu = \mu_g(p, T)$ by varying n_0, where μ_g is the chemical potential of gaseous phase.

Statistical error estimation

In order to estimate the error for the calculated μ consider an ensemble of pieces of nonstationary Markov trajectories with fixed μ. Distinguish the interval for μ: $[\mu_-, \mu_+]$ which includes comparable number of trajectories of all three types: desintegration, overfilling and a stop at a finite length of the trajectory (for shorter trajectories this interval would evidently widen). The average is determined by the centre of the interval $[\mu_-, \mu_+]$. The average value of μ over the finite portion of M trials has a dispersion $(\mu_+ - \mu_-)^2/M$ and the error $\delta\mu \sim \Delta\mu/\sqrt{M}$, where $\Delta/\mu = \mu_+ - \mu_-$, M is the number of trails inside this interval($\Delta\mu = 0.4$, $M = 9$ on Figure 1.)

So the physical meaning is attributed to an average over the ensemble of MC-trajectories. With the account of total number of microstates in the whole group of generated MC-trajectories, the computer effort for the estimated critical size is not greater than in a usual MC calculations of the configurational energy.

3. CALCULATION OF THE THERMODYNAMICAL PROPERTIES BASED ON MC-DATA

We consider two opportunities for calculation of thermodynamical characteristics of a cluster. The first is direct calculation in a statistical ensemble with the restrictions on the number of microstates, corresponding to the defintion of a cluster. The second is the calculation of characteristics for a small system without any restrictions and further restoration of the characteristics of clusters.

Let $Z\ (N,\ V,\ T)$ be the NVT-partition function in the approximation of point noninteracting clusters (Frenkel-Band approximation [1]) and $Z^{cl}\ (n,\ T)$ the configurational integral over internal degrees of freedom for the n -particle cluster. Then

$$Z\,(N,\,V,\,T) = \sum_{\{\nu_n\}:\ \sum_n \nu_n n = N} \Big(\prod_n \nu_n!\Big)^{-1} \Big(\prod_n (Z^{cl}\,(n))^{\nu_n}\Big) V^{\sum \nu_n} \tag{6}$$

The expression for the NpT -partition function is obtained from (6) by integration over the volume V of the macrosystem:

$$\begin{aligned} Y\,(N,\,p,\,T) &\equiv e^{-\frac{G\,(N,p,T)}{kT}} = \frac{p}{kT}\int_0^\infty \mathrm{d}V\, e^{\frac{-pV}{kT}}\, Z\,(N,\,V,\,T) \\ &= \sum_{\{\nu_n\}\,:\,\sum_n \nu_n\cdot n\, =\, N} \left(\Big(\sum_n \nu_n\Big)!/\prod_n \nu_n!\right)\cdot\left(\prod_n (Z^{cl}\,(n,\,T))\right)^{\nu_n} \left(\frac{kT}{p}\right)^{\sum_n \nu_n} \\ &= \sum_{\{\nu_n\}\,:\,\sum_n \nu_n\cdot n\, =\, N} \left(\Big(\sum_n \nu_n\Big)!/\prod_n \nu_n!\right) \exp\left(-\frac{\sum_n \nu_n\, G^{cl}\,(n,\,p,\,T)}{kT}\right) \end{aligned} \tag{7}$$

The most probable size distribution $\{\nu_n\}$ corresponds to the maximum term in the sum (7):

$$\begin{aligned} \nu_n &= \nu_1 \exp\left[\ln\left(\frac{kT}{p} Z^{cl}\,(n,\,T)\right) - n\cdot\ln\left(\frac{kT}{p}\cdot Z^{cl}\,(1,\,T)\right)\right] \\ &= \nu_1 \exp\left[-\frac{-kT\ln\left[\frac{kT}{p} Z^{cl}\,(n,\,T)\right] - \mu_{ig}\cdot n}{kT}\right] \end{aligned} \tag{8}$$

where μ_{ig} is the chemical potential for the ideal gas. If the interaction of clusters is accounted for in excluded volume approximation we obtain instead of (8):

$$v_n = v_1 \exp\left[- \frac{-kT \ln\left[\frac{kT}{p} \mathrm{e}^{-\frac{pv_n}{kT}} Z^{cl}(n, T)\right] - \mu_g \cdot n}{kT} \right] \tag{9}$$

