The Translation–Rotation Paradox in the Nucleation Theory

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The factor of 10^{17} proposed by Lothe and Pound in the theory of nucleation of droplets from the vapor phase is studied using classical statistical mechanics. The controversial factor Φ is derived from partition functions for an isolated n-mer and for an n-molecular cluster imbedded in the bulk liquid phase. The rotational degrees of freedom have no place in Φ, in agreement with Reiss, Katz, and Cohen's treatment. It is proved that the surface free energy of a cluster is proportional to the surface area. The estimate of what Lothe and Pound called the replacement term is different from those of previous authors. It is concluded that Φ is written as a ratio $\Phi = v_g/v_l$, where v_g and v_l are the volumes per molecule in the gas phase and in the liquid phase, respectively. For water at $300°K$, Φ is approximately equal to 10^4.

1. INTRODUCTION

The controversy over the factor of 10^{17} in the theory of nucleation of droplets which was started when Lothe and Pound[1] proposed the factor in 1962 does not seem to have come to an accord in spite of the efforts of many investigators. Lothe and Pound's claim[1-3] is that the classical theory of nucleation had missed a large factor attributable to translational and rotational degrees of freedom of a cluster. In the latest contribution to the issue, Reiss, Katz, and Cohen[4,5] (RKC) argued that the factor should be much smaller, between 3×10^3 and 10^6. The present paper examines the partition functions as was done by RKC, but with emphasis on different aspects.

As a preparation for the later discussion, the expression for the number of n-mers is derived in Section 2. The formula agrees with that of RKC. A "molecular volume theorem" is proved in Section 3 as a general property of classical partition functions for interacting particles. This theorem separates the translational degrees

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of freedom from the relative coordinates. In Section 4, the partition function of the n-mer is calculated starting from a bulk liquid phase and removing the "outside" molecules to infinity. The translational degrees of freedom in the partition function are treated using the molecular volume theorem. The expression for the controversial factor is derived. Section 5 reformulates the derivation in mathematical terms. The surface free energy is treated in Section 6, and comments on previous treatments are given in Section 7.

We treat molecules of a certain chemical species condensing from the vapor phase into liquid droplets. Since a molecule behaves as an integral entity in both the vapor and the liquid phases, the internal degrees of freedom of a molecule do not play any role in the condensation phenomenon, and hence will be disregarded.

A general property of the classical statistical mechanics is that the partition function (p.fn.) is separated into the momentum part and the configurational part. When the momentum part is integrated, each degree of freedom contributes a factor $(2\pi mkT)^{1/2}/h$, where m is the mass of a molecule and h is Planck's constant. Consequently,

$$\gamma \equiv (2\pi mkT/h^2)^{3/2} \tag{1}$$

multiplies each volume element of the configurational part to make the p.fn. dimensionless. In the rest of the paper, we understand that the momentum part of the p.fn. has been integrated, and our main attention will be directed to the configurational p.fn.

2. THE NUMBER OF n-MERS

We derive the expression for the number of n-molecular clusters (or the n-mers) in the vapor phase based on a simple cubic lattice whose lattice constant is infinitesimally small. This lattice actually represents the continuum space. The advantage of the lattice treatment is that the number of configurations can be counted easily.

An n-mer in this lattice is formed by placing n molecules on lattice points not far away from each other, so that each molecule is within the force range of at least one other member of the cluster. Different relative configurations of the n-mer are numbered by $i = 1, 2,...$. They are relative configurations in the sense that we do not count two configurations different when the two can be superposed by translation of the whole cluster; however, two configurations which can be superposed by rotation are counted separately.

Each configuration (of a cluster) which is counted separately is thus designated by two numbers: n and i. The number of (n, i) clusters in the system is written as $N_{n,i}$, and the potential energy contained in this cluster is denoted by $\epsilon_{n,i}$. The latter is the sum of intermolecular potentials over all pairs within the cluster. The total potential energy in the system is then

$$E = \sum_{n,i} \epsilon_{n,i} N_{n,i} \tag{2}$$

A configurational state of the whole system is defined by placing clusters over the lattice. When the set of numbers $\{N_{n,i}\}$ is given, the number of different states (of the

system) sharing the same set is given by the number of distributing these clusters over the lattice points

$$\Omega = \frac{\hat{N}!}{N_0! \prod_{n,i} N_{n,i}!} \, (v_0\gamma) ** \sum_{n,i} n N_{n,i} \tag{3}$$

where $\hat{N}$ is the total number of lattice points in the system, and N_0 is defined by

$$N_0 = \hat{N} - \sum_{n,i} N_{n,i} \tag{4}$$

The double asterisk is the FORTRAN notation for "raised to the power of." This Ω is the weight factor after the integration over the momentum space has been done, so that one factor γ defined in Eq. (1) appears for one molecule. Here v_0 is the volume per lattice point, and appears in Ω because each lattice point actually represents $v_0\gamma$ states. The combinatorial factor in Ω is not perfectly accurate, since overlaps of clusters are not avoided in the expression. This inaccuracy of counting configurations, however, is characteristic of the "droplet" model of nucleation theory and is acceptable for the early stage of nucleation, where the number and sizes of clusters are small.

The Helmholtz free energy F for the system is constructed using Eqs. (2) and (3) as

$$F = E - kT \ln \Omega - \mu \left[\sum_{n,i} n N_{n,i} - N_a \right] \tag{5}$$

Here, μ is the Lagrange multiplier, and the bracketed terms are added anticipating that F is to be minimized under the subsidiary condition

$$N_a = \sum_{n,i} n N_{n,i} \tag{6}$$

where N_a is the total number of molecules in the system.

The most probable distribution $\{N_{n,i}\}$ is derived by minimizing F with respect to $N_{n,i}$ keeping $\hat{N}$, T, μ, and N_a fixed:

$$N_{n,i} = N_0 (v_0\gamma)^n \exp(n\mu\beta - \epsilon_{n,i}\beta) \tag{7}$$

The meaning of μ is derived from Eq. (5) as

$$(\partial F/\partial N_a)_T = \mu \tag{8}$$

which indicates that μ is the chemical potential. The total number of n-mers N_n is obtained as a sum of $N_{n,i}$ over i:

$$N_n = N_0 e^{n\mu\beta} (v_0\gamma)^n \sum_i \exp(-\epsilon_{n,i}\beta) \tag{9}$$

The physical meaning of this is easy to understand. It is a sum of the Boltzmann

factors for all possible configurations of n-clusters including different orientations and different locations. The different locations are taken care of by the factor N_0. We rewrite Eq. (9) using the total volume of the system V:

$$V = \hat{N} v_0 \approx N_0 v_0 \tag{10}$$

where the last approximate equality is legitimate for the droplet model. Then Eq. (9) is written in the form

$$N_n = e^{n\mu\beta} V \gamma \sum_i (v_0 \gamma)^{n-1} \exp(-\beta \epsilon_{n,i}) \tag{11}$$

A more familiar way of writing Eq. (11) is in the integral form, since v_0 is an arbitrarily small volume. Reiss et al.[5] write the same equation in their Eqs. (10) and (14) as

$$N_n = e^{n\mu\beta} \frac{\gamma^n}{n!} V z_{\text{isol}} \tag{12a}$$

with

$$z_{\text{isol}} = n^3 \int \cdots \int d\mathbf{r}_1' \cdots d\mathbf{r}_{n-1}' \exp[-\beta \epsilon(\mathbf{r}_1',..., \mathbf{r}_{n-1}')] \tag{12b}$$

where $\mathbf{r}_j'$ is the coordinate of the jth molecule relative to the center of mass (the center-of-mass coordinate). The factor n^3 is the Jacobian. The division by $n!$ is necessary in order to make n particles indistinguishable. It is easy to interpret Eq. (11) or (12) and say that the sum or the integral in it is the p.fn. relative to the center of mass, and the V in front of it represents the mass motion. In the integral of Eq. (12b), the center of mass is regarded fixed at the origin. In this sense, z_{isol} or the sum in Eq. (11) may be called the *fixed-point p.fn.*, or the relative p.fn., and may be designated by $Q_{\text{FP}}^{(n)}$. The important characteristic of $Q_{\text{FP}}^{(n)}$ is that the translational degrees of freedom for the center of mass or the fixed point are not included in the p.fn.

