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Treatment of Droplike Clusters in Nucleation Theory Using Reiss's Method

Ryoichi Kikuchi[1]

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The expression of the correction factor Φ in nucleation theory is derived by extending the method Reiss used recently. Φ is the factor appearing in the number of critical nuclei (formed as a vapor condenses into liquid drops) as a correction to the conventional theory. It is shown that $\Phi = p_l v_g/kT$, where p_l is the pressure of the liquid phase inside the drop, v_g is the volume per molecule in the vapor phase, k is the Boltzmann constant, and T is the absolute temperature. The difference between this Φ and Reiss's expression is p_l, which replaces his p_g (the vapor pressure in equilibrium with the drop). The Φ derived in this paper is compatible with the expression $\Phi = v_g/v_l$ (v_l is the molecular volume in the liquid phase) previously proposed by the present author.

KEY WORDS: Nucleation; condensation; rate; partition function; clusters; surface layer; unstable equilibrium; fluid.

1. INTRODUCTION

In a recent publication,(1) Reiss reviewed the theory of condensation from supersaturated vapor into liquid drops and then, looking at the problem from a novel angle, proposed a theory which shed new light on the controversial "translation-rotation paradox." The point of issue is the expression of the number of critical-sized nuclei, particularly the preexponential factor in the expression. Since this factor comes often in our discussion, we will call it Φ. It corresponds to Γ_i/N in Reiss's Eq. (R25) (we write R to indicate the equation in Reiss's paper(1)). Historical background and the significance of Φ are found in Ref. 1. Reiss derived that Φ is expressed as

$$\Phi_R = p_g v_g/kT \tag{1}$$

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[1] Hughes Research Laboratories, Malibu, California.

where p_g (written as p_i in Reiss's paper) is the pressure required to compress the drop or the pressure of the gas in equilibrium with the drop, v_g is the volume per molecule in the gas phase, k is the Bolzmann constant, and T is the absolute temperature.

A remarkable consequence of Reiss's result is that the factor Φ_R reduces to unity when the drop is in equilibrium with the (supersaturated) vapor phase, since the vapor can be approximated as ideal. This fact further suggests that even when the drop is not in equilibrium with the vapor, the factor Φ_R is not expected to be much different from unity.

On the other hand, the present author(2) derived the following expression for Φ:

$$\Phi_K = v_g/v_l \tag{2}$$

in which v_l is the volume per molecule in the liquid phase. The purpose of the present paper is to propose a modification of Reiss's Φ_R and to reconcile the apparent discrepancy between Φ_R and Φ_K.

2. AN INEQUALITY TO BE OBEYED BY Φ

Reiss showed in his Eq. (R42) that the partition function of a vapor system that contains n_i drops of i molecules is written as

$$Q = \sum_{\mathbf{n}} \prod_{i} [(q_i)^{n_i}/(n_i!)] \tag{3}$$

where q_i is the partition function of a cluster of size i:

$$q_i = (V/i!\,\Lambda^{3i}) \int \cdots \int_{R_i} \exp(-\beta u_i)\, d\mathbf{r}_2' \cdots d\mathbf{r}_i' \tag{4}$$

The coordinate of the kth molecule is denoted by $\mathbf{r}_k$ and the relative coordinate with respect to the first molecule is written as $\mathbf{r}_k'$:

$$\mathbf{r}_k' \equiv \mathbf{r}_k - \mathbf{r}_1 \qquad \text{for} \quad k = 2, 3, \ldots, i \tag{5}$$

V is the volume of the vapor phase, Λ is the factor resulting from the momentum integral:

$$\Lambda \equiv h/(2\pi mkT)^{1/2} \tag{6a}$$

and

$$\beta = 1/kT \tag{6b}$$

We define that the integration range designated by R_i in (4) is over all possible relative configurations of the i molecules that are within a sphere of radius r and thus in the volume $v_i = 4\pi r^3/3$. Each relative configuration is counted only once; in other words, when two configurations are within the sphere and are superposable on top of each other, they are counted only once in R_i. With this definition of R_i, the partition function Q in (3) is proportional to the probability of finding a spherical drop of radius r. Reiss uses q_i in two meanings. Our q_i in (4) is different from his q_i defined in (R43) and (R37), but is exactly the mathematical expression of q_i in (R64).

Since the potential energy u_i of the i molecules is a function of $\mathbf{r}_2',\ldots,\mathbf{r}_i'$ and is independent of the absolute location of $\mathbf{r}_1$, the front factor V in (4) results when we linearly translate the first molecule $\mathbf{r}_1$, keeping a relative configuration fixed, over the entire volume V of the vapor phase.

We are interested in the relation between (4) and a second phase integral defined in (R50) and (R52):

$$q_i^{(d)} = (1/i!\,\Lambda^{3i}) \int_{v_i} \cdots \int \exp(-\beta u_i)\, d\mathbf{r}_1 \cdots d\mathbf{r}_i \tag{7}$$

The constraint on the integration indicated by v_i is that all i molecules are contained within a spherical surface of volume v_i. The integration is done for the i molecules, in contrast to (4), which is for the relative coordinates only. Reiss derived the following relation for q_i to be used in (3):

$$q_i = \beta p_g V q_i^{(d)} \tag{8}$$

Combining this with the general definition

$$\Phi = N^{-1} q_i / q_i^{(d)} \tag{9}$$

he obtained the expression Φ_R in (1).

