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Coordinate Transformation for Separating the Classical Phase Integral and the Rotational Partition Function of a Small Liquid Cluster of Molecules

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A liquid cluster of identical molecules is considered, and it is concluded that in the case of classical systems: (i) The macroscopic rotation can be defined irrespective of the molecular mobility. (ii) The canonical partition function is approximately separable into translational, rotational, and internal partition functions, and the numerical value of the rotational partition function is approximately the same as that of a rigid system with the same density and shape. (iii) The rotational symmetry number need not be considered when dealing with the usual phase integral of nonrigid systems, such as that used in this paper. (iv) These considerations lead to a value of about 10^9 for the rotational partition function of a cluster of about 100 water molecules.

I. INTRODUCTION

It has been assumed by Lothe and Pound[1-3] in the theory of homogeneous nucleation of liquid from vapor, that the canonical partition function Q of a small liquid cluster of molecules (typically about 100 molecules) can be approximated by the product of the translational partition function Q_t, the rotational partition function Q_r, and the internal partition function Q_i, i. e,,

$$Q \cong Q_t Q_r Q_i . \tag{1}$$

Lothe and Pound[1] further assumed that Q_r is approximately given by taking the cluster to be rigid and by using a symmetry number of unity. In this case, the rotational partition function is of the order of 10^9 in a typical case.

It has been shown[4-9] that the approximation (1) is valid in the case of semirigid systems like polyatomic molecules or crystallites. The rotational partition function of these semirigid systems is well defined,[4-9] and the symmetry number associated with the rotational partition function is clearly understood.[10] It should be emphasized, however, that the possibility of defining the lattice sites in these systems has crucial importance for the validity of the approximations used.

In the case of nonrigid systems like liquid clusters, it is impossible to define the lattice sites. Hence, the validity of the Lothe-Pound approximation is by no means obvious. On the basis of qualitative considerations, Abraham and Pound[11] concluded that the rotational partition function of a liquid cluster could approach unity for liquids of high molecular mobility. However, the qualitative considerations used by them are not satisfactory in the present authors's opinion. Since Lothe and Pound's approximation has critical importance in the capillarity-approximation theory of homogeneous nucleation, it is desirable to investigate its validity in a quantitative way.

II. DEFINITION OF ROTATION

The concept of rotation is well defined in semirigid systems like polyatomic molecules or crystallites. Since the molecular structure or the lattice sites can be defined in those systems, one can use the reference axes fixed to those structures to describe the rotation.[4-9] On the other hand, the concept of rotation of a nonrigid system, a liquid cluster in the present case, is not clear, because the lattice on which one can fix the reference axes is not defined in this case. Recently Meyer and Günthard[12] used the internal-motion axis system to define the rotation of a general asymmetric-top molecule undergoing almost arbitrary deformations. The angular velocity of the reference axes is well defined in their treatment, but the angular orientation of the reference axes is not explicitly defined. The internal-motion axis system will be extended and applied to a liquid cluster in the following.

Consider a liquid cluster of n identical molecules. Assume monatomic molecules for simplicity. The atoms can be treated as particles according to the adiabatic approximation[13] and the particles are assumed to be interacting quite strongly to form a liquid cluster. The classical statistical mechanics is assumed to be applicable throughout this paper, and this is usually a good approximation for liquids.[14]

The system (a liquid cluster) may be translating in space and colliding with the other clusters, monomer molecules or the walls, as in the case of homogeneous nucleation of liquid from vapor. However, the collision time is very short compared with the time period between successive collisions, and hence the system can be represented by an ensemble of systems which are free from all external forces.[15] It is noted, however, that this may not be the case for a system whose temperature is close to the critical temperature, because the period of interaction between a cluster and other clusters and monomers becomes appreciable, and correspondingly the classical states corresponding to this time period will contribute appreciably to the partition function of the entire system of supersaturated vapor. A situation of this kind is excluded from the following argument.[16]