where $\mu_g = - kT \ln[kT/p] + pv_1$ is the chemical potential of the gas, obtained in the excluded volume approximation, and v_n is the volume of the n-particle cluster. The expression under logarithm in the numerator of (9) represents NpT-partition function of a cluster with the fixed centre of mass:

$$y_c^{cl}(n, p, T) = \exp\left(-\frac{G_c^{cl}(n, p, T)}{kT}\right) = \frac{p}{kT}\int_{v_n}^{\infty} \mathrm{d}V\, \mathrm{e}^{-\frac{pV}{kT}} Z^{cl}(n, T)$$

$$= \exp\left(-\frac{pv_n}{kT}\right) Z^{cl}(n, T)$$

So the whole numerator in the exponent (9) represents the variation of the Gibbs free energy caused by formation of a cluster from the monomer gas - the isothermic-isobaric formation work of a cluster.

$$A(n, p, T) = - kT \ln\left[y_c^{cl}(n, p, T)\frac{kT}{p}\right] - \mu_g \cdot n$$

$$= - kT \ln\frac{kT}{p} + G_c^{cl}(n, p, T) - \mu_g n \tag{10}$$

It follows from (10) that it is the ensemble with the fixed centre of mass that should be used for a formation work calculation.

Fixation of the centre of mass brings some inconvenience in MC calculations. Elementary estimations based on considering a cluster as a spherical hard particle show that G_c^{cl} is related to G^{cl} in the following way:

$$G^{cl}(n, p, T) = G_c^{cl}(n, p, T) - kT \ln\frac{kT}{p\Lambda^3} + 0\left(\frac{pv_n}{kT}\right)^{1/3} kT$$

Difference between G^{cl} and $G_c^{cl} - kT \ln kT/p\Lambda^3$ per one particle in the kT units has an order of $\Delta = 1/n\,(pv_n/kT)^{1/3} \sim l_l/l_g$ where l_g, l_l are average interparticle distances in the gaseous and condensed phases correspondingly. In the region far from the critical point the small value of Δ is guaranteed.

In computer experiment, as a rule, we do not simulate a single cluster but an n-particle system at given p and T. Determination of G^{cl} on the basis of these data represents a separate problem. Suppose that we managed to determine the Gibbs free energy of the n-particle system. It is possible to find $G^{cl}(n, p, T)$ on the basis of the known $G(n, p, T)$ by solution of a system of equations, which could be produced from (7) by putting N equal to $1, \ldots n$. For instance for $n = 2$ we have:

$$\exp(-G(1, p, T)/kT) = \exp(-G^{cl}(1, p, T)/kT)$$

$$\exp(-G(2, p, T)/kT) = \exp(-G^{cl}(2, p, T)/kT) + [\exp(-G^{cl}(1, p, T)/kT)]$$

Therefore

$$G^{cl}(1, p, T) = -kT \ln\left(\frac{kT}{p\Lambda^3}\right)$$

$$G^{cl}(2, p, T) = -kT \ln\left[\exp(-G(2, p, T)/kT) - \left(\frac{kT}{p\Lambda^3}\right)^2\right]$$

The solution of (7) is difficult for big clusters due to combinatorial problems. However, for large n, it is possible to leave only two terms in the sum (7) with $\{\nu_1 = n, \nu_i = 0\}$ and $\{\nu_n = 1, \nu_i = 0\}$ corresponding to the extreme states of completely condensed or completely gaseous system. All the intermediate states are excluded. It corresponds to the fact that the phase coexistence is almost impossible even for small n in NpT-ensemble. As a result we obtain:

$$G^{cl}(n, p, T) = -kT \ln\left[\exp(-G(n, p, T)/kT) - \exp\left(-\frac{n \cdot \mu_g}{kT}\right)\right] \quad (11)$$

Systems with electrostatic interaction, where the formation of stable small clusters (ionic pairs, triads) is possible [2], demand a particular approach in application of such an approximation.