In connection with this interpretation, it is noticed that the volume V in which the center of mass may move is normalized with γ, and the mass in this factor is m, as shown in Eq. (1). Then a legitimate question one may ask is, "Why is the mass associated with the mass motion in Eq. (11) or (12) the mass of a single molecule m rather than nm for the n-mer?" This question is answered in Appendix A.

It is to be noted that the configurational p.fn., z_{isol} in Eq. (12) or the corresponding sum in Eq. (11), contains different outside shapes of the n-mer. The need arises later for different shapes to be treated separately. Two outside shapes are defined as different when a part of the boundary differs more than l (the average intermolecular distance) after best effort to superpose them, not by a rotation, but by a linear translation.

3. THE "MOLECULAR VOLUME" THEOREM

Before proceeding to the next step of imbedding the n-mer in the liquid phase, we prove a theorem of general validity for classical partition functions. The theorem is stated as:

Theorem.   The configurational p.fn. of a homogeneous system of molecules is the product of the molecular volume and the fixed-point p.fn.

We first prove the theorem assuming the periodic boundary condition. The configurational p.fn. for a system of N molecules in a volume V is written as

$$Q = \frac{1}{N!} \int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 \cdots \int d\mathbf{r}_N \exp[-\beta\epsilon(N)] \tag{13}$$

where $\epsilon(N)$ is the potential energy of the N molecules and depends on the relative coordinates only. The $N!$ makes molecules indistinguishable. The $d\mathbf{r}_i$ integration is done in the volume V of the system. Under the periodic boundary condition, the result of integrations over $\mathbf{r}_2, ..., \mathbf{r}_N$ is independent of $\mathbf{r}_1$. Thus, we can write Q as

$$Q = \frac{V/N}{(N-1)!} \int_V d\mathbf{r}_2 \int_V d\mathbf{r}_3 \cdots \int_V d\mathbf{r}_N \exp[-\beta\epsilon(N)] \tag{14}$$

The number of molecules to be made indistinguishable is now $N - 1$, since the molecule No. 1 is fixed at the origin in the integration. Therefore, the integral divided by $(N - 1)!$ is the fixed-point p.fn., as defined in the previous section, and Q is proved to be the product of this quantity and the molecular volume V/N as the theorem claims.

We next examine the boundary which is not periodic. First, we note that the analysis in Eqs. (13) and (14) counts the number of independent configurations correctly, and the difference between the two boundary conditions lies only in the evaluation of the potential energy. The nonperiodic case can be derived from the periodic one by imposing an extra requirement that the interaction across the boundary vanishes. Or we may write

$$\epsilon_{\text{p.b.}} = \epsilon_{\text{non-p.b.}} + \epsilon_{\text{across}} \tag{15}$$

When the system is large, and hence the boundary area is large, the fluctuation of ϵ_{across} relative to the rest is small, so that we can justifiably neglect its variation for different configurations. Under this interpretation, we can apply the same analysis as Eqs. (13) and (14) to the nonperiodic boundary case by subtracting a constant value ϵ_{across} from the energy, to come to the same conclusion. Thus, the theorem is proved for the nonperiodic boundary condition also.

The physical interpretation of the theorem is as follows. We fix one of the molecules (to be called the center molecule) at the origin and consider all configurations made by moving around the remaining $N - 1$ molecules. The p.fn. constructed with these configurations is the fixed-point p.fn., Q_{FP}. When we *linearly translate* one of the configurations, the center molecule steps out of the origin, which is then left vacant. (In the *linear translation*, the system is treated as a rigid body with the relative distances of molecules in the configuration fixed, and then is moved parallel to itself, keeping the same orientation.) The configuration in which the origin is not occupied by a molecule is certainly distinguishably different from the one in which it is occupied. However, if the configuration is shifted too far, another molecule may come to the

origin, and then this configuration is not new any more, since it is one of the configurations counted in the p.fn. Q_{FP}. The volume in which the center molecule may move and still give rise to distinguishably different configurations of the system is roughly within a "molecular polygon" bounded by planes each of which bisects a line connecting the center molecule to one of its neighbors in the given configuration. The volume of this polygon is, on the average, equal to the volume per molecule $V/N = v_l$. Thus, we can say that distinguishably different configurations of the system are obtained when the center molecule, and hence the whole configuration, translates linearly within the molecular polygon whose volume is v_l on the average. Thus, the complete configurational p.fn., Q, is a product of v_l and Q_{FP}.

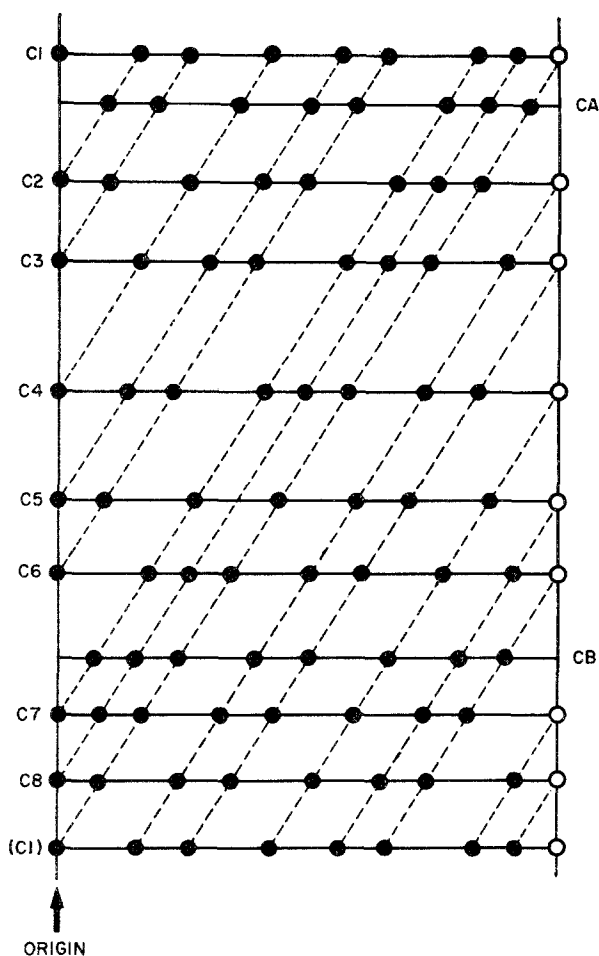The same technique can be used in deriving the volume v_l rigorously rather

Fig. 1. A linear translation in a one-dimensional system. A horizontal line defines a configuration. Dotted lines show how molecules shift. Since the periodic boundary is assumed, a molecule disappearing at the left reappears from the right.

than "on the average." If we move the center molecule in the entire volume V, during this process, all of the N molecules pass the origin one after another. This means the volume V is shared by N different fixed-point configurations, and thus the volume per configuration is rigorously $V/N = v_l$, as we wanted to show. An example of a one-dimensional system of eight molecules is shown in Fig. 1. In the configuration $C1$, a molecule sits at the origin (i.e., the left end of the system), and hence it is a fixed-point configuration. We shift $C1$ toward the left; dotted lines indicate traces of molecules. As $C1$ is shifted, configurations like CA emerge, which have not been counted in Q_{FP}. However, as the shifting continues, $C2$ appears, which is no longer new, since it is one of the fixed-point configurations counted in Q_{FP}. During the sweep of the entire length, $8v_l$ shown in Fig. 1, eight different fixed-point configurations $C1, C2,..., C8$ appear. Taking into account the fact that under the periodic boundary condition we have $\epsilon_{C1} = \epsilon_{C2} = \cdots = \epsilon_{C8} = \epsilon_{CA}$ and that these equalities also hold approximately when the boundary is not periodic, we can write

$$8v_l \exp(-\beta\epsilon_{C1}) = v_l[\exp(-\beta\epsilon_{C1}) + \exp(-\beta\epsilon_{C2}) + \cdots + \exp(-\beta\epsilon_{C8})] \quad (16)$$

as a contribution to the complete p.fn. The right-hand side is what is claimed in the theorem.

4. THE IMBEDDED CLUSTER

Our aim is to write the right-hand side of the expression (11) for N_n in terms of the free energy of the bulk liquid and of the surface tension of the droplet. For this purpose, we work on each shape of the n-mer separately. We pick up configurations $i = 1, 2,...$ of the prescribed shape of the isolated n-mer and place them inside the boundary of the same shape on the small-meshed lattice, which is the same as the one used in Section 2. These are the fixed-point configurations $Q_{FP}^{(n)}$ defined in Section 2. We then surround the cluster by additional N molecules over the rest of the lattice in such a way that a homogeneous liquid phase of the same density as the n-mer results. We call the molecules in the first-placed n-mer the "inside" molecules and those added the "outside" molecules. Different configurations of the N outside molecules are numbered by $I = 1, 2,...$. The configurations of $n + N$ molecules thus constructed exhaust all we need for the fixed-point p.fn., $Q_{FP}^{(n+N)}$. However, the following comment concerning the shape of the cluster should be noted.