In this section, we do not discuss the derivation of (8), but rather compare (8) with an inequality which q_i and $q_i^{(d)}$ should satisfy. We start with (7) and change coordinates to the relative coordinate system:

$$q_i^{(d)} = (1/i!\,\Lambda^{3i}) \int \cdots \int \exp(-\beta u_i)\, d\mathbf{r}_2' \cdots d\mathbf{r}_i' \int d\mathbf{r}_1 \tag{10a}$$

In the integral $\int d\mathbf{r}_1$, the relative coordinates $\mathbf{r}_2',\ldots,\mathbf{r}_i'$ are fixed and the configuration is linearly translated within the spherical boundary. How far the linear translation can be done depends on the configuration, and the volume within which $\mathbf{r}_1$ can move is denoted by $\hat{v}(\mathbf{r}_2',\ldots,\mathbf{r}_i')$. Thus, we write (10a) as

$$q_i^{(d)} = (1/i!\,\Lambda^{3i}) \int_{R_i} \cdots \int \exp(-\beta u_i)\, \hat{v}(\mathbf{r}_2',\ldots,\mathbf{r}_i')\, d\mathbf{r}_2' \cdots d\mathbf{r}_i' \tag{10b}$$

The limit of integration is the same as (4), as is indicated by R_i. Here, $\hat{v}(\mathbf{r}_2',\ldots,\mathbf{r}_i')$is the volume in which the first molecule can move while the entire i molecules linearly translate rigidly within the fixed spherical boundary. From its physical meaning, we maintain that $\hat{v}$ is roughly of the order of the volume per molecule in the condensed phase; however, for our present purpose, it is sufficient to take the absolutely safe upper limit of $\hat{v}$:

$$\hat{v}(\mathbf{r}_2',\ldots,\mathbf{r}_i') < v_i \tag{11}$$

which says that $\hat{v}$ is smaller than the entire volume of integration, i.e., the volume of the sphere. When we combine (11) with (10), we see

$$q_i^{(d)} < (v_i/i!\,\Lambda^{3i}) \int_{R_i} \cdots \int \exp(-\beta u_i)\, d\mathbf{r}_2' \cdots d\mathbf{r}_i' \tag{12}$$

Now, the integration part of the right-hand side is the same as the one in q_i in (4), so that we can derive

$$q_i^{(d)} < (v_i/V)\, q_i \tag{13}$$

Substitution of (13) in (9) leads to the inequality

$$\Phi > v_g/v_i = v_g/iv_l \tag{14}$$

The number on the right-hand side is 10^2 when we use the values for water vapor: $v_g = 4 \times 10^{-19}\ \mathrm{cm}^3$, $v_l = 3 \times 10^{-23}\ \mathrm{cm}^3$, and $i = 100$. As was commented in deriving (11), v_i is a vast overestimation of $\hat{v}$; a more reasonable value of $\hat{v}$ is the individal molecular volume v_l in the liquid phase. Φ_K in (2) is equivalent to saying that $\hat{v}$ can be equated to v_l.

We now notice that v_g/v_i in (14) and hence Φ do not become close to unity, contrary to Reiss's claim in his Section 5. The question why our estimate of Φ is different from Reiss's is anwered in the rest of this paper.

3. REVIEW OF REISS'S TREATMENT

We want to review the key steps of Reiss's treatment. The surface free energy, which Reiss did not explicitly take into account, will be included in the formulation.

Reiss wants to construct q_i in (4) using $q_i^{(d)}$ in (7). The latter is the partition function of a drop of i molecules contained inside a fixed spherical surface. When we move the sphere to a location not overlapping the previous sphere, we have another partition function $q_i^{(d)}$ made of states which are completely different from those in the previous $q_i^{(d)}$. Roughly speaking, q_i in (4) is obtained when we move the sphere around over all the volume V and sum up contributions from $q_i^{(d)}$ from each location of the sphere. In this summing-up process, however, care must be taken when two spheres overlap; when they do, states contained in two $q_i^{(d)}$'s are not necessarily different.

Suppose we shift the sphere from the location S_1 to S_0 in Fig. 1 and want to calculate the fresh contribution ΔZ to the partition function q_i. We define V_0 as the volume inside S_0 but outside S_1. The shaded area in Fig. 1 is a section of V_0. Now, ΔZ is a sum over states in which i molecules are within the sphere S_0 with an additional requirement that at least one molecule lies within V_0. It is written as

$$\Delta Z = Z[S_0] - Z[S_0 - V_0] \tag{15}$$

where $Z[S_0]$ is the partition function of i molecules when all of them are in the sphere

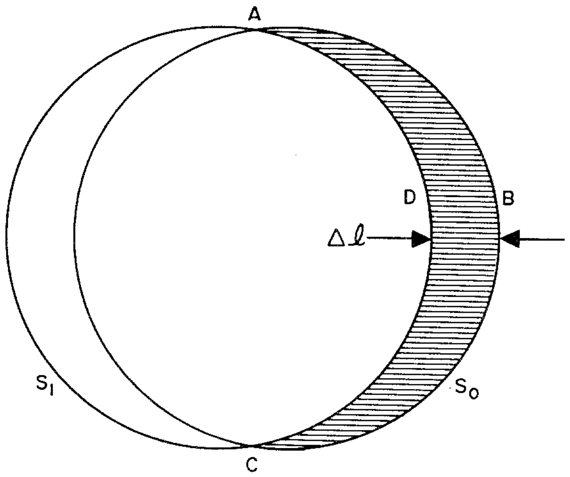


Fig. 1. Unit shift of a spherical drop.

