

Equilibrium Cluster-size Distribution in a Finite System

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1. Introduction

The theoretical aspect of the problem was studied in Refs [1—11]. The case $T, V, N = \text{const}$ was largely considered, where N = number of particles (atoms, molecules) in the system, T = temperature, V = volume occupied by the system. The natural potential in this case is the Helmholtz free energy (F).

The equilibrium state of the system is characterized by a certain size distribution of clusters. The authors of Refs [1—8] believed that the main features of this distribution can be elucidated by studying the free energy of the system, $F(a, j)$, calculated on the assumption that the system consists of a single cluster of size j and $N-j$ monomers (here and below we will use for short the notation $\vec{a} = (N, T, V)$). In so doing, the size-distribution function of clusters was assumed to be described by the Boltzmann relation as

$$(1.1) \quad f_i \sim \exp[-\beta F(\vec{a}, j)],$$

where $\beta = 1/kT$ and k is the Boltzmann constant.

It was shown that with transition from unsaturated vapour to supersaturated one, $F(a, j)$ changes its form from one-stable (with a minimum at $j=1$) to bistable (with minimums at $j=1$ and $j=j_s \sim N$). The appearance of the minimum at $j=j_s$ corresponds to the formation of a large stable cluster being in equilibrium with the ambient vapour. It represents a new phase. In accordance with (1), the distribution function acquires a two-peak form instead of a one-peak form for unsaturated vapour.

Besides, the states in which the system contains several clusters of identical size (and the other particles as monomers) were considered in Refs [1, 8]. It was revealed that the free energy of such states, especially for large clusters, is considerably higher than the above free energy corresponding to the existence of a single cluster of the same size in the system. For that reason a probability for simultaneous presence of two and more large clusters in the system is to be small.

The described behavior of the cluster size distribution function agrees with computer simulation data, but in the qualitative aspect only. In particular, if we use the expression for $F(a, j)$ from Ref. [3] or [4,7] and formula (1.1) to calculate the value f_1/f_{j_s} , then for the conditions of Fig. 2 it will be by several orders smaller than in computer simulation [2, 4, 7].

The reason of such a discrepancy was ascertained in our previous works Refs [9, 10]. In the same papers a "one drop vapour" approximation adapting the Mayer cluster-expansion formalism to heterogeneous equilibrium state of a finite system was proposed, which allows us to remove the discrepancy. In the scope of the chemical reaction formalism a similar approximation was given by Hendriks [11].

In Refs [9, 10] an analytical solution describing mean number cluster size distribution function for high values of the system supersaturation was obtained. This paper presents calculation results in general case (from unsaturated to supersaturated vapour conditions).

2. General relations

The case $\vec{a}=(N, T, V)=\text{const}$ will be under consideration, to which corresponds a canonical ensemble. Following Mayer [12], we will write the partition function of the system in the form

$$(2.1) \quad Q(\vec{a}) = \sum_{\vec{N}} \prod_1^N q_j^{N_j} / N_j!$$

where q_j is the partition function of a cluster of size j , and N_j is the number of such clusters. We treat the Mayer clusters as physical ones, which seems reasonable, if the system is far enough from the critical point. In the simplest case when the particles are atoms,

$$(2.2) \quad q_j = (2\pi mkT/h^2)^{3/2j} V b_j,$$

where $b_j = b_j(V, T)$ are Mayer's cluster integrals, m is the atom mass, and h is Planck's constant [12]. The summation in (2.1) is taken with respect to all the possible sets $\vec{N}=(N_1, \dots, N_N)$ obeying the conservation condition

$$(2.3) \quad \sum_1^N j N_j = N.$$

Every term in the right side of (2.1) may be related to the probability for existence of the set of clusters \vec{N}

$$(2.4) \quad P(\vec{N}|\vec{a}) = \frac{1}{Q} \prod_1^N q_j^{N_j} / N_j!$$

Then, the size distribution function of clusters is defined by the expression

$$(2.5) \quad f(N_j|\vec{a}) = \sum_{\vec{x}} \delta(N_j - x_j) P(\vec{x}|\vec{a}),$$

and the mean number cluster size distribution function is

$$(2.6) \quad f(j|\vec{a}) = \sum_{N_j} N_j f(N_j|\vec{a}).$$

Here $\delta(\dots)$ is Kronecker's symbol. The first one obeys the condition $\sum_1^N \sum_{N_j} f(N_j|\vec{a}) = 1$,

and the second one that of $\sum_j j f(j|\vec{a}) = N$.