Unless the shape of the inside cluster is prescribed, some of the outside configurations are counted more than once. As seen in Fig. 2, a configuration of the $n + N$ molecules is counted twice when a configuration B of the inside cluster is derived from another one A by removing one or more molecules C from A and adding the same number of molecules D to A. In this case, a configuration E (of the $n + N$ molecules) which contains A together with D contains both A and B. Then E is counted twice, once starting from A and adding N outside molecules to it (when the molecules D are part of the added N) and next starting from B (when the molecules C are part of the added N). The restriction that the outside shape of the n-cluster is no more different that the average intermolecular distance l anywhere on the surface, as was stated at the end of Section 2, prevents the possibility of including A and B

A : ● AND ✖

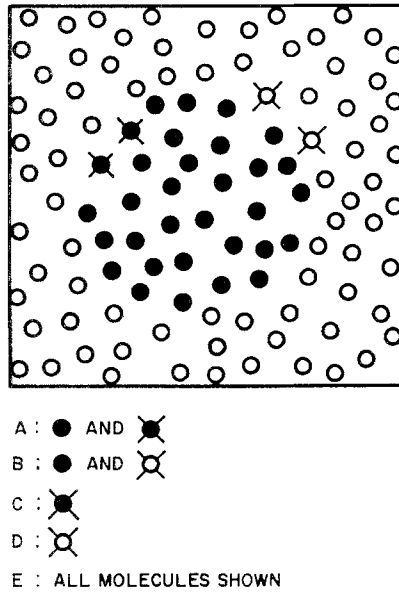B : ● AND ✖

C : ✖

D : ✖

E : ALL MOLECULES SHOWN

Fig. 2. An example of a configuration which is counted twice.

shown in the example as belonging to the same shape of the cluster. Therefore, when we deal with a prescribed shape of the cluster, each configuration is counted only once.

In order to conform with the proof of the molecular volume theorem, it is needed to place one of the molecules at a fixed point in space. We pick a certain point inside the cluster and call it the origin. When the origin is not occupied by a molecule in a configuration, we shift the configuration linearly so that a molecule which has located near the origin now occupies it. The shift can be less than half of the intermolecular distance l. Since no two configurations of the inside cluster are superposable by a linear translation, the one-to-one correspondence is maintained between the shifted and the original configurations. The shifted configuration is ready for the molecular volume theorem.

In order to write the p.fn. explicitly, we define ϵ_I for the potential energy of the Ith configuration of the outside molecules and $\epsilon_{i,I}$ for the potential energy between the ith configuration of the inside molecules and the Ith configuration of the outside molecules. (The two subscripts i and I have a different meaning from those in Section 2, but no confusion is expected.) Using these definitions, $Q_{FP}^{(n+N)}$ is written as

$$Q_{FP}^{(n+N)} = \sum_i v_0^{n-1} \exp(-\beta\epsilon_i) \sum_I v_0^N \exp[-\beta(\epsilon_{i,I} + \epsilon_I)] \qquad (17)$$

where $\sum_i$ sums over the $n-1$ inside molecules (since the center molecule is always at the origin) and the second summation goes over the outside N molecules.

The p.fn. for the whole system built by the n inside and N outside molecules can be written as $\exp[-\beta(n+N)f - \sigma A_{n+N}\beta]$, where f is a function of internal

variables only (of the density and the temperature), because each molecule is exactly equivalent on the average, except for the edge effect near the external surface. Here, σ is the surface tension, and A_{n+N} is the external surface area of the system. The molecular volume theorem tells us that the complete configurational p.fn. is written as $v_l Q_{\mathrm{FP}}^{(n+N)}$. Taking into account the momentum p.fn., we can then write

$$
\begin{aligned}
&\exp[-(n+N)\,f\beta - \sigma A_{n+N}\beta] \\
&= \gamma v_l \sum_i (\gamma v_0)^{n-1} \exp(-\epsilon_i \beta) \sum_I (\gamma v_0)^N \exp[-(\epsilon_{i,I} + \epsilon_I)\beta]
\end{aligned}
\tag{18}
$$

It is seen that for each three degrees of freedom, a factor γv_0 appears. Since $(n+N)f$ is the Helmholtz free energy for $n+N$ molecules, the chemical potential μ_l for a liquid molecule is related to f as

$$
f = \mu_l - pv_l
\tag{19}
$$

where p is the pressure. In our problem, μ_l for the liquid phase is smaller than μ in Eq. (8) for the vapor phase, so that the vapor condenses into liquid.

When the range of intermolecular interaction is finite, the molecules inside the cluster do not interact with those molecules that are far from the cluster. Therefore, it is expected that $e^{-nf\beta}$ for the cluster can be written in terms of the cluster itself and the surface term which is contributed from outside molecules in the neighborhood. For a given inside configuration i, we may sum over the outside configurations I and define the surface free energy $\hat{\sigma}_i$ as

$$
\exp(\beta\hat{\sigma}_i) = \sum_I (\gamma v_0)^N \exp[-\beta(\epsilon_{i,I} + \epsilon_I)]/\exp(-Nf\beta - \sigma A_{n+N}\beta)
\tag{20}
$$

The caret on $\hat{\sigma}_i$ indicates that it has a dimension of energy; the dimension of σ is energy per area. It is to be noted that Eq. (20) does not depend on γ, since $(\gamma v_0)^N$ in $e^{-Nf\beta}$ cancels the same in the numerator. Also, the edge effect near the external surface cancels on the right-hand side. Using the average surface factor of Eq. (20), we can transform Eq. (18) as

$$
e^{-nf\beta} = \gamma v_l \sum_i (\gamma v_0)^{n-1} \exp[-(\epsilon_i - \hat{\sigma}_i)\beta]
\tag{21}
$$

The separation of the whole system into two parts can be achieved by a boundary of any shape. Therefore, Eq. (21) holds for a cluster of any size n and any shape; also, it is exact, although it is not easy to evaluate $\hat{\sigma}_i$. When the infinite separation is taken as the zero of the potential energy, $\epsilon_{i,I}$ is negative; the sign in front of $\hat{\sigma}_i$ is so chosen that $\hat{\sigma}_i$ is positive.

If we move all the outside molecules away to infinity, the bonds $\epsilon_{i,I}$ across the surface are cut and the work $\hat{\sigma}_i$ has to be done. As is proved in Section 6, this work is proportional to the surface area of the cluster A_n and is the surface free energy (of the isolated cluster), which is written as

$$
\hat{\sigma}_i = \sigma A_n
\tag{22}
$$

Since the outside shape of the configurations in Eq. (21) is fixed, the surface free energy σA_n depends on i very little, so that we can bring this term to the front of the summation in Eq. (21) to write

$$\lambda_n \equiv \exp[-(nf + \sigma A_n)\beta] = \gamma v_l \sum_i (\gamma v_0)^{n-1} \exp(-\beta\epsilon_i) \qquad (23)$$

The summation in Eq. (23) is over the fixed-point configurations and is exactly the same as a part of the sum in Eq. (11) for the corresponding outside shape of the cluster. Elimination of the sum from the two equations leads to the expression

$$N_n = (V/v_l) \sum_{\text{shapes}} \Theta \exp\{-[n(f - \mu) + \sigma A_n]\beta\} \qquad (24)$$

where the factor Θ takes into account the orientation degeneracy. For a sphere, $\Theta = 1$. If we define the controversial factor Φ based on the spherical area $A_n^{(0)}$ as

$$N_n = \Phi N_a \exp\{-[n(\mu_l - \mu) + \sigma A_n^{(0)}]\beta\} \qquad (25a)$$

$$A_n^{(0)} = 4\pi(3nv_l/4\pi)^{2/3} \qquad (25b)$$

then the expression for Φ is

$$\Phi = (v_g/v_l) \exp(pnv_l\beta) \left\{ 1 + \sum_{\substack{\text{shapes} \\ \neq \text{ sphere}}} \Theta \exp[-(A_n - A_n^{(0)})\,\sigma\beta] \right\} \qquad (26)$$

where N_a is the total number of molecules and $v_g = V/N_a$ is the volume per molecule, both in the gas phase. In Eq. (26), v_l is the molecular volume, i.e., the volume per molecule, in the liquid phase, p is the pressure, and n the number of molecules in the cluster.