4. THE STATIONARY METHOD

Description

For numerical calculation of $G(n, p, T)$ it is convenient to use a special (contracted) μpT ensemble. In this ensemble the only allowed microstates are those with two possible particle numbers n: $n = m, n = m + 1$. The ratio of probabilities to find the system in the states with the allowed n remains the same as that in the complete ensemble

$$\frac{W(m)}{W(m+1)} = \exp(-\tilde{\mu}/kT) \exp(G(m+1, p, T) - G(m, p, T)) \quad (12)$$

The left side of (12) can be easily estimated by MC-method for the input $\tilde{\mu}$. So for $\mu(m, p, T) \equiv \Delta G(m + 1, p, T) = G(m + 1, p, T) - G(m, p, T)$ we obtain:

$$\mu(m, p, T) = \tilde{\mu} + kT \ln \frac{W(m)}{W(m+1)} \quad (13)$$

It is clear that the result for μ according to (13) should not depend on the input value of $\tilde{\mu}$. However the statistical error of the second term of (13) which has an order of $\delta W/\min(W(m), W(m + 1))$ attains minimum for $W(m) = W(m + 1)$. So the optimum value for $\tilde{\mu}$ is $\Delta G(m + 1, p, T)$. The initial arbitrary value of $\tilde{\mu}$ can be improved according to the preliminary estimation of μ.

The result of calculation is the chemical potential in the fixed n, p, T-point. It is possible to obtain the Gibbs potential by "integration" of such data:

$$G(n, p, T) = \sum_{m=1}^{n} \Delta G(m, p, T)$$

In the stationary method the involvement of a restricted submultitude of the microstates provides on one hand the stationary character of Markov chains and on the other hand concentrates computational efforts in a narrow range of n values. The nonstationary approach involves into MC-game a large number of microstates. It can quickly provide a general picture of microdrop stability. The stationary method pretends on high precision which can be achieved by the increase of the MC-chain length.

Results and discussion

The dependence of $\mu^{cl}(n) = \Delta G^{cl}(n + 1, p, T)$ obtained for $p = 0.002$, $T = 0.51$ is presented on Figure 2 and in Table 1. Two ways of determination of a cluster are compared. In the first approach, the Markov process and consequently the statistical averages involve only low-energy configurations with the potential energy of each particle less than $-3/2\,(n - 1/n)\,kT$ (the transition probabilities for other congfigurations are being made equal to zero). Such a method corresponds to the cluster definition introduced in [3]. In the second method the Markov process includes all the configurations. $G^{cl}(n)$ are being determined according to (7) on the base of the $G(n)$ data (Figure 3). As it is seen on Figure 2, $n_c = 17$ for the first cluster determination and $n_c = 22$ in the second case.

The p-T conditions Figure 2 correspond to conditions of the MD simulations of an argon microdrop in a spherical cavity [3]. Since the microdrop observed in [3] is in equilibrium with the gas, it should be considered as a critical nucleus. The stability of the equilibrium is caused by smallness of the system as a whole. The size of the nucleus in [3] for $p = 0.002$, $T = 0.51$ was estimated as 15.5 particles.

The results (Figure 3) correspond to the contracted μpT-ensemble in which the phase coexistence is impossible. If the ensemble parametres vary, the transition from one phase to another in the whole system occurs in a manner of a jump. It should be expected that at proper values of p and T and gradual increase of n there occurs a qualitative change – the transition from gaseous to liquid state – the drop formation.

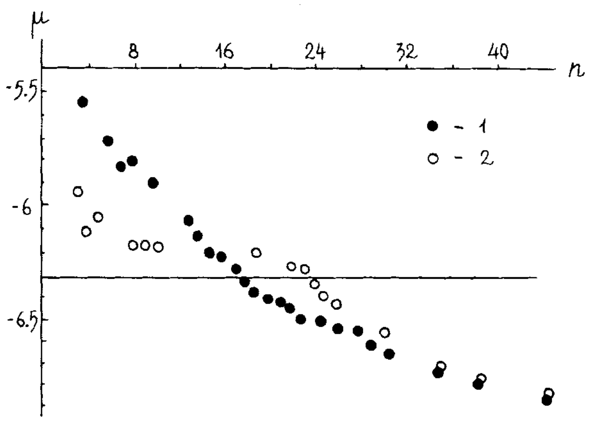

Figure 2 Dependence of the cluster chemical potential on the number of particles at $p = 0.002$, $T = 0.51$ 1-MC data in the ensemble with the restriction upon energy, 2-calculation according to (15), horizontal line-chemical potential of the gaseous phase.