3. Formalism of the conditional free energies

For convenience of the interpretation of the results we will use the formalism of Ref [10]. It is the following.

Bearing in mind well-known relation $\exp [-\beta F(\vec{a})] = Q(\vec{a})$, where $F(\vec{a})$ is the free energy and $Q(\vec{a})$ is the partition function of the system, every term in the right side of (2.1) may be considered as the conditional free energy corresponding to the existence in the system of a set of clusters \vec{N}

$$(3.1) \quad \exp [-\beta F(\vec{a} | \vec{N})] = \prod_1^N q_j^{N_j / N_j!}.$$

Then (2.4) takes the Boltzmann relation form

$$(3.2) \quad P(\vec{N} | \vec{a}) = \exp \{ \beta [F(\vec{a}) - F(\vec{a} | \vec{N})] \}.$$

In a similar manner it is possible to introduce the conditional free energy corresponding to the existence of N_j clusters of size j in the system

$$(3.3) \quad \exp [-\beta F(\vec{a} | N_j)] = \sum_{\vec{x}} \delta(N_j - x_j) \exp [-\beta F(\vec{a} | \vec{x})]$$

with allowance for which (2.5) takes the form

$$(3.4) \quad f(N_j | \vec{a}) = \exp \{ \beta [F(\vec{a}) - F(\vec{a} | N_j)] \}$$

and the conditional free energy corresponding to the existence of a cluster of size j

$$(3.5) \quad \exp [-\beta F(\vec{a} | j)] = \sum_{N_j} N_j [-\beta F(\vec{a} | N_j)],$$

so (2.6) may be written as

$$(3.6) \quad f(j | \vec{a}) = \exp \{ \beta [F(\vec{a}) - F(\vec{a} | j)] \}.$$

The last relation shows that formula (1.1) should include $F(\vec{a} | j)$ (3.5) instead of $F(\vec{a} | j)$. These values are different: $F(\vec{a} | j)$ is calculated with respect to all the states of the system in which it contains a cluster of size j , and $F(\vec{a}, j)$ is only with respect to the states in which there are no other clusters in the system but of size j . It is clear that for a heterogeneous equilibrium state of the system, when a large cluster of size $\sim N$ exists, the difference between $F(\vec{a} | j)$ and $F(\vec{a}, j)$ for small j will be considerable. For that reason, if we use formula (1.1), there appears the aforementioned discrepancy between the numbers of small and large clusters.

To perform detailed calculations, it is necessary to work out a procedure of summation with respect to \vec{N} and to specify the form of q_j .

4. Summation procedure

A procedure of the summation in (2.1) is complicated by the conservation condition (2.3). For that reason one prefers to deal with the grand canonical ensemble, for which a number of particles in the system is allowed to be unlimited [12]. As a consequence, it is naturally assumed that there exist clusters of however large size and, moreover, there are many such clusters. The latter makes it possible to use the method of most probable distribution to find the size distribution of clusters.

In a real system the cluster size cannot exceed the number of particles in the system, N , and the number of clusters of size $\sim N$ must be ~ 1 . For unsaturated vapour such a difference between the real system and the grand canonical ensemble is not important, since the ground state of the system is occupied by monomers, and the probability of the appearance of large clusters is extremely small. The situation drastically changes with transition to supersaturated vapour. Here the system in the ground state contains clusters of size $\sim N$, therefore they should be considered carefully.

For that purpose we use the "one drop-vapour" approximation [9, 10]. In accordance with the approximation it is proposed that in the heterogeneous equilibrium state the system contains only one cluster of size $\sim N$ which can fluctuate in size (it will be referred to as a drop and the number of particles in it will be denoted g). The remaining particles as monomers and small clusters make up the ambient vapour (they will be denoted i).