The orientation degeneracy factor Θ is estimated as follows. As was mentioned at the end of Section 2, two outside shapes of a cluster are not distinguishable unless they differ more than l. We divide the spherical surface $A_n^{(0)}$ into unit areas of l^2 and then count the number of different orientations the outside shape can take treating the solid angle $4\pi l^2/A_n^{(0)}$ as one distinguishable orientation. For example, if a surface of an n-mer has one molecule outside of a sphere, the number of distinguishable ways of orienting this shape is equal to the number of unit areas l^2 on the surface:

$$\Theta = A_n^{(0)}/l^2 \approx 5n^{2/3} \qquad (27)$$

Another example of Θ is schematically illustrated by the two shapes of a two-dimensional cluster in Fig. 3. The orientational degeneracy factor Θ_a for (a) is twice as large as Θ_b because (a) can be rotated for $360°$ to produce distinguishably different configurations, while (b) can be rotated only for $180°$ due to the twofold rotational symmetry of the figure.

For water at $300°$ K, the data are

$$v_g = 4 \times 10^{-19} \text{ cm}^3, \qquad v_l = 3 \times 10^{-23} \text{ cm}^3, \qquad \sigma = 70 \text{ dyn/cm} \qquad (28)$$
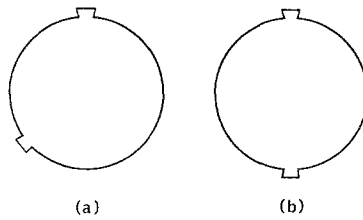
Fig. 3.   Two configurations of a cluster having different orientation degeneracies Θ.

Since we can approximately use the ideal-gas equation of state $pv_g\beta = 1$ for the gas phase, we see $pnv_l\beta \approx 10^{-2}$ for $n = 100$. Thus, the factor $\exp(pnv_l\beta)$ can be disregarded. When a boundary deviates from the spherical shape by the distance $l = v_l^{1/3}$ anywhere on the surface, the increase in the surface area is larger than the order of $2\pi l^2$ which causes the increase in the surface free energy of $2\pi l^2 \sigma/kT \approx 10$. Thus, the sum over nonspherical shapes in Eq. (26) can also be neglected, so that with a sufficient accuracy we can write

$$\Phi = v_g/v_l \tag{29}$$

For the data in Eq. (28), Φ has the value

$$\Phi = 10^4 \tag{30}$$

As a check of the consistency of our theory, we may examine a special case, when the cluster is a rectangular parallelepiped. In this case, the partition function of the cluster can be calculated without being imbedded in the matrix bulk liquid phase, since the steps in the proof of the molecular volume theory can be applied to the cluster itself. This procedure leads directly from Eq. (18) to Eq. (23) by disregarding the "outside" and putting $N = 0$; this shows the internal consistency of the theory.

5. ALTERNATIVE DERIVATION

In this section, we reformulate the results of the previous section using integrations. It is more mathematical, but may be more straightforward. The complete p.fn. for the $n + N$ molecules is written as

$$\exp[-(n + N)f\beta - \sigma A_{n+N}\beta] = \frac{\gamma^{n+N}}{(n+N)!} \int dr_1 \cdots \int dr_{n+N} \exp[-\beta\epsilon(n + N)] \tag{31}$$

where each integral goes over the entire volume of the system. As was done in Section 3 in the proof of the molecular volume theorem, we can do the integration of r_1 over the entire volume $(n + N)v_l$:

$$\exp[-(n + N)f\beta - \sigma A_{n+N}\beta] = \frac{\gamma^{n+N}v_l}{(n+N-1)!} \int dr_2 \cdots \int dr_{n+N} \exp[-\beta\epsilon(n + N)] \tag{32}$$

because this integral is independent of $\mathbf{r}_1$. Now we draw a boundary which contains the volume nv_l and also contains the origin, where the molecule No. 1 is always placed. We now divide $n + N - 1$ molecules into two groups of $n - 1$ and N, and place $n - 1$ molecules inside the boundary and N outside. The number of ways of choosing $n - 1$ molecules is $(n + N - 1)!/[(n - 1)!\,N!]$. Thus, Eq. (32) may be written as

$$\exp[-(n + N)f\beta - \sigma A_{n+N}\beta] = \gamma v_l \frac{\gamma^{n-1}}{(n - 1)!} \int d\mathbf{r}_2 \cdots \int d\mathbf{r}_n\, e^{-\beta\epsilon(n)}$$

$$\times \frac{\gamma^N}{N!} \int d\mathbf{R}_1 \cdots \int d\mathbf{R}_N \exp\{-\beta[\epsilon(n, N) + \epsilon(N)]\} \quad (33)$$

where $\epsilon(n, N)$ is the inside–outside interaction corresponding to $\epsilon_{i,I}$ in Eq. (18). The first group of integrations is over all the relative configurations of the n molecules inside the fixed boundary and exactly corresponds to the summation $\sum_i$ in Eq. (18). The second group of integrations is for the N outside molecules and corresponds to the sum $\sum_I$ in Eq. (18). Thus, Eq. (33) is the integral expression of Eq. (18).

The effect of the outside molecules on the inside cluster is written in the form of the surface free energy, defined as

$$\exp[\beta\hat{\sigma}(n)]$$

$$= \frac{\gamma^N}{N!} \int d\mathbf{R}_1 \cdots \int d\mathbf{R}_N \exp\{-\beta[\epsilon(n, N) + \epsilon(N)]\}/\exp[-Nf\beta - \sigma A_{n+N}\beta] \quad (34)$$

Use of Eq. (34) in Eq. (33) leads to

$$e^{-nf\beta} = \gamma v_l \frac{\gamma^{n-1}}{(n - 1)!} \int d\mathbf{r}_2 \cdots \int d\mathbf{r}_n \exp\{-\beta[\epsilon(n) - \hat{\sigma}(n)]\} \quad (35)$$

This relation is exact and holds for any shape of the inside cluster. If we remove the outside molecules to infinity, the work $\hat{\sigma}(n)$ must be done. The work is proportional to the surface area, and is written as σA_n. When σA_n depends little on the coordinates $\mathbf{r}_j$, we may take this out of the integral and write

$$\lambda_n \equiv \exp[-(nf + \sigma A_n)\beta] = \gamma v_l \frac{\gamma^{n-1}}{(n - 1)!} \int d\mathbf{r}_2 \cdots \int d\mathbf{r}_n\, e^{-\beta\epsilon(n)} \quad (36)$$

On the other hand, the number of n-mers, Eq. (11), can be written in the integral form as

$$N_n = e^{n\mu\beta}\gamma V \frac{\gamma^{n-1}}{(n - 1)!} \int d\mathbf{r}_2 \cdots \int d\mathbf{r}_n\, e^{-\beta\epsilon(n)} \quad (37)$$

where the integration is done inside the fixed boundary in which we are interested. The difference between $n!$ of Eq. (12) and $(n - 1)!$ in Eq. (37) occurs because in Eq. (12b) all n molecules are equivalent, while in Eq. (37), the molecule No. 1 is fixed relative to the boundary of integration, so that only $n - 1$ molecules are equivalent.

Although it is not shown explicitly, the integral in Eq. (37) includes various different outside shapes of the cluster, while Eq. (36) is for one of them. Except for this difference in the outside shapes, integrals in Eqs. (36) and (37) are exactly the same, so that we can eliminate them to arrive at the results expressed in Eqs. (25) and (26).

6. SURFACE FREE ENERGY

In writin Eq. (23), we stated that $\hat{\sigma}_i$ defined in Eq. (20) is proportional to the surface area as in Eq. (22). If it is not, an extra factor is to be multiplied by v_i in Eq. (23), and then Φ in Eq. (26) or (29) is to be divided by this extra factor. This section is devoted to the proof of Eq. (22), which consequently denies such an extra factor. We have to be content with a qualitative and heuristic proof. Our particular attention is directed toward the translational and rotational oscillations of the inside cluster as a rigid body, or the equivalent motions of the "outside" when the inside is kept fixed.