In the absence of external forces on the system, the angular momentum $\vec{L}$ is conserved. The angular momentum about the origin O of the laboratory Cartesian coordinate system Σ is given by

$$\vec{L}=\sum_{i=1}^{n}\vec{r}_i\times m\dot{\vec{r}}_i,\tag{2}$$

where m is the mass of each particle, and $\vec{r}_i$ is the position vector with origin at O. Equation (2) can be rewritten as follows[17, 18] in terms of the position vector $\vec{R}$ of the center of mass O', the position vector $\vec{r}_i'$ of particles with the origin at O', the velocity $\vec{v}_i$ of the particles relative to the translating and rotating Cartesian coordinate system Σ' whose origin is at the center of mass O', and the angular velocity $\vec{\omega}$ of Σ' relative to Σ:

$$\vec{L}=\vec{R}\times nm\dot{\vec{R}}+m\sum_{i=1}^{n}\vec{r}_i'\times\vec{v}_i'+m\sum_{i=1}^{n}\vec{r}_i'\times(\vec{\omega}\times\vec{r}_i').\tag{3}$$

The first term in (3) is the angular momentum of the c. m. about O, the second term is the angular momentum about O' and relative to Σ', and the third term is due to the rotation of Σ'. The sum of the last two terms in (3) is the angular momentum due to the spin of the system about O', and we denote it by $\vec{S}$, i. e.,

$$\vec{S}=\vec{L}-\vec{R}\times nm\dot{\vec{R}}=m\sum_{i=1}^{n}\vec{r}_i'\times\vec{v}_i'+m\sum_{i=1}^{n}\vec{r}_i'\times(\vec{\omega}\times\vec{r}_i').\tag{4}$$

Let us define $\vec{\omega}$ such that the first term on the right-hand side in (4) vanishes, i. e., zero angular momentum relative to Σ'. Since the last term in (4) can be rewritten

$$m\sum_{i=1}^{n}\vec{r}_i'\times(\vec{\omega}\times\vec{r}_i')=\mathscr{I}\vec{\omega},\tag{5}$$

where $\mathscr{I}$ is the instantaneous moment of inertia tensor, the defining equation of $\vec{\omega}$ is

$$\vec{S}=\mathscr{I}\vec{\omega}.\tag{6}$$

Since $\vec{S}$ and $\mathscr{I}$ are known functions of positions and velocities of the particles, $\vec{\omega}$ can be obtained at any instant by solving (6).

Since $\mathscr{I}\vec{\omega}$ is the spin angular momentum of the system, it is reasonable to define the rotational angular velocity of the system by $\vec{\omega}$, in analogy with the case of rigid systems. In order to complete the definition of rotation, we need to define the angular orientation of the system. Let us define the orientation of the system by the orientation of Σ' relative to Σ. Once the orientation of Σ' is arbitrarily chosen at some instant t_o, the orientation is defined at any instant t. Thus, it is concluded that the rotation of a liquid cluster of molecules can be defined by specifying the orientation and the angular velocity of Σ' relative to Σ. It is noted, however, that the specification of time t is necessary to define the orientation. The argument given above is applicable to any nonrigid system as well as to a liquid cluster.

III. COORDINATE TRANSFORMATION FOR SEPARATING THE CLASSICAL PHASE INTEGRAL

The classical phase integral of a conservative system of n identical particles is given by the following, in terms of the position vectors $\vec{r}_i$ and their conjugate momenta $\vec{p}_i$ with respect to the laboratory coordinate system Σ:

$$Q=\frac{1}{n!\,h^{3n}}\int\cdots\int\exp[-H(\vec{r},\vec{p})/kT]\,d\vec{r}\,d\vec{p},\tag{7}$$

where H is the classical Hamiltonian and $\vec{r}$ and $\vec{p}$ stand for $\vec{r}_1, \ldots, \vec{r}_n$ and $\vec{p}_1, \ldots, \vec{p}_n$. The integration domain covers the entire phase space.