Table 1 Dependence of the cluster chemical potential on the number of particles at $T = 0.51, p = 0.002$ (MC data in the ensemble with the restriction upon energy).

n	$\Delta G\ (n)$	n	$\Delta G\ (n)$
5	5.56	22	6.42
7	5.73	23	6.47
8	5.86	24	6.51
9	5.82	26	6.51
11	5.89	27	6.57
14	6.07	28	6.57
15	6.17	30	6.63
16	6.25	32	6.68
17	6.21	36	6.76
18	6.31	40	6.80
19	6.34	46	6.87
20	6.40	49	6.91
21	6.42		

This change should be expressed in n-dependence of chemical potential $\mu(n)$ as a break which we really observe on Figure 3. The chemical potential is constant to the left of this break and is equal to μ_{ig}. It is also seen that for pressure ten times greater-$p = 0.02$-the critical size becomes smaller (may be less than 1)-all the curve has a liquid drop character.

The value of the critical size obtained in μpT ensemble with the definition of a cluster similar to [3] differs from that of [3] by 1.5 atoms (see Figure 2). This difference slightly surpass the statistical error and is possibly caused by two reasons: the use of different ensembles and different ways of pressure calculations.

To compare MC calculations with the classical theory of capillarity (CTC), the chemical potential of an argon cluster at $T = 84°K$ was calculated. According to CTC chemical potential of a cluster at given p and T is defined as

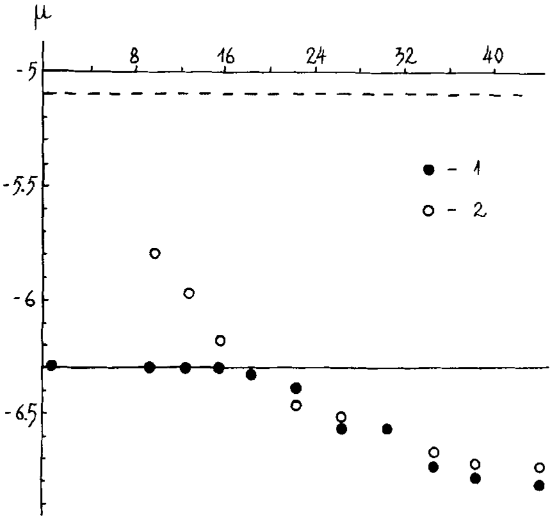

Figure 3 Dependence of the chemical potential on the number of particles at $T = 0.51$ and $p = : 1 - 0.002$, $2 - 0.02$; horizontal line-chemical potential of the gaseous phase: solid at $p = 0.002$, dots-at $p = 0.02$

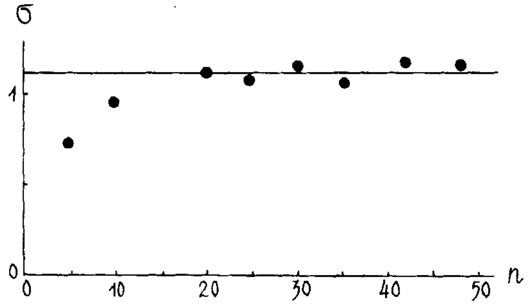

Figure 4 Dependence of the surface tension on the number of particles calculated from MC data according to (15); $T = 84°\mathrm{K}$, $p = 6p_0 =$ Horizontal line is the experimental data [7].

$$\mu\,(n, p, T) = \mu_0\,(p, T) + \left(\frac{\partial \mu_l}{\partial p}\right)_T \left(p - p_0 + \frac{2\sigma}{r}\right) \tag{14}$$

where p_0, μ_0 are pressure and chemical potential of the saturated vapor at given temperature, σ-surface tension, r-radius of the cluster, μ_l-chemical potential of the liquid phase at pressure p. Since $\partial\mu_l/\partial p = v'$ (where v' is the specific volume of the liquid phase) the equation (14) could be reduced to

$$\mu\,(n, p, T) = \mu_0\,(T) + v'\,(p - p_0) + \frac{8\pi\sigma}{3} v'^{2/3}\, n^{-1/3} \tag{15}$$