S_0, and $Z[S_0 - V_0]$ is the corresponding partition function when the i molecules are in S_0 but outside of V_0.

By definition, $Z[S_0]$ is identical to $q_i^{(d)}$ in (7). It is written as

$$q_i^{(d)} = Z[S_0] = Z(v) = \exp[-\beta f(v) - \beta\hat{\sigma}(a)] \tag{16a}$$

where v is the volume of the sphere, $f(v)$ is the Helmholtz free energy of the interior, and $\hat{\sigma}(a)$ is the surface free energy. $\hat{\sigma}(a)$ depends on the surface area a, which in turn is a function of v. Although the shape of the volume $S_0 - V_0$ is slightly deformed from a sphere, we assume

$$Z[S_0 - V_0] = Z(v - \Delta v) \tag{16b}$$

where Δv is the volume of V_0. Substitution of (16) in (15) leads to

$$\Delta Z = [dZ(v)/dv]\,\Delta v = \beta(p_l\,\Delta v - \sigma\,\Delta a)\,Z(v) \tag{17}$$

where

$$p_l = -df(v)/dv \tag{18}$$

is the pressure inside the sphere, σ is the surface free energy per area, and Δa is the increase in area due to Δv.

When the drop is a sphere of radius r and when the distance of the shift is Δl as in Fig. 1, the volume change and the area increase are

$$\Delta v = \pi r^2\,\Delta l, \qquad \Delta a = 2\pi r\,\Delta l \tag{19}$$

Substitution of these in (17) leads to

$$\Delta Z = \beta p_g(\Delta v)\,Z[S_0] \tag{20}$$

where

$$p_g = p_l - (2\sigma/r) \tag{21}$$

It should be noticed that p_g in (20) is not the inside pressure p_l of the drop, but is the outside pressure which is in equilibrium with the drop.

We can also interpret the result (20) as follows. Suppose the surface ABC in Fig. 1 is pushed back quasistatically to the position ADC. During this process, any part of the surface is in equilibrium with the outside pressure p_g, and the work done on the surface, which is the increase in the free energy, is $p_g\,\Delta v$. The inside pressure p_l always balances with the surface tension and does not appear explicitly in the final expression.

ΔZ in (20) corresponds to a shift of Δl in Fig. 1, and represents a new term to be added to form q_i for the entire volume. When we repeat the Δl shift numerous times, the resulting shift is as shown in Fig. 2. At each Δl shift, the same analysis holds, so that the resultant contribution to q_i is the sum of ΔZ in (20) or the integral which is written as

$$\int \Delta Z = \beta p_g \pi r^2 L q_i^{(\bar{a})} \tag{22}$$

where Γ is the length of the total shift in Fig. 2 and $\pi r^2 L$ is the volume covered by the sphere. It should be noted that during this shift, the surface area increases by $2\pi r L$.

The relations (20) and (22) agree with (R56) and (R60), confirming that our procedure of treating the inside free energy $f(v)$ and the surface free energy $\hat{\sigma}(v)$ separately as in (16) is equivalent to Reiss's interpretation, although the latter treats the sum $f + \hat{\sigma}$ as the free energy of the droplet. So far, we have simply confirmed Reiss's result, and thus the question raised at the end of Section 2 remains unanswered. We now come to two- and three-dimensional constructions and see the difference.

4. OMISSION OF THE SURFACE TERM

It may be noticed that Fig. 2, by which we confirmed Reiss's result, is a one-dimensional construction. The volume covered by the linearly translating sphere forms a rod-shaped volume. In order to derive q_i which is for the entire volume, we must continue shifting the sphere in a three-dimensional volume.

For illustrative purposes, we show in Fig. 3 how a two-dimensional space is

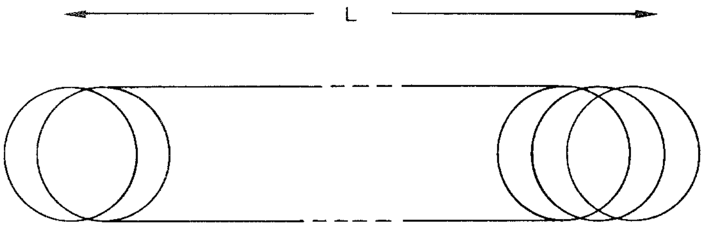


Fig. 2. One-dimensional shift of a spherical drop.