The variables in the phase integral are not limited only to $\vec{r}$ and $\vec{p}$, but any other variables can be used if the following conditions are satisfied: (a) The new variables are canonical variables. (b) There is one-to-one correspondence between the sets of values of old and new variables. (c) If the new Hamiltonian does not represent the total energy, the Hamiltonian in the phase integral is replaced by the total energy.

Liouville's theorem holds when the first condition is satisfied.[19] Hence, the distribution function of the phase points in the new phase space remains a function of constants of motion at thermodynamic equilibrium, and the canonical partition function is given by the same form as that in (7). It is noted that the second condition assures that all the classical states are counted once and only once in the new-variable system. When the Hamiltonian is not the total energy under the new variables, the Hamiltonian in (7) has to be replaced by the total energy in order to associate $-kT \ln Q$ with the Helmholtz free energy. Since it is shown, for example by Tolman,[19] that the volume elements in the old and in the new phase space have exactly the same numerical magnitudes under canonical transformation of variables, the three conditions given above will assure that the classical phase integral in terms of the new variables has exactly the same numerical value as that in terms of the old variables.

The argument given above holds generally for canonical transformations, including those which involve time explicitly. Consider a special canonical transformation which transforms from $\vec{r}$ and $\vec{p}$, at a time t, to their initial values $\vec{r}_0$ and $\vec{p}_0$, at $t=0$. The equations of transformation are

$$\begin{aligned}\vec{r}_0&=\vec{r}_0(\vec{r},\vec{p},t),\\ \vec{p}_0&=\vec{p}_0(\vec{r},\vec{p},t).\end{aligned}\tag{8}$$

The Eqs. (8) are uniquely determined when the Hamiltonian is given. In order to make a one-to-one correspondence between the old variables $(\vec{r}, \vec{p})$ and the new variables $(\vec{r}_0, \vec{p}_0)$, the time in (8) has to be fixed at a value $t=t_1$. Since the solution of the equations of motion is unique, (8) can be inverted as

$$\begin{aligned}\vec{r}&=\vec{r}(\vec{r}_0,\vec{p}_0,t_1),\\ \vec{p}&=\vec{p}(\vec{r}_0,\vec{p}_0,t_1),\end{aligned}\tag{9}$$

where the time is taken to be t_1. The phase integral can be evaluated in terms of $(\vec{r}_0, \vec{p}_0)$, given by (8) with $t=t_1$, and obviously the same is true in terms of $(\vec{r}, \vec{p})$, as given by (9).

Let us introduce a new set of variables as follows:

$$\begin{aligned}&\vec{R}=\frac{1}{n}\sum_{j=1}^{n}\vec{r}_j,\\ &\dot{\vec{R}}=\frac{1}{n}\sum_{j=1}^{n}\dot{\vec{r}}_j,\\ &\vec{r}_i{}'=\vec{r}_i-\vec{R}, \qquad (i=1,2,\ldots,n),\\ &\vec{\omega}=\mathcal{I}^{-1}\vec{S},\\ &\vec{v}_i=\dot{\vec{r}}_i-\dot{\vec{R}}-\vec{\omega}\times\vec{r}_i{}', \qquad (i=1,2,\ldots,n),\end{aligned}\tag{10}$$

where $\vec{R}$, $\dot{\vec{R}}$ are the position vector of the center of mass and its velocity relative to the laboratory frame Σ; $\vec{r}_i{}'$ are the position vectors of particles relative to the center of mass; $\vec{v}_i{}'$ are velocities of particles relative to Σ' which was introduced in Sec. II; $\vec{\omega}$ is the angular velocity of Σ' relative to Σ as defined in Sec. II; and $\mathcal{I}^{-1}$ is the inverse matrix of the instantaneous moment of inertia tensor under the matrix representation. Of course $\dot{\vec{r}}_i$ are given by $\vec{p}_i/m$. It can easily be seen that the following relations exist between $\vec{r}_i{}'$ and $\vec{v}_i{}'$, on account of the definition of $\vec{R}$, $\dot{\vec{R}}$ and $\vec{\omega}$:

$$\begin{aligned}&\sum_{i=1}^{n}\vec{r}_i{}'=0,\\ &\sum_{i=1}^{n}\vec{v}_i{}'=0, \quad \sum_{i=1}^{n}\vec{r}_i{}'\times\vec{v}_i{}'=0.\end{aligned}\tag{11}$$