The experimental thermophysical properties of argon at 84°K are $p_0 = 0.7052$ bar (0.00168), $v' = 0.7075\,\mathrm{Dm}^3/\mathrm{kg}$ (1.197), $v'' = 241.2\,\mathrm{Dm}^3/\mathrm{kg}$ (408.1) [6] $\sigma = 13.5$ din/sm [7] where v'' is the specific volume of the saturated vapor. The chemical potential of the cluster was calculated by stationary MC procedure in the μpT ensemble with the restriction upon energy (see above). Then the values of σ were obtained according to (15) on the basis of the calculated values of μ. The results of MC calculations are in accordance with CTC (Figure 4).

5. STATIONARY METHOD IN μVT ENSEMBLE

Analogous to (13), it is possible to calculate Helmholtz free energy $F_c\,(n, V, T)$ in the contracted μVT ensemble. We carried out such calculations with fixed centre of mass in the volume $V = 45$ at $T = 0.50$. The initial configuration for each next n, V, T-point was obtained from the final configuration of the preceding one. There exists data in [4] for free energy of the same system. In [4] F_c was calculated in the ensemble with fixed centre of mass by a different and independent method-thermodynamical integration over volume: $F_c\,(13, V, T) = -65.75$. Our calculations for $n = 13$ in the contracted μVT ensemble gave the value $F_c = -65.62$ which does not differ from [4] within statistical error.

6. APPLICATION TO THE MACROSYSTEMS

It is possible to apply the contracted ensemble method to macrosystems according to the following scheme. Usual periodical boundary conditions [5] are imposed, the described above Markov chain in μpT ensemble with states $n = m$ and $n = m + 1$ in periodical box is being arranged, $\Delta G\,(m + 1, p, T)$ is calculated and m is increased by 1; the procedure is repeated until ΔG ceases to depend on m. This saturation level should be considered as the chemical potential $\mu\,(p,T)$ of the macrosystem.

For rough but quick estimation of the chemical potential it is possible to use the nonstationary method: collapse or overfilling of the periodical box could testify the nearest to the sought value of μ.

It should be pointed out that the idea of calculation of the free energy difference for two neighboring states can be carried out by variation not necessarily of n but of any other parameter. For calculation of $\Delta F = F\,(\alpha + \delta) - F\,(\alpha)$, were α is an arbitrary parameter, it is possible to arrange a statistical ensemble with the partition function

$$Z\,(\eta) = \int e^{\frac{\alpha\eta}{kT}}\,F\,(\alpha)\,\mathrm{d}\alpha$$

and organize a random walk in such a way, that only transitions between $\alpha + \delta$ and α states take place. Then the difference ΔF would be expressed analogous with (13):

$$F\,(\alpha + \delta) - F\,(\alpha) = \eta - kT\ln\frac{W\,(\alpha + \delta)}{W\,(\alpha)}$$

As an example consider calculation of the chemical potential by means of a smooth switching on of an additional particle. This method can be useful in the case of homogeneous periodical systems at considerable densities since the insertion and removal of a particle in a single MC step in such a case has too small probabilities (it presents no great problem in simulations of clusters as far as the birth and removal of particles could occur here in the peripheral areas of the cluster). Consider modified statistical ensemble (ηNpT) with the partition function:

$$K\,(\eta, n, p, T) = \int_0^1 \mathrm{d}\alpha\; \mathrm{e}^{\frac{\eta\alpha}{kT}}\,J\,(\alpha, n, p, T)$$

$$J\,(\alpha, n, p, T) = \frac{p}{kT}\int \mathrm{d}V\,\mathrm{e}^{-\frac{pV}{kT}}\frac{1}{\Lambda^{3n}\,n!}\left(\frac{V}{\Lambda^3\,n}\right)^{\alpha-1}\int \mathrm{d}\,x_1 \ldots \mathrm{d}x_n \exp$$