In the definition of $\hat{\sigma}_i$ in Eq. (20), we keep the inside cluster fixed and sum over all configurations of the outside cluster. The difference between this $\hat{\sigma}_i$ and the ordinary concept of surface tension is that the latter is defined for an infinitely wide, flat surface, while our $\hat{\sigma}_i$ is for a finite closed surface. We ask if this difference makes $\hat{\sigma}_i$ violate Eq. (22).

Figure 4 shows an example of a cluster imbedded in the bulk liquid phase. When the inside cluster is taken out, the intermolecular bonds across the surface are broken. As is seen in Eq. (20), the surface free energy $\hat{\sigma}_i$ is the average of the potential energies $\epsilon_{i,I}$ for these bonds when the outside takes all possible configurations. The bonds contributing most to $\hat{\sigma}_i$ are marked by lines in Fig. 4. The surface tensions are the same for the flat and curved surfaces if (1) the density (denoted by b) of the cross-surface bonds per unit curved surface is the same as that for a flat surface, and (2) the number of molecules sitting within the distance a from the surface is the same for the two cases.
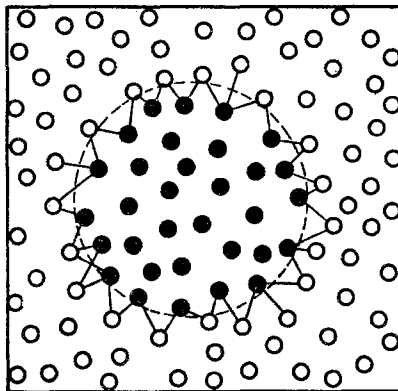

Fig. 4. An imbedded cluster and bonds across its boundary. Lines mark bonds which contribute most to the surface free energy. The bonds connect molecules on S_+ (black circles) and those on S_- (white circles).

There is a thermodynamic theory[6] which says the surface tension decreases with the radius. We believe this effect is of a different nature from the factor Φ we are concerned with, and we decide to neglect it in order not to confuse the issue, although it may be necessary to take this effect into account when our theory is to be compared with experiments.

In Fig. 4, we can distinguish the outside surface S_+ of the inside cluster and the inside surface S_- of the "outside." By examining the curvature of the surfaces in Fig. 4, we can see that the density b_- of cross-surface bonds measured at S_- is smaller than b_0 for the flat surface (in the same bulk phase), and that b_+ measured at S_+ is larger than b_0. Therefore, there is a surface S_0 around midway between S_+ and S_- at which the density of the cross-surface bonds is equal to the flat-surface value b_0. This means that when we choose the surface area of S_0 as A_n, the condition 1 is satisfied. Halfway between S_+ and S_- is exactly the place where the boundary surface for the inside cluster lies, as indicated by a broken curve in Fig. 4; the special case $A_n^{(0)}$ for the sphere is given in Eq. (25b).

The volume between the spheres of radii $r + a$ and $r - a$ is

$$(4\pi/3)[(r + a)^3 - (r - a)^3] = (4\pi r^2)(2a)[1 + (a^2/3r^2)] \tag{38}$$

Each molecule within the distance about $l/2$ from the boundary surface represents three degrees of freedom at an end of a cross-surface bond, which contributes to the p.fn. counted in the surface free energy. For $a = l/2$ and $r = 3l$ (corresponding to $n \approx 100$), we see $a^2/3r^2 \ll 1$, and Eq. (38) is equal to the surface area times the thickness; this means condition 2 is satisfied. Thus, we conclude that the surface tensions for the flat surface and the curved surface are equal.

It may still be argued that the relative translational and roational oscillations of the "outside" with respect to the inside cluster gives rise to p.fn.'s of the form of $kT/\hbar\omega$ and that these p.fn.'s induce in $\hat{\sigma}_i\beta$ a term of the form of $kT\ln(kT/\hbar\omega)$ which is not proportional to the surface area. This argument is answered heuristically as follows.

When the intermolecular potential $\varphi(r)$ is as shown in Fig. 5, we can approximate it near its minimum as

$$\varphi(r) = \epsilon + [\kappa(r - r_0)^2/2] \tag{39}$$

where κ is the spring constant near the bottom. The average around $r = r_0$ leads to the p.fn. of

$$\gamma_1 \int_{-\infty}^{\infty} e^{-\beta\varphi(r)} \, dr = e^{-\beta\epsilon} kT/\hbar\omega \tag{40a}$$

where

$$\gamma_1 \equiv (2\pi mkT)^{1/2}/h \tag{40b}$$

and

$$\omega \equiv (\kappa/m)^{1/2} \tag{40c}$$

is the frequency of oscillation. If we could treat each bond as independent, then

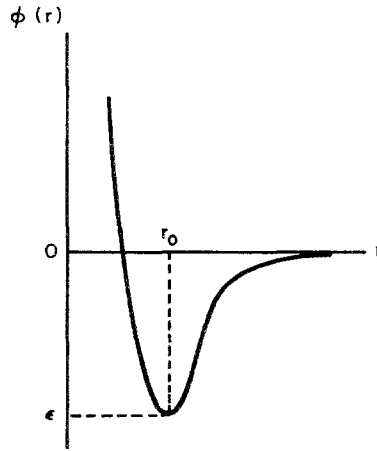$$\exp(\hat{\sigma}_i\beta) = [e^{-\beta\epsilon}(kT/\hbar\omega)/\gamma_1 l]^{**} (b_0 A_n) \tag{41}$$

Fig. 5.   Intermolecular potential $\varphi(r)$. The minimum value ϵ (< 0) is at $r = r_0$.

where b_0A_n is the total number of cross-surface bonds. The denominator $\gamma_1 l$ is introduced in order to show that $\exp(\hat{\sigma}_i\beta)$ is a ratio of two p.fn.'s and that it is independent of γ_1; the value of the length l is unimportant for the present discussion. Equation (41) shows that $\hat{\sigma}_i\beta$ is proportional to the surface area.

In Eq. (41), we interpret each bond as a simple harmonic oscillator oscillating around its minimum point (although this kinetic description is somewhat misleading, because the momentum p.fn., γ_1, cancels after all). There is another and equally valid description of these oscillators using collective modes. Due to the latter, Eq. (41) may be written as

$$\exp(\hat{\sigma}_i\beta) = \exp(-\epsilon\beta b_0 A_n)\, J \prod_j \frac{kT/\hbar\omega_j}{\gamma_1 l} \tag{42}$$

where j goes up to the total number of bonds b_0A_n. The multiplication factor J results from the Jacobian between the original and the transformed coordinates. It is to be emphasized that although the proportionality of $\hat{\sigma}_i\beta$ to the surface area is not obvious in Eq. (42), it is clearly demonstrated in Eq. (41). The analysis done up to this point is good for a closed, finite surface like Fig. 4, as well as for a flat, infinite surface.

There are special kinds of collective oscillations we are concerned with. For a flat surface, we denote by T_{flat} the relative oscillation of the two sides of the surface *en masse* perpendicular to the flat surface. For a closed surface, we denote by T_{closed} the relative oscillation of the inside and outside along a certain fixed direction; and R_{closed} denotes the relative rotational oscillation of the inside and outside. The key question we ask is if T_{closed} and R_{closed} lead to factors which make $\hat{\sigma}_i\beta$ not proportional to the area.