The angular orientation of Σ' can be represented by three Eulerian angles θ, ϕ and ψ, which describe the relative orientation of three unit vectors $\vec{e}_1$, $\vec{e}_2$, and $\vec{e}_3$ along the Cartesian axes of Σ' to three unit vectors $\vec{i}$, $\vec{j}$, and $\vec{k}$ along the Cartesian axes of Σ. $\vec{e}_1$, $\vec{e}_2$, and $\vec{e}_3$, are given by integrating the following equations under an arbitrary chosen initial orientation at $t=0$:

$$\frac{d\vec{e}_i}{dt}=\vec{\omega}\times\vec{e}_i, \quad (i=1,\ 2,\ 3)\ .\tag{12}$$

The initial condition can be chosen, for example, as follows:

$$\vec{e}_1 \parallel \vec{r}_n{}' , \qquad \vec{e}_2 \parallel \vec{r}_n{}' \times \vec{r}_{n-1}{}' ,$$
$$\vec{e}_3 = \vec{e}_1 \times \vec{e}_2 , \quad \text{at } t = 0 . \tag{13}$$

It is noted that (13) does not give a proper initial condition if $\vec{r}_n{}' \parallel \vec{r}_{n-1}{}'$. However, since those states form a subset of measure zero in the set of all the classical states, they can be neglected in evaluating the classical phase integral. Equation (13) implies the following:

$$y_n{}' = z_n{}' = y_{n-1}{}' = 0 , \quad \text{at } t = 0 , \tag{14}$$

where $y_n{}' = \vec{r}_n{}' \cdot \vec{e}_2$, $z_n{}' = \vec{r}_n{}' \cdot \vec{e}_3$,

and $y_{n-1}{}' = \vec{r}_{n-1}{}' \cdot \vec{e}_2$.

Since $\vec{\omega}(t)$ is a known function of t if $(\vec{r}_0 , \vec{p}_0)$ are given, $\vec{e}_1$, $\vec{e}_2$, and $\vec{e}_3$ can be known by solving (12); hence θ, ϕ, and ψ can be known as functions of time. Thus θ, ϕ, and ψ can be formally written

$$\theta = \theta(\vec{r}_0, \vec{p}_0, t) ,$$
$$\phi = \phi(\vec{r}_0, \vec{p}_0, t), \tag{15}$$
$$\psi = \psi(\vec{r}_0, \vec{p}_0, t) .$$

Similarly all the new variables defined by (10) can be written as functions of $\vec{r}_0$, $\vec{p}_0$, and t. Inasmuch as there are $6n+12$ new variables, there must be 12 constraint equations on them.

The phase integral can be evaluated in terms of $(\vec{r}_0, \vec{p}_0)$, as seen by taking $t=0$ in (8). The phase integral can also be evaluated in terms of the new variables if we choose t to be a constant t_1 in (15) and in the other new variables expressed as functions of $\vec{r}_0$, $\vec{p}_0$, and t. Let us choose $t_1 = 0$. The variables which will be used in the phase integral are now $6n$ new variables. These are obtained by eliminating 12 variables from $6n+12$ variables [$6n+9$ new variables defined by (10) together with θ, ϕ, and ψ] through 12 constraint equations given by (11) and (14).