$$\left(-\frac{1}{kT}\left(\frac{1}{2}\sum_{i,j d\neq 1}\phi\,(x_i - x_j) + \sum_{j\neq 1}\psi\,(x_1 - x_j, \alpha)\right)\right) \tag{16}$$

where $\psi\,(x, \alpha)$ is a function of the switching parameter α and $\psi\,(x, 1) = \phi(x)$, $\psi\,(\chi, 0) = 0$. $J\,(\alpha = 0;1, n, p, T)$ is the NpT partition function with the number of particles $n - 1$ and n per periodical box. The ensemble with the partition function (16) corresponds to the smooth switching on of the first particle. The parameter η in (16) is the analogue of the chemical potential.

The chemical potential μ can be expressed in the following way:

$$\mu\,(p, T) = -\,kT\ln\,(J\,(1, n, \mathrm{p}, T)) + kT\ln\,(J\,(0, n, p, T)) \tag{17}$$

In order to obtain difference (17) we shall consider ηpT-ensemble with two values of α: $\alpha = \alpha_m$ and $\alpha = \alpha_{m+1}$, $0 \leqslant \alpha_m < \alpha_{m+1} \leqslant 1$ (the interval [0,1] is devided into M intermediate values of α). Number of particles n is supposed to be sufficiently large to provide independence of $\mu(p, T)$ on n. Each microstate in this ensemble is characterised by the volume of the system, particle configuration and by one of two neighbouring values of α: $\alpha = \alpha_m$, $\alpha = \alpha_{m+1}$. Transition probabilities between states should provide the distribution over α in the form

$$(V/\Lambda^3 n)^{\alpha-1} \exp(\eta\alpha/kT) \exp\left(-\frac{pV+E}{kT}\right)$$

where E is the instant value of configurational energy. It is convenient to choose the transition probabilities fulfilling the detailed balance condition in the form:

$$\frac{W_{\alpha_m \to \alpha_{m+1}}}{W_{\alpha_{m+1} \to \alpha_m}} = \left[\frac{V}{\Lambda^3 n} \exp \frac{\eta}{kT}\right]^{\alpha_{m+1}-\alpha_m} \mathrm{e}^{\frac{E_m - E_{m-1}}{kT}}$$

Transition probabilities with the change of volume in such an ensemble are also dependent on α, since the volume distribution is of the following form: $V^{\alpha-1} \exp(-pV/kT)$. Let W_{m+1}/W_m be the ratio of probabilities to find the system in the states with $\alpha = \alpha_{m+1}$ and $\alpha = \alpha_m$:

$$\frac{W_{m+1}}{W_m} = \exp(\eta(\alpha_{m+1} - \alpha_m)/kT) \frac{J(\alpha_{m+1}, n, p, T)}{J(\alpha_m, n, p, T)}$$

Then

$$-kT \ln \frac{J(\alpha_{m+1}, n, p, T)}{J(\alpha_m, n, p, T)} = \eta(\alpha_{m+1} - \alpha_m) - kT \ln \frac{W_{m+1}}{W_m} \tag{18}$$

The value of W_{m+1}/W_m in the right side of (18) is estimated in a MC run. Note that the values of η could be different for different m.

Ultimately the chemical potential of the system can be expressed as follows

$$\mu(p, T) = \sum_{m=0}^{M-1} \left[\eta_m(\alpha_{m+1} - \alpha_m) - kT \ln \frac{W_{m+1}}{W_m}\right]$$

7. CONCLUSION

Numerical approbation of the proposed open ensemble methods proved their effectiveness in applications. Comparison of our approach with other direct methods of chemical potential calculation [8] shows that is resembles the "particle insertion method" of Widom based on estimation of canonical average of the exp $(-\beta U)$, where U is the interaction of the trial particle with the rest particles of the system. It is known that the use of conventional (Boltzman) sampling in calculation of $\langle \exp(-\beta V) \rangle$ often results in a poor convergence as far as the most probable canonical ensemble microstates are far from the maximum of the averaged function. Therefore specific (nonboltzman) types of sampling are used, which preferentially involve phase regions located "between" n-particle and $n+1$-particle canonical ensembles (umbrella sampling). Our method is equivalent in some way to umbrella sampling, but the sampling is "physical" (Boltzman) and therefore possibly optimal.