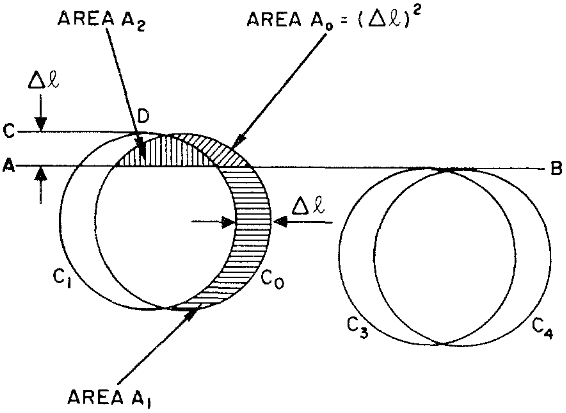


Fig. 3. Two-dimensional shift of a circle.

covered by shifting a *circle*. The part below the line AB has been covered by moving the circle as shown in $C_3 \to C_4$. After this, the circle is raised by Δl and the part below the line CD is covered. The circle C_1 is the last position of the circle.

Now, we move the circle to the right by Δl to the C_0 position. The area increase is the diagonally hatched part A_0, whose area is $(\Delta l)^2$. The important point which should be noted is that the surface length does not increase at all as the circle is shifted, because the surface curve after the rightward shift is exactly of the same shape as before, with the only difference being that the curve has shifted to the right by Δl, and this shift is equivalent to moving the length Δl from the AB line to the CD line. We can understand this also by measuring the arc lengths carefully; in Fig. 4, which is a close-up of circles C_1 and C_0 in Fig. 3, we see $\overset{\frown}{RQ} = \overset{\frown}{EP} = \Delta l$ and $\overset{\frown}{RE} = \overset{\frown}{QP}$.

We examine in detail ΔZ, which is the new addition to the partition function after the shift from C_1 to C_0 in Fig. 3 or 4. ΔZ is the sum of the Boltzmann factors

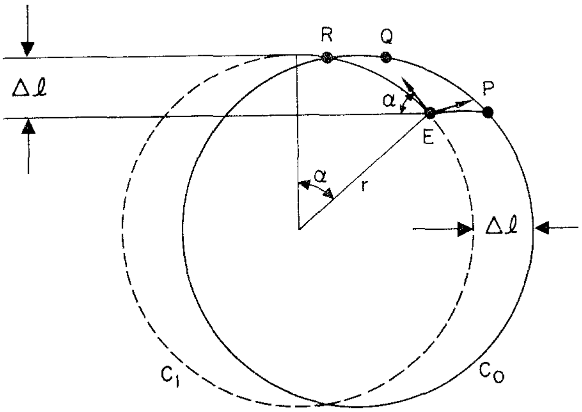


Fig. 4. Close-up of two circles C_0 and C_1 in Fig. 3.

contributed from configurations that have not been counted before, and our task is to count these new configurations. There are two categories of ΔZ, and we discuss them separately.

I. When at least one of the i molecules of a configuration lies in the area A_0 in Fig. 3, the configuration is new because the molecule lies outside of the previously covered area. When some molecules lie in the area A_1 (but none in A_0), this configuration was new in Fig. 1, but is not necessarily so in the present construction in Fig. 3 because any point in A_1 belongs to a circle (actually, to many circles) which has already been constructed below the line AB.

The new contribution ΔZ_I to the partition function is then

$$\Delta Z_I = Z[C_0] - Z[C_0 - A_0] \tag{23}$$

$Z[C_0]$ is the partition function for the whole circle C_0, which can be written, analogous to (16), as

$$Z[C_0] = Z(a) = \exp[-\beta f(a) - \beta\hat{\sigma}] \tag{24}$$

where a is the area of the circle and $\hat{\sigma}$ is the surface free energy. $Z[C_0 - A_0]$ is the partition function, i.e., the sum of the Boltzmann factors, of configurations contained in C_0 less the area A_0. The term $C_0 - A_0$ denotes not only the area, but also the shape of this area. The area difference between C_0 and $C_0 - A_0$ is $\Delta a = (\Delta l)^2$, as shown in Fig. 3. The surface length of the $C_0 - A_0$ figure is exactly the same as that of C_0, and the local radius of curvature of $C_0 - A_0$ is always the same as the radius r of C_0. The main difference between C_0 and $C_0 - A_0$ is the existence of a cusp E (Fig. 3 or 4) in the latter.

We now assume that $Z[C_0 - A_0]$ can be written also in the form of (24):

$$Z[C_0 - A_0] = Z(a - \Delta a) = \exp[-\beta f(a - \Delta a) - \beta\hat{\sigma}] \tag{25}$$

Then, we can differentiate to derive

$$\Delta Z_I = [dZ(a)/da]\,\Delta a = \beta p_l(\Delta a)Z[C_0] \tag{26}$$

where

$$p_l = -df(a)/da \tag{27}$$

It should be noted that the term corresponding to $\sigma\,\Delta a$ in (17) is missing because the surface length does not increase in the present shift, and hence p_l is the pressure inside the circle rather than the outside pressure p_g in (20). Another way of looking at (26) is that the pressure p_l (not p_g) is needed and the work $p_l\,\Delta a$ is to be done in order to compress starting from the whole circle and make a dent of the area A_0 to end up with the $C_0 - A_0$ shape.