Since these new variables are not canonical variables, we need to introduce canonical variables in terms of them in order to get the Jacobian of the transformation to be unity. It seems to be reasonable to assume that the Lagrangian L of the system is given by $T-U$ under the new variables, where T is the kinetic energy and U is the potential energy. The kinetic energy is given by the following[5]:

$$T = \tfrac{1}{2} M (\dot{X}^2 + \dot{Y}^2 + \dot{Z}^2) + \frac{1}{2} \sum_{i=1}^{n} m(\dot{x}_i'^2 + \dot{y}_i'^2 + \dot{z}_i'^2)$$
$$+ \tfrac{1}{2} A\omega_{x'}^2 + \tfrac{1}{2} B\omega_{y'}^2 + \tfrac{1}{2} C\omega_{z'}^2 + D\omega_{x'}\omega_{y'}$$
$$+ E\omega_{y'}\omega_{z'} + F\omega_{z'}\omega_{x'} , \tag{16}$$

where $M = nm$, $A = \sum_{i=1}^{n} m(y_i'^2 + z_i'^2)$,

$$B = \sum_{i=1}^{n} m(z_i'^2 + x_i'^2) ,$$

$$C = \sum_{i=1}^{n} m(x_i'^2 + y_i'^2), \quad D = -\sum_{i=1}^{n} m x_i' y_i' ,$$

$$E = -\sum_{i=1}^{n} m y_i' z_i', \quad F = -\sum_{i=1}^{n} m z_i' x_i' ,$$

$$\omega_{x'} = \dot{\phi} \sin\theta \sin\psi + \dot{\theta} \cos\psi ,$$
$$\omega_{y'} = \dot{\phi} \sin\theta \cos\psi - \dot{\theta} \sin\psi , \tag{17}$$
$$\omega_{z'} = \dot{\phi} \cos\theta + \dot{\psi} ,$$

$$\dot{X} = \dot{\vec{R}} \cdot \vec{i} , \quad \dot{Y} = \dot{\vec{R}} \cdot \vec{j} , \quad \dot{Z} = \dot{\vec{R}} \cdot \vec{k},$$

$$x_i' = \vec{r}_i{}' \cdot \vec{e}_1 , \quad y_i' = \vec{r}_i{}' \cdot \vec{e}_2 ,$$

$$z_i' = \vec{r}_i{}' \cdot \vec{e}_3 ,$$

$$\dot{x}_i' = \vec{v}_i{}' \cdot \vec{e}_1 , \quad \dot{y}_i' = \vec{v}_i{}' \cdot \vec{e}_2 ,$$

$$\dot{z}_i' = \vec{v}_i{}' \cdot \vec{e}_3 , \quad (i = 1, 2, \ldots, n) .$$

Using the constraint equations (11) and (14), we can eliminate 12 variables from T. For example, we can eliminate x_n', y_n', y_{n-1}', y_{n-2}', z_n', z_{n-1}', $\dot{x}_n'$, $\dot{y}_n'$, $\dot{y}_{n-1}'$, $\dot{y}_{n-2}'$, $\dot{z}_n'$, and $\dot{z}_{n-1}'$. It can be easily seen that

$$y_n' = y_{n-1}' = z_n' = 0, \quad x_n' = -\sum_{i=1}^{n-1} x_i' ,$$

$$y_{n-2}' = -\sum_{i=1}^{n-3} y_i' , \quad z_{n-1}' = -\sum_{i=1}^{n-2} z_i' ,$$

and that $\dot{x}_n'$, $\dot{y}_n'$, $\dot{y}_{n-1}'$, $\dot{y}_{n-2}'$, $\dot{z}_n'$, and $\dot{z}_{n-1}'$ are functions of

$$(x'_{n-1}, \ldots, x'_1, \dot{x}'_{n-1}, \ldots, \dot{x}'_1, y'_{n-3}, \ldots,$$

$$y'_1, \dot{y}'_{n-3}, \ldots, \mathring{y}'_1, z'_{n-2}, \ldots, z'_1, \mathring{z}'_{n-2}, \ldots, \dot{z}'_1).$$

The potential energy is formally written

$$U = U(x'_1, \ldots, x'_{n-1}, y'_1, \ldots, y'_{n-3}, z'_1, \ldots, z'_{n-2}).$$