Here, in contrast to Refs [9, 10], we shall consider the whole interval of the system supersaturation, in particular, unsaturated vapour. Therefore, every term in the right side of (2.1) may be written as

$$(4.1) \quad \prod_1^N q_i^{N_i} / N_i! \quad \text{or} \quad q_g \prod_1^{i_0} q_i^{N_i} / N_i!.$$

The first form is related to unsaturated vapour and the second does to supersaturated one. The upper limit of the summation for the second form is determined by the conservation law

$$(4.2) \quad \sum_1^{i_0} i N_i + g = N.$$

Note that here $i_0 < g$.

For small clusters it is possible to assume that $N_i \gg 1$. Therefore, using the Stirling formula $N_i! \approx (N_i/e)^{N_i}$ and applying the Lagrange multipliers method to (4.1) (i. e. varying the expressions (4.1) with respect to N_i under corresponding conditions (2.3) or (4.2)), we can find the most probable sets \tilde{N}_i which mainly contribute to (2.1). In this way we obtain [10]

$$(4.3) \quad \tilde{N}_i = q_i \exp(\beta i \mu_1),$$

where μ_1 is the chemical potential of the vapour.

Thus, the relation (2.1) may be written as

$$(4.4) \quad Q(\vec{a}) = \prod_1^N q_i^{\tilde{N}_i} / \tilde{N}_i! + \sum_{g=2}^N q_g \prod_{i=1}^{i_0} q_i^{\tilde{N}_i} / \tilde{N}_i!$$

or, in terms of the conditional free energies, as

$$(4.5) \quad \exp[-\beta F(\vec{a})] = \exp[-\beta F(\vec{a} | \tilde{N}_1, \dots, \tilde{N}_N)] \\ + \sum_{g=2}^N \exp[-\beta F(\vec{a} | \tilde{N}_1, \dots, \tilde{N}_g, 1 g)].$$

5. The form of q_j

To define q_j (2.2) we use the modification of the capillary approximation given in Ref [9]. In accordance with it

$$q_j = V n_\infty \exp \{ -\beta [\mu_{l_\infty} j + \alpha (j^{2/3} - 1)] \}.$$

Here μ_{l_∞} is the chemical potential of the liquid, $n_\infty = n_\infty(T)$ is the density of saturated vapour, and

$$\alpha = (36\pi v_{l_\infty}^2)^{1/3} \gamma_\infty,$$

where v_{l_∞} is the volume per molecule in the liquid and γ_∞ is the surface tension. The index ∞ means that the values refer to the bulk liquid phase.

If we take into account the well-known relation $\mu_1 \approx \mu_{l_\infty} + kT \ln \left(\frac{N_1}{n_\infty V} \right)$, the expression for q_j may be written as follows:

$$(5.1) \quad q_j = \tilde{N}_1 \exp \{ -\beta [\mu_{l_\infty} (j-1) + \mu_1 + \alpha (j^{2/3} - 1)] \}.$$

Then, (4.3) takes the form

$$(5.2) \quad \tilde{N}_i = \tilde{N}_1 \exp \{ -\beta [(\mu_{l_\infty} - \mu_1) (i-1) + \alpha (i^{2/3} - 1)] \}.$$

6. Expressions for the conditional free energies and mean number cluster size distribution function

The expressions for the conditional free energies may be found by matching (4.4) against (4.5). Using the Stirling formula for $\tilde{N}_i!$ and replacing q_j and \tilde{N}_i by corresponding expressions (5.1) and (5.2), we obtain

$$(6.1) \quad F(\vec{a} | \tilde{N}_1, \dots, \tilde{N}_N) = \mu_1 N - kT \sum_1^N \tilde{N}_i$$

$$(6.2) \quad F(\vec{a} | \tilde{N}_1, \dots, \tilde{N}_g, 1, g) = \mu_{l_\infty} (g-1) + \mu_1 + \alpha (g^{2/3} - 1) \\ + \mu_1 (N-g) + kT \ln (1/\tilde{N}_1) - kT \sum_1^{i_0} \tilde{N}_i.$$

Note that the last terms in (6.1) and (6.2) correspond to pV , where p is the pressure.

To make those expressions ready to use, it is necessary to define the values μ_1 , \tilde{N}_1 and $\sum \tilde{N}_i = pV$ depending on the number of the particles in vapour phase $N_V = \sum i \tilde{N}_i$, which (with allowance for (2.3) and (4.2)) takes the meanings N and $N-g$ for (6.1) and (6.2), respectively.