The following objection may be raised. In the compressed shape $C_0 - A_0$, the radius of curvature is everywhere the same as r and hence the surface is balanced with the outside pressure p_g. Therefore, p_g, not p_l, must be enough to achieve the compression, with the consequence that the change of free energy must be $p_g\,\Delta a$ rather than $p_l\,\Delta a$ in (26).

This objection is anwered as follows. On the surface of $C_0 - A_0$, there is one point at which the surface tension and the pressures do not balance; this is the cusp point E. At E, the surface tension tends to pull the point back out to the circular surface. In other words, an extra work, beside $p_g(\Delta l)^2$, is required to push in the cusp point from the surface to the point shown in Fig. 3 or 4. This extra work w is shown in (30) to be $(\sigma/r)(\Delta l)^2$, which is equal to $(p_l - p_g)(\Delta l)^2$ in the two-dimensional circle. Thus, the total work done, which is the sum of $p_g(\Delta l)^2$ and $(\sigma/r)(\Delta l)^2$, is $p_l(\Delta l)^2$ as shown in (26).

The extra work w needed to push the arc $\overset{\frown}{QP}$ of Fig. 4 into the position $\overset{\frown}{RE}$ is calculated as follows. Suppose this pushing-in operation is done by sliding the arc $\overset{\frown}{QP}$ parallel to itself, keeping the point P on the arc $\overset{\frown}{CP}$. At the point E, the surface tension σ acts along two directions as shown by the arrows. The net horizontal component of these forces is $\sigma(1 - \cos\alpha)$, neglecting the higher-order effect due to the curvature of $\overset{\frown}{EP}$. Since the arc $\overset{\frown}{PQ}$ is slid parallel to itself, the net force acting on P at any point during the sliding operation is also $\sigma(1 - \cos\alpha)$. The work done against this component in bringing P to E is

$$w = \sigma(1 - \cos\alpha)\,\Delta l \tag{28}$$

On the other hand, the geometrical construction in Fig. 4 gives

$$\Delta l = r(1 - \cos\alpha) \tag{29}$$

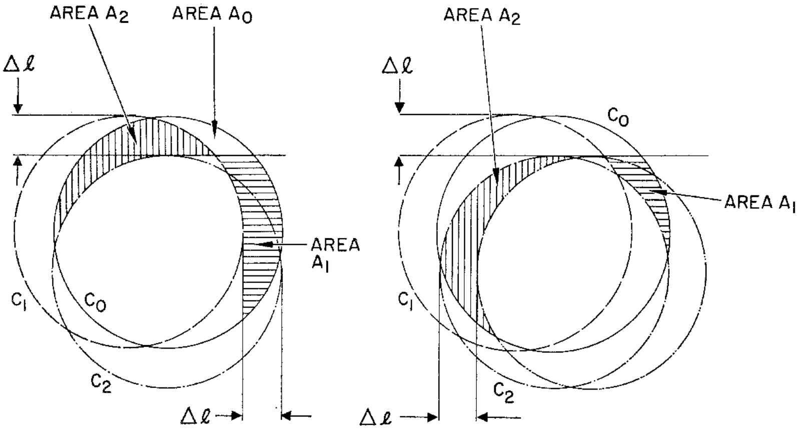
Combination of the two leads to

$$w = (\sigma/r)(\Delta l)^2 \tag{30}$$

Another objection may be raised, this time against (25). It may be argued that the internal free energy f in (24) or (25) may depend not only on the area of the figure, but also on its shape, particularly when the circle is of a microscopic size, since the dent A_0 has a sharp cusp. To the present author, this objection is a valid one and makes the result (26) questionable for a circle of small size. If the drop is small, the density fluctuation on the surface becomes large so that the dent we are interested in may be regarded as a natural occurrence. This means the work to be done to form the dent is expected to be much smaller than $(\sigma/r)\,\Delta a$, to result in a change of p_l to a smaller value. We will come back to this point again at the end of Section 5 and in the discussion in Section 6.

II. The second category of new configurations is made of those for which each molecule (of the i molecules in the configuration) belongs to one of the old circles but there are at least two molecules that are not covered by a *single* old circle. An example is based on the area A_k, $k = 0, 1, 2$, in Fig. 5(a) and satisfies the following three conditions simultaneously: (i) no molecule is in the area A_0, (ii) at least one molecule lies in the area A_1, and (iii) at least one molecule lies in the area A_2. Such a configuration is new because A_2 is inside the dashed circle while A_1 is outside, and a part of A_1 is inside the dot-dash circle while A_2 is outside.