The generalized momenta are given as follows:

$$p_X = \frac{\partial L}{\partial \dot{X}} = M\mathring{X}, \quad p_Y = M\mathring{Y}, \quad p_Z = M\mathring{Z},$$

$$p_{x'_i} = \frac{\partial L}{\partial \dot{x}'_i} = m\dot{x}'_i + m\dot{x}'_n \frac{\partial \dot{x}'_n}{\partial \dot{x}'_i} + m\dot{y}'_n \frac{\partial \mathring{y}'_n}{\partial \mathring{x}'_i} + m\mathring{y}'_{n-1} \frac{\partial \mathring{y}'_{n-1}}{\partial \mathring{x}'_i}$$

$$+ m\dot{y}'_{n-2} \frac{\partial \dot{y}'_{n-2}}{\partial \dot{x}'_i} + m\dot{z}'_n \frac{\partial \mathring{z}'_n}{\partial \mathring{x}'_i} + m\dot{z}'_{n-1} \frac{\partial \mathring{z}'_{n-1}}{\partial \dot{x}'_i},$$

$$(i = 1, 2, \cdots, n-1); \tag{18}$$

and similarly for $p_{y'_i}$ and $p_{z'_i}$:

$$p_\theta = \frac{\partial L}{\partial \dot{\theta}} = A \cos\psi\, \omega_{x'} - B \sin\psi\, \omega_{y'}$$

$$+ D(\cos\psi\, \omega_{y'} - \sin\psi\, \omega_{x'}) - E \sin\psi\, \omega_{z'} + F \cos\psi\, \omega_{z'},$$

$$p_\phi = \frac{\partial L}{\partial \dot{\phi}} = A \sin\theta \sin\psi\, \omega_{x'} + B \sin\theta \cos\psi\, \omega_{y'}$$

$$+ C \cos\theta\, \omega_{z'} + D(\sin\theta \sin\psi\, \omega_{y'} + \sin\theta \cos\psi\, \omega_{x'})$$

$$+ E(\sin\theta \cos\psi\, \omega_{z'} + \cos\theta\, \omega_{y'})$$

$$+ F(\cos\theta\, \omega_{x'} + \sin\theta \sin\psi\, \omega_{z'}),$$

$$p_\psi = \frac{\partial L}{\partial \dot{\psi}} = C\omega_{z'} + E\omega_{y'} + F\omega_{x'}.$$

The total energy is

$$E = T + U$$

$$= \frac{1}{2M}(p_X^2 + p_Y^2 + p_Z^2) + T_i(p_{x'}, p_{y'}, p_{z'}, x', y', z')$$

$$+ (f_1 p_\theta^2 + f_2 p_\phi^2 + f_3 p_\psi^2 + f_4 p_\theta p_\phi$$

$$+ f_5 p_\phi p_\psi + f_6 p_\psi p_\theta) + U(x', y', z'), \tag{19}$$

where the second term T_i is the kinetic energy due to the motion of the particles relative to $\sum'$ and will be called the internal kinetic energy. $f_1, \ldots, f_6$ are known functions of x', y', z', θ, and ψ; $p_{x'}$, $p_{y'}$, and $p_{z'}$ stand for $p_{x'_i}$, etc., as defined by (18), and similarly x', y', and z' represent the $3n-6$ variables x'_i, etc. The first bracket in (19) is the translational kinetic energy of the c.m. and will be called the translational energy, while $T_i + U$ may be termed the internal energy. The third bracket is the kinetic energy due to the rotation of Σ' and will be called the rotational energy.