Figure 6 shows schematically that these three collective modes can be defined both for the flat and the closed surfaces. For the flat surface, we know that ω_j corresponding to those in Fig. 6 appear among the factors for calculating $\hat{\sigma}_i\beta$ in the form of Eq. (42) and then, in turn, in the form of Eq. (41), which shows $\hat{\sigma}_i\beta$ is proportional
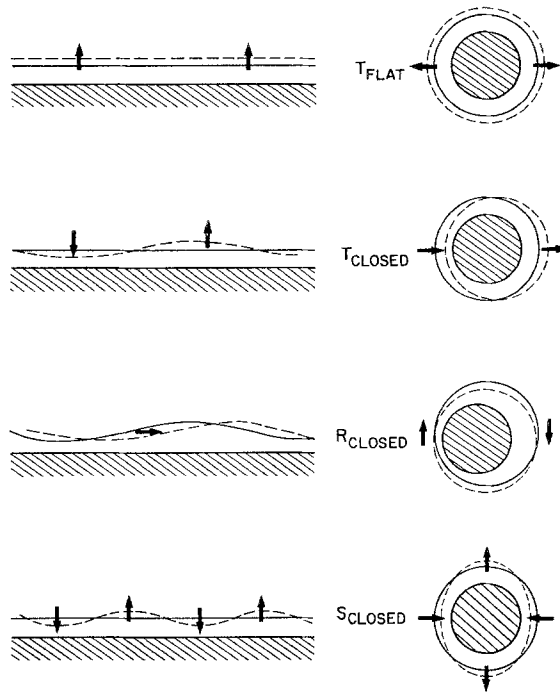
Fig. 6. Four modes of oscillation schematically shown for a flat surface and a closed surface. In order to exaggerate the effect, the inside and the outside for rotation mode R are drawn non-concentric.

to A_n . In analogy, we reason that for the closed surface also, the three collective modes of Fig. 6 and those not shown here lead to the corresponding ω_j in Eq. (42), which, in turn, can be rewritten in the form of Eq. (41), and hence we conclude that $\hat{\sigma}_i\beta$ is proportional to the surface area. In other words, it is not justified to single out $(kT/\hbar\omega)$'s corresponding to T_{closed} and R_{closed} and say that $\hat{\sigma}_i\beta$ is not proportional to A_n .

7. DISCUSSION

1. It is significant to note that the theory presented in Sections 4 and 5 becomes almost identical with Lothe and Pound's (LP) when the identification of the surface free energy is changed. They reason[7] that $\hat{\sigma}_i\beta$ in Eq. (20) is not proportional to the surface area and that Eq. (22) is to be replaced by

$$\exp(\hat{\sigma}_i\beta) = [\exp(\sigma A_n\beta)] \, \Gamma_{\text{tr}}\Gamma_{\text{rot}} \tag{43}$$

where the two Γ factors are contributions from T_{closed} and R_{closed} in Fig. 6. In estimating the surface free energy, we may keep the "outside" fixed and move the inside instead of the reversed operations in Fig. 6. Corresponding to T_{closed} , Lothe and Pound write

$$\Gamma_{\text{tr}} = (kT/\hbar\omega_{\text{tr}})^3/(\gamma v_l) \tag{44a}$$

where ω_{tr} is the frequency of translational oscillation of the imbedded cluster when the outside is fixed. The second factor Γ_{rot} is written as

$$\Gamma_{rot} = (\Delta\theta/2\pi)^3 \tag{44b}$$

where $\Delta\theta$ is the angular amplitude of rotational oscillation of the inside cluster when the outside is fixed. If Eq. (43) is used instead of Eq. (22), the factor Φ in Eq. (29) is replaced by

$$\Phi = [\gamma v_g/(kT/\hbar\omega_{tr})^3][2\pi/\Delta\theta]^3 \tag{45}$$

which is the Lothe–Pound factor, 10^{17}.

Since we proved in Section 6 that Eq. (43) is not the case, Lothe and Pound's claim, Eq. (45), is denied. However, it seems worthwhile to present arguments which reiterate our stand.

a. We can argue that as far as the calculation of the surface free energy goes, other modes like T_{flat} and S_{closed} in Fig. 6 are of the similar nature as T_{closed} and R_{closed}, so that if Γ_{tr} and Γ_{rot} are to be factored out as in Eq. (43), there is no reason why, for example, Γ_{shear} [which is of the same qualitative form as Γ_{tr} in Eq. (44a)] for the S_{closed} mode is not factored out in Eq. (43) also.

b. Another difficulty in the interpretation of Eq. (43) lies in the nonspherical clusters. For such a cluster, the orientation degeneracy factor Θ is to be multiplied as in Eq. (26). If we follow Eq. (43) and replace v_g/v_l in Eq. (26) by Eq. (45), the resulting Φ has two factors, $1/\Gamma_{rot}$ and Θ, of similar nature.

The original proposal of Lothe and Pound[1] was that the rotational degrees of freedom which are frozen in the bulk liquid are liberated in the vapor phase. Our Θ represents exactly this effect, although the estimated value of Θ in Eq. (27) is much smaller than 10^9 which they proposed.[1-3] Either one of the factors Θ or $1/\Gamma_{rot}$ is extra and has no place in their original concept.

c. In order to further elucidate our argument, we examine the one-dimensional model treated in Appendix B. The surface free energy is identified in (B.2) as

$$\exp(2\hat{\sigma}_1\beta) = e^{-\epsilon\beta}(kT/\hbar\omega)/(\gamma_1 l) \tag{46}$$

The $(kT/\hbar\omega)$ factor originates in the mutual oscillation of the inside and outside, l is the length per molecule, and ϵ is the minimum of the potential energy as defined in Fig. 5 and Eq. (39). Abraham and Canosa[8] identify only $-\epsilon$ as the surface free energy $2\hat{\sigma}_1$, and include the rest of the right-hand side of Eq. (46) in the "replacement" term. The following qualitative reasoning justifies Eq. (46) against their stand: The product $e^{-\beta\epsilon}(kT/\hbar\omega)$ results from one integral shown in Eq. (40a) and should be treated as a unit, since $kT/\hbar\omega$ contains the potential energy contribution no less than $e^{-\beta\epsilon}$ does.

This example of one dimension clearly shows that in the three-dimensional expression (43) it is also not justified to separate Γ's to be included in the Φ as in Eq. (45), since the Γ factors are simply a part of one integral of the qualitative form of Eq. (40a) which leads to the coordinate p.fn. In other words, if the Γ's in Eq. (44)

are ever to be included in the Φ factor as in Eq. (45), a part of the potential energy contribution of the form of $e^{-\alpha\epsilon\beta}$ should also be in Φ.

d. We can also comment that the surface free energy should not depend on the moment of inertia I_{cluster} which depends on the mass distribution deep inside the cluster. Nevertheless, the published replacement factor of Lothe and Pound[1-3] explicitly depends on I_{cluster}. This shows that either their replacement factor is not of the nature of the surface free energy, or I_{cluster} cancels after all. The expression (44b) is based on the latter interpretation.[7]

2. There is a second, and probably the original, interpretation of the LP theory. In this interpretation, the proportionality of the surface free energy to the surface area, Eq. (22), is assumed accepted. For this case, we argue against the LP theory[1-3] as follows.

When we compare the p.fn.'s in Eqs. (11) and (23), a particular emphasis is to be placed on the rotation of the cluster. Suppose the shape of the cluster is spherical. Since the two sums over the relative configurations in these expressions are identical, there is no difference between the two as far as the rotational degrees of freedom are concerned, and thus there is no room for the rotation to influence the factor Φ. This reasoning and conclusion agree with that of Reiss et al.[4,5]

It may still be argued that the rotation in the isolated droplet is free, while the rotation of the n-cluster in the condensed phase, if it is pictured as a rigid rotating top, is an oscillation of only a small amplitude. This argument, however, does not invalidate the above conclusion, because the rotated state of the cluster can be reached by a succession of small displacements of many molecules in the imbedded cluster, and what counts in the partition function is the *accessibility*[9] and not how the state is reached. The last statement is a result of the situation that the momentum p.fn. is taken care of separately by the factor γ, and therefore we are concerned with the configurational p.fn. only.

For a nonspherical shape of the cluster, we do take into account the contribution from the "rotation" in the form of the degeneracy factor Θ as in Eq. (26). This factor Θ is sometimes called the weight factor and is a familiar concept in statistical mechanics of cooperative phenomena (Kikuchi and Brush;[10] also see Guggenheim[11]). We regard this Θ as closest to LP's original concept of liberation of the ratotional degrees of freedom, as we commented in 1(b). It gives rise to the summation over shapes in Eq. (26). However, when this term is small, as is the case for water at 300° K, Θ, and hence the "rotation," do not appear in the final expression for Φ at all.

If our arguments on the rotation are agreed upon, LP's theory[2,3] is interpreted as replacing the v_i in Eq. (29) by the free volume v_f in which the center of mass of an n-cluster (regarded as a rigid body) can move inside a cage formed by the outside molecules. This free volume is of the order of n^{-2} of the free volume of a single molecule in the liquid phase and is several orders of magnitude smaller than our v_i in Eq. (28). From the point of view of the molecular volume theorem, we interpret that the "cage" itself is formed by summing Boltzmann factors for the outside molecules as shown in Eq. (20). As the imbedded cluster (regarded as the rigid body) moves, the configurations (of the outside molecules) which contribute most to the surface

free energy $\hat{\sigma}_i$ move accordingly. In other words, we say that the cage itself shifts as the cluster shifts. However, if the cage and the cluster move too far a distance, the configurations formed at the new location are no more distinguishably different from those counted in the old location. The molecular volume theorem says that the limit of the range in which the cage and the cluster can move and still form meaningfully new configurations is the molecular volume v_l .