The contribution ΔZ_{IIa} (to the partition function) due to the new configurations



(a) (b)

Fig. 5. Overlapping areas of three circles corresponding to Figs. 3 and 4.

defined in Fig. 5(a) is estimated in two steps. First, we calculate the contribution $\Delta Z'_{\text{IIa}}$ due to those configurations which satisfy the conditions (i) and (ii) only. This is evaluated as

$$\Delta Z'_{\text{IIa}} = Z[C_0 - A_0] - Z[C_0 - A_0 - A_1] \tag{31}$$

where $Z[C_0 - A_0 - A_1]$ is the partition function of configurations for which molecules are in the circle C_0 but outside of A_0 and A_1. The next step is to find the fraction of $\Delta Z'_{\text{IIa}}$ that is due to those configurations that which satisfy (i) and (iii) only. We estimate it by using a simple proportion:

$$\Delta Z_{\text{IIa}} = \Delta Z'_{\text{IIa}}(Z[C_0 - A_0] - Z[C_0 - A_0 - A_2])/Z[C_0 - A_0] \tag{32}$$

In order to evaluate these expressions, we assume a relation similar to (16a):

$$Z[C_0 - A_0] = Z(a) = \exp[-\beta f(a) - \beta\hat{\sigma}(s)] \tag{33a}$$

where a and s are respectively the area and the surface length of the $C_0 - A_0$ figure. $f(a)$ and $\hat{\sigma}(s)$ are the internal free energy and the surface free energy, respectively. We further assume

$$Z[C_0 - A_0 - A_1] = Z(a - \Delta a) = \exp[-\beta f(a - \Delta a) - \beta\hat{\sigma}(s - \Delta s)] \tag{33b}$$

When we examine Fig. 5(a), we see

$$\Delta a = r\,\Delta l + o(\Delta l), \qquad \Delta s = \Delta l + o(\Delta l) \tag{34}$$

where $o(\Delta l)$ is a small quantity of order higher than Δl. Combining (33) and (34), we derive

$$\begin{aligned} Z[C_0 - A_0] - Z[C_0 - A_0 - A_1] &= \beta(p_l\,\Delta a - \sigma\,\Delta l)\,Z[C_0 - A_0] \\ &= \beta p_g r(\Delta l)\,Z[C_0 - A_0] \end{aligned} \tag{35}$$

where we used

$$p_l = p_g + (\sigma/r) \tag{36}$$

for the circle.

We see that (34) holds for the difference between $C_0 - A_0$ and $C_0 - A_0 - A_2$ also, and hence (35) holds when A_1 is read A_2 on the left-hand side. Substitution of the original (35) and the modified one into (31) and (32) leads to

$$\Delta Z_{\text{IIa}} = (\beta p_g r\,\Delta l)^2\, Z[C_0 - A_0] \tag{37}$$

Comparing this with (26), we see

$$\Delta Z_{\text{IIa}}/\Delta Z_{\text{I}} = (p_g r^2/kT)(p_g/p_l) \tag{38}$$

Figure 5(a) is not the only case of category II; those configurations that satisfy the conditions (i), (ii), and (iii) based on Fig. 5(b) also belong to category II. We do not go into the details, but ΔZ_{IIb} and other contributions due to group II are of the same order of magnitude as ΔZ_{IIa} in (38). Thus, we may write

$$\Delta Z_{\text{II}}/\Delta Z_{\text{I}} = \alpha(p_g r^2/kT)(p_g/p_l) \tag{39}$$

where α is of the order of unity. Under ordinary circumstances, the ratio (39) is much smaller than unity, so that ΔZ_{I} in (26) is the main contribution. Comparison of (26) with (20) shows that Reiss's derivation is good for a one-dimensional construction but not for two, and suggests how the three-dimensional case is to be treated. It is done in the next section

5. THREE-DIMENSIONAL SPACE

In this section, we let the sphere cover a three-dimensional space. We move the sphere by Δl each time, and the center of the sphere occupies a lattice point of a simple cubic lattice as shown in Fig. 6. Due to the difficulty of drawing stacked overlapping spheres, we draw only their centers in Fig. 6. In each layer perpendicular to the z axis, the sphere is moved on a line parallel to the y axis ($A \to B$); after a line is finished, the sphere is shifted by Δl to the x direction and moved onto the next line ($C \to D$). After one layer is finished, the sphere is moved by Δl to the z direction and the next layer is covered. Figure 6 shows an intermediate stage where S_0 is the next position of (the center of) the sphere.

When we stack N spheres as is shown in Fig. 6, the total volume is $(\Delta l)^3 N$. Therefore, the new volume which is added when the sphere is shifted from S_1 to the S_0 position is

$$\Delta v = (\Delta l)^3 \tag{40a}$$

We will call this added volume V_0. As this volume is added, the surface area does not increase, because the situation is analogous to Fig. 3 for the two-dimensional case and the same surface area simply shifts position:

$$\Delta a = 0 \tag{40b}$$

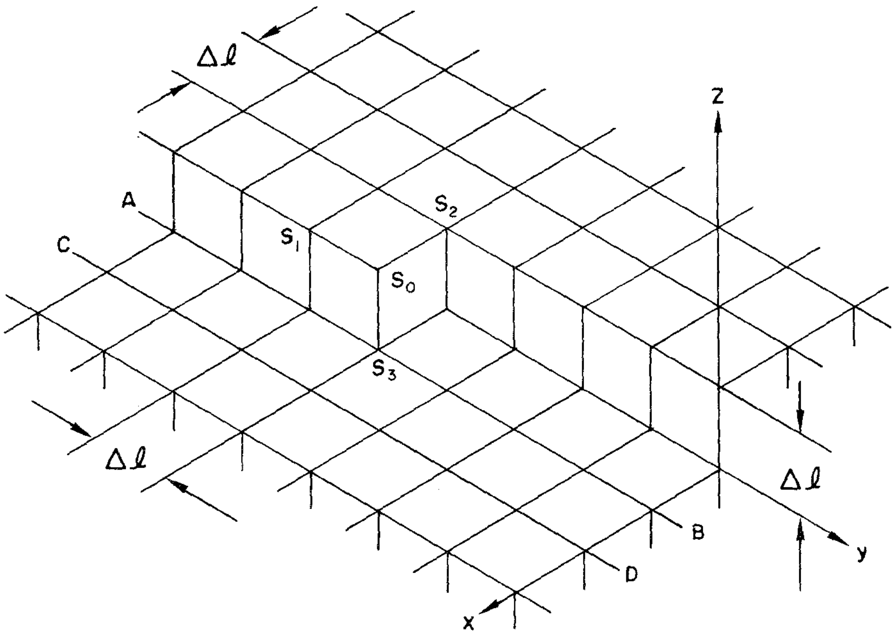


Fig. 6. Positions of the center of a spherical drop as it is shifted three-dimensionally.

The contribution to the partition function ΔZ_{I} by those configurations for which at least one molecule is in V_0 is calculated, using

$$Z[S_0] = Z(v) = \exp[-\beta f(v) - \beta\hat{\sigma}] \tag{41a}$$

$$Z[S_0 - V_0] = Z(v - \Delta v) = \exp[-\beta f(v - \Delta v) - \beta\hat{\sigma}] \tag{41b}$$

as

$$\Delta Z_{\mathrm{I}} = [dZ(v)/dv]\,\Delta v = \beta p_l(\Delta v)\, Z[S_0] \tag{42}$$

where $Z[S_0] = q_i^{(d)}$ is the partition function of i molecules when they are inside the sphere S_0, and p_l is defined in (18).

It is significant that p_g in (20) is now replaced by p_l. The appearance of p_l in (42) corresponds to the existence of the cusp-shaped edges on the corner volume V_0. As was discussed in Section 4.I, extra work is needed to push in the spherical surface against the surface tension, keeping the cusp-shaped edges. Working with straightforward but tedious geometry, we can prove that the extra work is $(2\sigma/r)\,\Delta v$, so that the total work done is

$$p_g\,\Delta v + (2\sigma/r)\,\Delta v = p_l\,\Delta v \tag{43}$$

In the two-dimensional case of the previous section, we showed that there were two categories of new configurations, I and II. The ΔZ_{I} calculated in (42) corresponds to category I. In the three-dimensional case, we can classify two other categories II and III. In understanding them, we define volumes V_k, $k = 1, 2, 3$, based on Fig. 6 such that V_k is the volume in the sphere S_0 but outside of the sphere S_k. Also, we define the volume V_{kl} as the volume common to V_k and V_l. An example of a configuration in group II contains at least one molecule in each of V_1 and V_{23} (and cyclic changes). A configuration in group III contains at least one molecule in each of V_k, $k = 1, 2, 3$. It does not seem worthwhile to go into the details of groups II and III, since contributions from them are negligible under ordinary circumstances as we saw in Section 4.II. Therefore, in the present discussion, we regard (42) as the total contribution to the partion function as the volume increases by Δv.

When the shift of the sphere is continued over the entire volume V of the system, the resultant contribution to q_i in (4) is the sum of (42):

$$q_i = \int \Delta Z_{\mathrm{I}} = \beta p_l V q_i^{(d)} \tag{44}$$

$Z[S_0]$ in (42) is the partition function of i molecules when all of them are in the sphere S_0, and is identified ith $q_i^{(d)}$ as in (16a). Equation (44) is the same as Reiss's result (18) except that his p_g is now replaced by p_l. Since q_i and $q_i^{(d)}$ in (44) are those used in defining Φ in (19), the new relation (44) leads to the revised expression

$$\Phi_R' = p_l v_g / kT \tag{45}$$

It is important to note that the macroscopic expressions are used for $Z[S_0]$ and $Z[S_0 - V_0]$ in (41), and in the differentiation procedure of (42). As was commented at the end of Section 4.I, when the size of a drop is microscopic, the expression of $Z[S_0 - V_0]$ in (41b) is particularly questionable because the surface has a sharp dent in it; it is likely that the argument presented in the last paragraph of Section 4.I works and p_l in (45) is to be replaced by a smaller value. In any event, the nature of the approximations involved in (41) should be clarified before the result (45) can be accepted with full confidence.

6. CONCLUDING REMARKS

What we have shown in this paper is that the "correction" factor Φ_R in (1) which Reiss derived should be written as Φ_R' in (45), the change being to replace Reiss's p_g, which is the pressure outside of a drop, by the inside pressure p_l. The basis of this change is the three-dimensional construction presented in Section 5 in contrast to Reiss's analysis, which is good only in a one-dimensional system shown in Section 3. The modified expression Φ_R' satisfies the required inequality presented in Section 2.