IV. ROTATIONAL PARTITION FUNCTION

The canonical partition function of the system is given by the following, in terms of the new variables:

$$Q = \frac{1}{n!\,h^{3n}} \int \cdots \int \exp(-E/kT)$$

$$\times dX\, dp_X \cdots d\psi\, dp_\psi \cdots dz'_{n-2}\, dp_{z'_{n-2}}, \tag{20}$$

where E is expressed by (19). Transforming the variables from p_θ, p_ϕ, and p_ψ into ω'_x, ω'_y, and ω'_z, (20) becomes

$$Q = Q_t\, Q_{r,i}, \tag{21}$$

where Q_t is the translational partition function

$$Q_t = \frac{1}{h^3} \int \cdots \int \exp[-(p_X^2 + p_Y^2 + p_Z^2)/2MkT]$$

$$\times dX dY dZ dp_X dp_Y dp_Z; \tag{22}$$

and $Q_{r,i}$ is the rotational and internal partition function

$$Q_{r,i} = \frac{1}{n!\,h^{3n-6}} \int \cdots \int \exp[-(T_i + U)/kT]$$

$$\times dx'_1\, dp_{x'_1} \cdots dz'_{n-2}\, dp_{z'_{n-2}} \frac{1}{h^3} \int \cdots \int$$

$$\times \exp[-(\tfrac{1}{2} A\omega_{x'} + \cdots + F\omega_{z'}\, \omega_{x'})/kT]$$

$$\times d\theta d\phi d\psi d\omega'_x\, d\omega'_y\, d\omega'_z\, /J, \tag{23}$$

in which J is given by

$$J = \frac{\partial(\omega_{x'}, \omega_{y'}, \omega_{z'})}{\partial(p_\theta, p_\phi, p_\psi)} = \left(\frac{\partial(p_\theta, p_\phi, p_\psi)}{\partial(\omega_{x'}, \omega_{y'}, \omega_{z'})}\right)^{-1}$$

$$= [(ABC - AE^2 - BF^2 - CD^2 + 2DEF)\sin\theta$$

$$- (EF^2 \cos\psi - E^2 F \sin\psi)\cos\theta]^{-1}. \tag{24}$$

The first integral in (23) corresponds to the internal motion of the particles, and the second part corresponds to the rotational motion of Σ'. However, it should be noted that those two parts in (23) are coupled, because the integrand (including J) of the latter part is a function of the internal coordinates x', y', and z'. And yet, since $U(x', y', z')$ is a strong function of the distribution of the particles in the case of a liquid, only the configurational states which correspond approximately to the minimum value of U will contribute appreciably to the configurational integral. The moment of inertia coefficients and the products of inertia A, B, C, D, E, and F are nearly constants for those configurations. Thus the following approximation should be valid:

$$\int\cdots\int\frac{1}{J(x', y', z', \theta, \psi)}\exp\{-[T_i(x', y', z', p_{x'}, p_{y'}, p_{z'})+U(x', y', z')+\tfrac{1}{2}A(x', y', z')$$
$$\times\omega_{x'}^2+\cdots+F(x', y', z')\omega_{z'}\omega_{x'}]/kT\}\,dx_1'\cdots dz_{n-2}'\cong\frac{1}{J_0}\exp[-(\tfrac{1}{2}A_0\omega_{x'}^2+\cdots+F_0\omega_{z'}\omega_{x'})/kT]$$
$$\times\int\cdots\int\exp[-(T_i+U)/kT]dx_1'\cdots dz_{n-2}' , \tag{25}$$

where $J_0, A_0, \cdots, F_0$ are the values corresponding to the distribution of particles which minimizes U. Under this approximation,

$$Q_{r,i}\cong Q_rQ_i , \tag{26}$$

where $$Q_r=\frac{1}{h^3}\int\cdots\int\frac{1}{J_0}\exp[-(\tfrac{1}{2}A_0\omega_{x'}^2+\cdots+F_0\omega_{z'}\omega_{x'})/kT]d\theta d\phi d\psi d\omega_{x'}d\omega_{y'}d\omega_{z'}; \tag{27}$$

$$Q_i=\frac{1}{n!\,h^{3n-6}}\int\cdots\int\exp[-(T_i+U)/kT]dx_1'\,dp_{x_1}'\cdots dz_{n-2}'dp_{z_{n-2}}' . \tag{28}$$

Q_r can be referred to as the rotational partition function, and Q_i as the internal partition function.