The method for the cluster formation work calculation developed in this paper could be used in applications to heterogenous nucleation and adsorbtion on the flat surface or in the micropores.

APPENDIX

Algorithms for calculation of the chemical potential by the stationary and nonstationary methods in μpT ensemble.
In both (stationary and nonstationary) methods four types of steps were used: variation of volume, displacement of a particle, increasing and decreasing by 1 of the number of particles.

Variation of volume

1. A uniformly distributed in the interval $[-\Delta V, \Delta V]$ random number v is generated; $\Delta V = \text{const}$.
2. $V \to V + v$ (v is added to V).
3. If $V \leqslant 0$, the step is rejected (new state coincides with the previous one).
4. If $|\vec{x}_i| > R = (3V/4\pi)^{1/3}$, $i = 1 \ldots N$, the step is rejected.
5. A uniformly distributed in [0,1] interval random number C is generated.
6. If $\exp(-pv/kT) < C$, the step is rejected.

Displacement of a particle

1. Random vector $\vec{\xi}$, ξ_i ($i = 1,2,3$) uniformly distributed in $[-\Delta x, \Delta x]$ interval, is generated.
2. j-th particle, $j = 1 \ldots N$, is chosen with the uniform probability.
3. $\vec{x}_j \to \vec{x}_j + \vec{\xi}$

3A. If a system with the fixed centre of mass is being simulated, a new position of the centre of mass is calculated and difference between old and new position is added to all particle coordinates.

4. If $|\vec{x}_i| > R = (3V/4\pi)^{1/3}$, $i = 1 \ldots n$, the step is rejected.
5. A uniformly distributed in [0,1] interval random number C is generated.
6. If $\exp(-\text{new energy} + \text{old energy}/kT) < C$, the step is rejected.

Insertion of a particle

1. The $n + 1$-th particle is inserted into a cube centred at the coordinate origine and with the edge $2R$, $R = (3V/4\pi)^{1/3}$. The probability density of insertion is uniform. Attempts to insert a particle are repeated until the condition $|\vec{x}_{n+1}| < R$ is being fulfilled and this $\vec{x}_{n+1}$ is accepted as the position of new particle.

1A. For the fixed centre of mass $R = (3V/4\pi)^{1/3}(1 + 1/N)$ as far as the condition $|\vec{x}_{n+1}| \leqslant R$ is attained, the position of the centre of mass and all the coordinates are recalculated according to the point 3A of preceding step. After that the $|\vec{x}_i| \leqslant (3v/4\pi)^{1/3}$, $i = 1 \ldots N + 1$ condition is being tested. If it is not fulfilled the step is rejected.

2. A uniformly distributed in [0,1] interval random number C is generated.
3. If $\exp[\mu - (n + 1\text{-th particle energy})/kT] < C\ (N + 1)\Lambda^3/V$ the step is rejected.

3A. For the fixed centre of mass the right side of the previous inequality is $C \cdot (N + 1) . \Lambda^3/(V(1 + 1/N)^3)$

Removal of a particle.

The j-th particle, $1 \leqslant j \leqslant N$, is being uniformly randomly chosen.

1A. For the fixed centre of mass the centre of mass of the system excluding the removed particle is being calculated, the coordinates of all particles are being corrected and if $|\vec{x}_i| > R = (3V/4\pi)^{1/3}$, $i \neq j$, the step is rejected.

2. A uniformly distributed in [0,1] interval random number C is generated.
3. If exp (j-th particle energy $- \mu/kT) < C\ V/N\Lambda^3$ the step is rejected.

3A. For the fixed centre of mass the constant in the right side should be $C.V.(1 + 1/(N-1))^3/(N\Lambda^3)$.

The ratio of the four types of steps were chosen 20:5:1:1 In the nonstationary method steps with birth and removal of particles followed one after another randomly. In the stationary method the birth of a particle follows when the particle number is minimal and removal - if it is maximal. The regular order of birth and removal steps breaks the detailed balance principle and results in an error at least in the stationary method. Special studies of the convergence speed dependence on the ratio of the number of steps of different types (in the stationary method) were not carried out.

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