It is instructive to compare Φ_R' and Φ_K. Taking into account the fact that the nucleus of critical size is in equilibrium with the vapor phase, we can construct the chemical potential versus the pressure isotherm schematically as in Fig. 7. The difffference $\mu - \mu_0$ is

$$\mu - \mu_0 = \int_{p_0}^{p} (\partial \mu / \partial p)_T \, dp = \int_{p_0}^{p} v \, dp \tag{46}$$

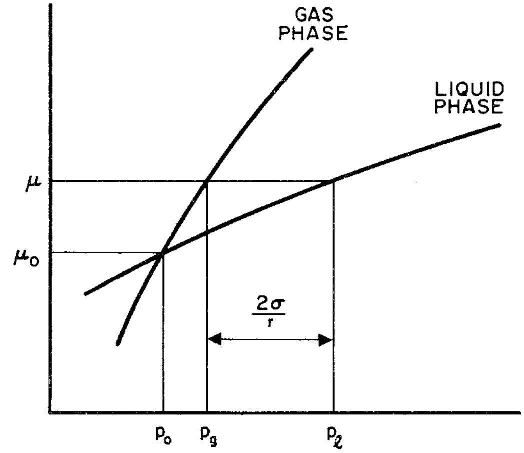


Fig. 7. Schematic illustration of the chemical potential versus pressure curves for the liquid and gas phases.

This can be calculated for the vapor phase and the liquid phase. For the former, we use the ideal gas equation of state, so that

$$\mu - \mu_0 = kT \ln(p_g/p_0) \tag{47}$$

For the liquid phase, we may use $v = v_l + v_l'(p - p_0)$ with constant v_l and v_l', so that

$$\mu - \mu_0 = v_l(p_l - p_0) + \tfrac{1}{2}v_l'(p_l - p_0)^2 \tag{48}$$

Usually, the right-hand side can be approximated by the first term $v_l p_l$. Equation (47) and (48), we obtain

$$\Phi_R'/\Phi_K = p_l v_l/kT = \ln(p_g/p_0) \equiv \ln S \tag{49}$$

The ratio p_g/p_0 is called the supersaturation and is often denoted by S; $\ln S$ is usually of the order of unity.(3) It may be noted that the relation (49) is used, by replacing p_l with $2\sigma/r$, in the form called the Thomson equation:

$$r = 2\sigma v_l/(kT \ln S) \tag{50}$$

to connect the size of the critical nuclei and the supersaturation.(4)

The ratio in (49) shows that the revised Reiss treatment Φ_R' and the author's previous expression Φ_K are compatible but not quite the same. The two expressions are greatly different when $\ln S$ is different from unity. However, it is not so bad as it looks. When $\ln S$ is less than unity, p_0 becomes important with respect to p_l in (48) and the right-hand side of (49) has additional positive terms; also, the configurations in categories II and III in Section 5 become important, as is seen from the right-hand side of (39). When $\ln S$ is large, however, the modified Reiss result (45) is questionable for the reason mentioned in the last paragraph of Section 5; it is reasoned that p_l is to be replaced by a smaller value to result in partly cancelling the ln S effect and hence in better agreement between Φ_R' and Φ_K in (49).

We do not imply that the author's previous result Φ_K is free from approximations. It is interpreted that both Φ_R' and Φ_K take advantage of simplifications made possible by approximations and emphasize different aspect of the problem. What exactly are the approximations in each method are still to be answered. Nevertheless, it is reassuring that the two methods. which proceed independently, lead to results which are essentially the same in cases of practical interest.[2]

As was described in the historial introductions in the papers by Reiss(1) and by the author,(2) the whole series of papers on the correction factor Φ were started by the proposal of the problem by Lothe and Pound.(5) They reasoned heuristically that the correction factor Φ is the ratio of the partition function for the translational and rotational degrees of freedom of a droplet to the partition function of the six degrees of freedom in the condensed phase and the value of Φ in a typical case is 10^{17}. The close agreement between Φ_R' in (45) and the previous result Φ_K in (2), both based on sound statistical mechanical ground, leaves no doubt that Φ_R' or Φ_K is the correct expression of the factor Φ except for possible future refinements. Acknowledging the credit to be given to Lothe and Pound for having stimulated the interest of the scientific community to the problem of the correction factor, we can now safely announce that the problem has been solved. We can thus repeat with more confidence the conclusion stated by Reiss in the last paragraph of Ref. 1: The controversy over 10^{17} is now replaced by a new challenging problem of evaluating the surface free energy of a droplet of a small size.

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[2] In a private communication, Dr. Howard Reiss agreed that this paper is the correct implementation of the program he initiated in Ref. 1 and he endorsed the result (45). The following observation of his contributed to this endorsement: Although the estimate of Φ using a thermodynamic cycle in the last section of Ref. 1 is valid as a consistency argument of his paper, it is to be modified in order to be compatible with the present analysis and thus does not contradict (45).