It is true that the center of mass of a rigid n-cluster oscillates only within the volume v_f if it is seen in a short time scale. However, we make recourse to the same argument as was used concerning the rotational degrees of freedom and say that the larger shift of the imbedded cluster is realized by a succession of small drifts and what counts in the p.fn. is the *accessibility*.

3. The RKC numerical estimate of Φ covers a range in which Eq. (30) lies, although the reasoning is somewhat different. The work of Reiss *et al.*[4,5] and the present paper both examine an imbedded cluster and try to find a volume in which the center of mass (or the "fixed" point) in the cluster can move while the cluster is confined in a prescribed boundary and after the fixed-point p.fn. has been constructed. We arrive at v_l in Eq. (29) by asking the question: What is the volume in which the "fixed point" can move to produce a distinguishably different configuration (to be summed in the p.fn.)? The RKC procedure and model for arriving at the corresponding volume v_{tr} are different from ours; it can be shown, however, that the two volumes are of the same physical meaning, as follows.

RKC define their v_{tr} as

$$v_{tr} = \int_v z(\mathbf{R})\, d\mathbf{R}/z(\mathbf{R} = 0) \tag{47}$$

where v is the volume of the n-cluster and $z(\mathbf{R})$ is defined as

$$z(\mathbf{R}) = n^3 \int_{v(R)} \cdots \int \exp[-\beta\epsilon(\mathbf{r}_1',...,\mathbf{r}_{n-1}')]\, d\mathbf{r}_1' \cdots d\mathbf{r}_{n-1}' \tag{48}$$

Here, $\mathbf{R}$ is the center of mass and $\mathbf{r}_j'$ is the center-of-mass coordinate as in Eq. (12). The integral is done in such a way that all molecules lie within the boundary of the cluster; therefore, the limits of the integral depend on $\mathbf{R}$ as signified by the symbol $v(\mathbf{R})$. The v_{tr} in Eq. (47) is interpreted as the sum of the volume elements $d(\text{volume})$ with the weight $z(\mathbf{R})/z(0)$. We can reason qualitatively that $z(\mathbf{R})$ is nearly equal to $z(0)$ when $\mathbf{R}$ is within the molecular polygon (defined in Section 3) around the origin, and that $z(\mathbf{R})$ decreases sharply as $\mathbf{R}$ goes further away from the origin. When this qualitative picture holds, RKC's v_{tr} is close to the volume of the molecular polygon v_l. This is the reason for the close similarity between the two numerical estimates of the volume.

8. SUMMARY

The controversial factor 10^{17} first proposed by Lothe and Pound[1–3] has been studied by carefully examining partition functions of an n-molecular cluster in the

isolated state and imbedded in the liquid phase. Different from previous treatments, the present paper is based on the principle that each distinguishably different state is counted exactly once in forming the partition function. Also, it is emphasized that the partition function is to be written for the equilibrium state using accessible configurations and should not be distorted by a kinetic picture, although we may use kinetic language in describing states to be summed in the partition function. A "molecular volume" theorem has been proved which says, "When a relative partition function of a homogeneous system is formulated keeping one of the molecules fixed at the origin, the complete partition function is the product of the relative one and the molecular volume." An implication of this theorem is that the replacement term of Lothe and Pound should be for a linear translation within a molecular volume v_l. This is to be compared with the molecular volume v_g in the gas phase in which the isolated n-mer can linearly translate. As a consequence, the form of the controversial factor has been shown to be $\Phi = v_g/v_l$. It was proved that the surface free energy of a cluster is written as a product of the surface area and the surface tension (defined for a flat surface); because of this proof, the rotational degrees of freedom do not contribute to Φ. For water at 300° K, the value of Φ is about 10^4.

APPENDIX A. THE MASS ASSOCIATED WITH THE CENTER OF MASS

In this appendix, we answer the question raised at the end of Section 2 concerning the mass to be associated with the motion of the center of mass of a cluster. For this purpose, we examine a simple example: three particles of equal mass in a linear space. The coordinates and momenta of the three particles are written as x_i and p_i ($i = 1, 2,$ and 3). We introduce a transformation:

$$X_0 = (x_1 + x_2 + x_3)/3, \qquad X_1 = (x_1 - x_3)/3, \qquad X_2 = (x_1 - 2x_2 + x_3)/3 \quad (A.1)$$

where X_0 is the center of mass. Using the Lagrangian function, the momenta conjugate to X_i are derived as

$$P_0 = 3m\dot{X}_0 = p_1 + p_2 + p_3$$
$$P_1 = \tfrac{9}{2}m\dot{X}_1 = 3(p_1 - p_3)/2 \qquad (A.2)$$
$$P_2 = \tfrac{3}{2}m\dot{X}_2 = (p_1 - 2p_2 + p_3)/2.$$

The transformation (A.1) was so chosen that cross terms P_iP_j do not appear in the transformed expression of the kinetic energy:

$$K = \frac{1}{2m}(p_1^2 + p_2^2 + p_3^2) = \frac{1}{2m}\left(\frac{1}{3}P_0^2 + \frac{2}{9}P_1^2 + \frac{2}{3}P_2^2\right) \qquad (A.3)$$

We are interested in the following expression, which appears in the partition function,

$$I = h^{-3}\int_{-\infty}^{\infty} dp_1 \int_{-\infty}^{\infty} dp_2 \int_{-\infty}^{\infty} dp_3\, e^{-K\beta}\, dx_1\, dx_2\, dx_3 \qquad (A.4)$$

After the integrations over the p_i, this becomes

$$I = \gamma_1^3\, dx_1\, dx_2\, dx_3 \,; \qquad \gamma_1 \equiv (2\pi m k T)^{1/2}/h \tag{A.5}$$

On the other hand, if we use the transformed coordinates, I is evaluated as

$$
\begin{aligned}
I &= h^{-3} \int_{-\infty}^{\infty} dP_0 \int_{-\infty}^{\infty} dP_1 \int_{-\infty}^{\infty} dP_2\, e^{-K\beta}\, dX_0\, dX_1\, dX_2 \\
&= d(\gamma_1 X_0 \sqrt{3})\, d(\gamma_1 X_1 \sqrt{9/2})\, d(\gamma_1 X_2 \sqrt{3/2})
\end{aligned}
\tag{A.6}
$$

where the result of the integral $h^{-1} \int dP_1$ is written next to X_i. This expression shows that the coordinates X_0, X_1, and X_2 are associated with the masses $3m$, $9m/2$, and $3m/2$, in agreement with (A.2). However, this association is not binding, because (A.6) is equivalent to

$$I = \tfrac{9}{2}\gamma_1^3\, dX_0\, dX_1\, dX_2 \tag{A.7}$$

in which the correspondence between X_i and its mass is lost. We can arrive at (A.7) directly from (A.5) by using the Jacobian for (A.1):

$$\left| \frac{\partial(X_0, X_1, X_2)}{\partial(x_1, x_2, x_3)} \right| = \frac{2}{9} \tag{A.8}$$

It is also instructive to see a case when the mass corresponding to a transformed coordinate cannot be defined. Let us examine the transformation

$$X_0' = (x_1 + x_2 + x_3)/3, \quad X_1' = (2x_1 - x_2 - x_3)/3, \quad X_2' = (-x_1 + 2x_2 - x_3)/3 \tag{A.9}$$

The conjugate momenta are

$$
\begin{aligned}
P_0' &= 3m\dot{X}_0' = p_1 + p_2 + p_3 \\
P_1' &= m(2\dot{X}_1' + \dot{X}_2') = p_1 - p_3 \\
P_2' &= m(\dot{X}_1' + 2\dot{X}_2') = p_2 - p_3
\end{aligned}
\tag{A.10}
$$

which brings the kinetic energy K of (A.3) into

$$K = \frac{1}{12m}\,[2P_0'^2 + (P_1' + P_2')^2 + 3(P_1' - P_2')^2] \tag{A.11}$$

Since this expression contains a cross term $P_1'P_2'$, we cannot uniquely define the corresponding mass from the integrations over P_1' or P_2'. Therefore, it is not possible to write I in the form corresponding to (A.6) multiplying X_i' with the factor containing its corresponding mass, whereas it is always possible to write I in the form (A.7) as a product of dX_i' with the appropriate Jacobian factor.