For that purpose we use the equation of state for nonideal gas taking into account the second virial coefficient

$$(6.3) \quad pV = N_V kT (1 + B_2 N_V/N).$$

This approach is equivalent to the consideration of monomers and dimers, so on the other hand, we have

$$(6.4) \quad pV = kT (\tilde{N}_1 + \tilde{N}_2).$$

Then, solving the system of the equations (6.3) and (6.4) simultaneously with the relation $N_V = \tilde{N}_1 + 2\tilde{N}_2$, we obtain

$$(6.5) \quad \tilde{N}_1 = N_V(1 + 2B_2 N_V/V)$$

and

$$(6.6) \quad \tilde{N}_2 = -B_2 N_V^2/V.$$

The chemical potential of the vapour may be found by the integration of the thermodynamical relation $d\mu = -sdT + vdp$ along the line $T = \text{const.}$ With taking into account the condition $\mu_1 = \mu_{l\infty}$ at $N_V/V = n_\infty$, it gives

$$(6.7) \quad \mu_1 = \mu_{l\infty} + kT [\ln(N_V/n_\infty V) + 2B_2(N_V/V - n_\infty)].$$

The second virial coefficient B_2 in the relations (6.3), (6.5) and (6.7) is the well-known value, it may be found everywhere. Nevertheless, to make the model to be selfconsistent, we define B_2 directly according to the modified capillary approximation used. The substitution of (6.5) and (6.6) into (5.2) gives the expression

$$B_2 = -\exp[-\beta \alpha (2^{2/3} - 1)]/n_\infty.$$

Now we have all we need to determine the mean number cluster size distribution function $f(j|\vec{a})$ (3.6). The series of the relations (3.1), (3.3) and (3.6) with allowance for the expressions (5.2), (6.1)–(6.2) and the summation procedure results in the following expression for the conditional free energy corresponding $f(j|\vec{a})$

$$(6.7) \quad \begin{aligned} \exp[-\beta F(\vec{a}|j)] &= \tilde{N}_j(N) \exp[-\beta F(\vec{a}|\tilde{N}_1, \dots, \tilde{N}_N)] \\ &+ \sum_{g=2}^N \tilde{N}_j(N-g) \exp[-\beta F(\vec{a}|\tilde{N}_1, \dots, \tilde{N}_g, 1, g)] \\ &+ \exp[-\beta F(\vec{a}|\tilde{N}_1, \dots, \tilde{N}_j, 1, j)], \end{aligned}$$

where the value N_V is given as an argument of \tilde{N}_j . It should be noted here that in the first and second terms of the right side of (6.7) we must consider the values of \tilde{N}_j at $j \geq 2$ only because the values at $j=1$ have been taken into account by the last term. On the other hand, j must be smaller, of course, than the critical cluster size $j_* = j_*(N_V)$, which obeys the Kelvin equation (7.1) as the stable cluster size j_S (it corresponds to the first, smaller, root of the equation).

The free energy of the system $F(\vec{a})$ in (3.6) is determined by formula (4.5).

7. Results and brief discussion

The calculation results given below correspond to the conditions of computer simulation by Rao et al. [2]: particles are argonlike atoms, $T=84$ K, $N=128$ and 256. In accordance with the data in Ref. [2] we used for the calculation the values of $v_{l\infty} = 52.10^{-30} \text{ m}^3$ and $\gamma_\infty = 12.10^3 \text{ N/m}$.

Fig. 1 shows a behaviour of the function $[F(\vec{a}|j) - F(\vec{a})]/kT = -\ln f(j|\vec{a})$ for $N=128$. As one can see, a condensation in the system occurs at $S > 6.3$ and does not at $S < 6.3$. The value $S_c \approx 6.3$ is a critical one for given T and N .

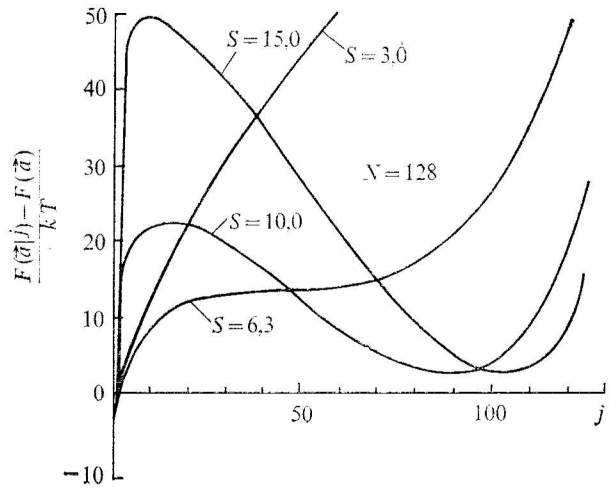


Fig. 1

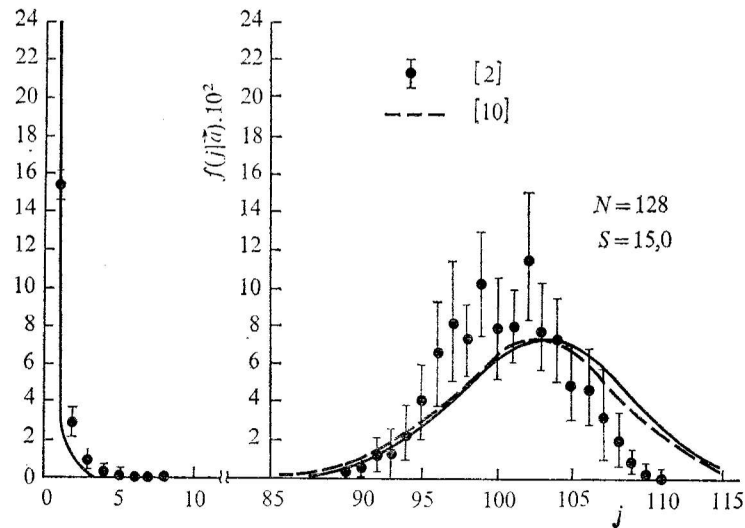


Fig. 2

At $S < S_c$ $F(\vec{a}|j)$ is consistent with $F(\vec{a}, j)$ considered by authors of the cited papers (see, for example, Refs [2, 6, 8]), but at $S > S_c$ there is the aforementioned discrepancy for small clusters. For illustration at $S=15.0$ the function is shown by the dashed line in which $F(\vec{a}|j)$ is replaced by $F(\vec{a}, j) = F(\vec{a}|N_1, \dots, N_b, 1j)$.

Fig. 2 gives a comparison of the mean cluster size distribution function calculated by using the data of Fig. 1 for $S=15$ with the computer simulation data of Ref. [2]. The analytical solution, obtained previously in Ref. [10], is the dashed line.

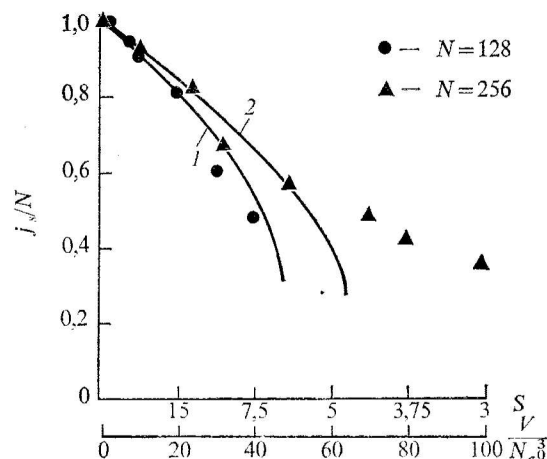


Fig. 3

Fig. 3 shows a stable drop size j_s corresponding to the minimum of $F(\vec{a}|j)$ at large values of j . With good accuracy it may be determined by the condition $\partial F(\vec{a}|\vec{N}_1, \dots, \vec{N}_l, 1j)/\partial j = 0$, which results in the Kelvin equation for non-ideal vapour:

$$(7.1) \quad \ln\left(S \frac{N-j_s}{N}\right) = \frac{2}{3} \frac{\alpha}{kT} j_s^{-1/3} - 2B_2 n_\infty S \left(1 + \frac{1}{N} - \frac{j_s}{N} - \frac{1}{S}\right).$$

The values j_s and S_c obtained from this equation show a good agreement with Fig. 1, as well as with the computer simulation results of Ref. [2] for $N=128$ (possible reason of the discrepancy for $N=256$ was pointed out in Ref. [10]).

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