Another example is shown when the three particles are bound by the potential of Fig. 5 and move in a linear space L. When the particles oscillate near the potential

minimum, the displacements from the state of minimum potential are written as x_1, x_2, and x_3. The equations of motion are

$$m \, d^2x_1/dt^2 = \kappa(x_2 - x_1)$$
$$m \, d^2x_2/dt^2 = \kappa(x_1 - x_2) + \kappa(x_3 - x_2) \qquad \text{(A.12)}$$
$$m \, d^2x_3/dt^2 = \kappa(x_2 - x_3)$$

where κ is the spring constant written in Eq. (39). When the X's in (A.1) are used, the equations (A.12) are brought to a normalized form, and the characteristic frequencies corresponding to X_i ($i = 0$, 1, and 2) are

$$\omega_0 = 0, \qquad \omega_1 = \omega, \qquad \text{and} \qquad \omega_2 = \omega \sqrt{3} \qquad \text{(A.13)}$$

where ω is the frequency defined in Eq. (40c).

The potential energy is

$$W = \tfrac{1}{2}\kappa[(x_1 - x_2)^2 + (x_2 - x_3)^2] + 2\epsilon \qquad \text{(A.14)}$$

Using (A.5), the partition function is written as

$$Q = \gamma_1{}^3 \int_0^L dx_1 \int_{-\infty}^{\infty} dx_2 \int_{-\infty}^{\infty} dx_3 \, e^{-\beta W} \qquad \text{(A.15)}$$

When x_1, $x_2 - x_1$, and $x_3 - x_2$ are used as the new set of variables, the Jacobian is unity and Q is integrated as

$$Q = \gamma_1 L (e^{-\beta\epsilon} kT/\hbar\omega)^2 \qquad \text{(A.16)}$$

where we used

$$\gamma_1 (2\pi/\beta\kappa)^{1/2} = kT/\hbar\omega \qquad \text{(A.17)}$$

It is to be remembered that $kT/\hbar\omega$ is the classical partition function of a simple harmonic oscillator of frequency ω. On the other hand, when we transform the potential energy W in (A.14) using the X's in (A.1), we can write Q in (A.15) as

$$Q = \int_0^L \gamma_1 \sqrt{3} \, dX_0 \int_{-\infty}^{\infty} \gamma_1\sqrt{\tfrac{9}{2}} \, dX_1 \int_{-\infty}^{\infty} \gamma_1\sqrt{\tfrac{3}{2}} \, dX_2 \exp[-\beta \tfrac{9}{4}\kappa(X_1{}^2 + X_2{}^2) - 2\epsilon\beta] \quad \text{(A.18)}$$

where we used (A.6). The result of this integration can be written as

$$Q = (\gamma_1 \sqrt{3}) \, L e^{-2\epsilon\beta} \frac{kT}{\hbar\omega_1} \frac{kT}{\hbar\omega_2} \qquad \text{(A.19)}$$

where ω_1 and ω_2 are defined in (A.13). The last two factors are for the two normal modes. The expression (A.19) is identical to (A.16), since (A.13) gives

$$\omega_1\omega_2 = \omega^2 \sqrt{3} \qquad \text{(A.20)}$$

and the factor $\sqrt{3}$ cancels the same in the center-of-mass motion $\gamma_1 \sqrt{3}$. It is easy to generalize the argument and write for a chain of n molecules,

$$\omega^{n-1} \sqrt{n} = \prod_{j=1}^{n-1} \omega_j \tag{A.21}$$

This relation was derived by Abraham and Canosa[8] and by Lothe and Pound.[12] It should be noted the the factor $\sqrt{n}$ originates in the coordinate transformation to the collective modes and expresses the fact that the mass associated with the center of mass in nm. However, it should also be noted that in (A.16) the mass associated with the mass motion of the cluster (linear translation of the cluster as a rigid body) is not nm but m, as shown by the factor $\gamma_1 L$.

We conclude from these examples that it is not justified to automatically write nm in the normalizing factor for the center-of-mass coordinate. The correct procedure is to start from the expression (A.5) in terms of the rectangular coordinates of individual particles, transform it using the Jacobian (A.8), and arrive at the expression (A.7).

This conclusion is equivalent to saying that the relative p.fn., i.e., the fixed-point p.fn., is meaningless unless it is specified what kind of mass is used in the center-of-mass p.fn.

APPENDIX B. SURFACE FREE ENERGY OF A LINEAR CHAIN

The surface free energy of a linear chain discussed in Appendix A is treated here. Consider a system of n molecules in a linear space. Each molecule is connected by springs to its two neighbors, except the two end ones, which are connected only on one side. The length of the system is nl, where l is not far from the stable spring distance r_0 in Eq. (39). The partition function of this system is, from (A.16),

$$Q(n) = \gamma_1 l (e^{-\beta\epsilon} kT/\hbar\omega)^{n-1} \tag{B.1}$$

The second factor is the fixed-point p.fn., and l is the molecular "volume;" thus, Eq. (B.1) is an example of the molecular volume theorem.

We start with a system of $n_1 + n_2$ molecules and divide it into two parts, one with n_1 molecules and the other with n_2, and place them separately in linear spaces of lengths $n_1 l$ and $n_2 l$, respectively. Now, the separated system has two more surfaces than the original ones, and hence the surface free energy per surface $\hat{\sigma}_1$ is derived from the ratio

$$\exp(2\hat{\sigma}_1\beta) = Q(n_1 + n_2)/Q(n_1) \, Q(n_2) = e^{-\beta\epsilon}(kT/\hbar\omega)/\gamma_1 l \tag{B.2}$$

This derivation of $\exp(2\hat{\sigma}_1\beta)$ is due to Cohen and Katz,[13] except for the interpretation of l.

An alternative derivation of (B.2) is from (B.1). The p.fn., $Q(n)$, can be written as a product of the bulk part $(e^{-\beta\epsilon}kT/\hbar\omega)^n$ and the two surfaces $\exp(-2\hat{\sigma}_1\beta)$:

$$Q(n) = (e^{-\beta\epsilon}kT/\hbar\omega)^n \exp(-2\hat{\sigma}_1\beta) \tag{B.3}$$

The comparison of (B.3) and (B.1) leads to (B.2).

As the third derivation of (B.2), we show that the definition in Eq. (20) leads to (B.2). We consider the molecule 0 in the inside and the molecules 1, 2, 3,..., N on the outside. The cross-surface potential corresponding to $\epsilon_{i,I}$ in Eq. (20) is

$$\epsilon_{0,1} = \epsilon + \tfrac{1}{2}\kappa(x_0 - x_1)^2 \tag{B.4}$$

The numerator of Eq. (20) corresponds to

$$Q_{\text{num}} = \gamma_1 \int_{-\infty}^{\infty} \exp(-\beta\epsilon_{0,1})\, dx_1 (e^{-\beta\epsilon}kT/\hbar\omega)^{N-1} \tag{B.5}$$

The second factor is the result of integrations over molecules 2, 3,..., N. The denominator of Eq. (20) corresponds to

$$Q_{\text{den}} = [Q(N)\exp(2\hat{\sigma}_1\beta)]\exp(-\hat{\sigma}_1\beta) \tag{B.6}$$

This needs some explanation. The two factors in the brackets correspond to $e^{-Nf\beta}$, since the difference between the latter and $Q(N)$ is the two surfaces, as shown in (B.3). The last factor corresponds to the effect of the external surface $\exp(-\sigma A_{n+N}\beta)$ in Eq. (20). Substituting these relations together with (B.1) for $Q(N)$ in the modified form of Eq. (20),

$$\exp(2\hat{\sigma}_1\beta) = [\exp(\hat{\sigma}_1\beta)]\, Q_{\text{num}}/Q_{\text{den}} \tag{B.7}$$

we arrive at (B.2). The gist of this procedure is the breaking of the 0–1 bond:

$$\exp(2\hat{\sigma}_1\beta) = \gamma_1 \int_{-\infty}^{\infty} \exp(-\beta\epsilon_{0,1})\, dx_1/(\gamma_1 l) \tag{B.8}$$

which leads to (B.2). The l in the denominator originates in the molecular volume theory, and it can be interpreted that dx_1/l is the average density of the molecule 1 in dx_1.

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