If we assume a macroscopically spherical-symmetric liquid cluster as the system, then

$$A_0=B_0=C_0,\quad D_0=E_0=F_0=0,\quad J_0=1/(A_0^3\sin\theta).$$

Hence, (27) becomes in this case

$$Q_r=\frac{1}{h^3}\int\cdots\int A_0^3\exp[-\tfrac{1}{2}A_0(\omega_{x'}^2+\omega_{y'}^2+\omega_{z'}^2)/kT]$$
$$\times\sin\theta\,d\theta d\phi d\psi d\omega_{x'}d\omega_{y'}d\omega_{z'}$$

$$=\frac{\sqrt{\pi}\,(8\pi^2kTA_0)^{3/2}}{h^3} . \tag{29}$$

The result given by (29) is the same as the rotational partition function of a spherical rigid system with the moment of inertia A_0.

V. ROTATIONAL SYMMETRY NUMBER

Although a rigorous treatment of the rotational symmetry number has to be carried out in terms of quantum mechanics,[20,21] it is also possible to understand it in terms of classical statistical mechanics when the classical approximation is valid. The canonical partition function of n identical particles is given by (7) in the classical approximation. It must be noted that the indistinguishability of identical particles is taken care of through the factor $1/n!$ and that all the identical particles are treated as if they were distinguishable in the integration; in other words all the classical states which differ only by permutation of particles have to be counted as distinct states. In the case of semirigid systems like polyatomic molecules, it is convenient to carry out the integration by assuming that each particle is localized at its site, for example, through the normal mode analysis. However, since the states which differ only by permutations of particles have to be counted as distinct, the result obtained under the localized situation has to be multiplied by $n!$ if the lattice does not have rotational symmetry. When the lattice has rotational symmetry, multiplication by $n!$ yields too large a result and this must be corrected by dividing it by the symmetry number in order to count all the classical states once and only once. Thus the symmetry number is defined only when the phase integral is performed under the localized situation. The details on this point are discussed by Ehrenfest and Trkal[22] and Mayer and Mayer,[10] and were recently reviewed by Nishioka and Pound.[23]

As discussed above, the symmetry number need not be considered when (7) is directly evaluated without using the localized situation. Since (7) and (20) are the same physical quantity represented by two different choices of variables, the symmetry number need not be considered in the present argument. Therefore the rotational partition function of a spherical liquid cluster is approximated by (29).

VI. CONCLUSION

The rotation of a liquid cluster of molecules can be defined irrespective of the molecular mobility. The canonical partition function of a liquid cluster can be approximately separated into translational, rotational and internal partition functions. The symmetry number need not be considered in nonrigid systems. The numerical value of the rotational partition function of a liquid cluster is approximately the same as that of a rigid system with the same density and shape and this yields a value of about 10^9 for a liquid cluster of about 100 water molecules, as assumed by Lothe and Pound.[1] It should be possible to extend the argument of this article to nonrigid systems in general.

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[1] J. Lothe and G. M. Pound, J. Chem. Phys. 36, 2080 (1962).

[2] J. Lothe and G. M. Pound, J. Chem. Phys. 45, 630 (1966).

[3] J. Lothe and G. M. Pound, J. Chem. Phys. 48, 1849 (1968).

[4] C. Eckart, Phys. Rev. 47, 552 (1935).

[5] E. B. Wilson, Jr., and J. B. Howard, J. Chem. Phys. 4, 260 (1936).

[6] H. H. Nielsen, Phys. Rev. 60, 794 (1941).

[7] G. Herzberg, Molecular Spectra and Molecular Structure (D. Van Nostrand Co., Inc., New York, 1945), Vol. II.

[8] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, Molecular Vibrations (McGraw-Hill Book Co., Inc., New York, 1955), pp. 273–284.

[9] J. E. Wollrab, Rotational Spectra and Molecular Structure (Academic Press Inc., New York, 1967), p. 399.

[10] J. E. Mayer and M. G. Mayer, Statistical Mechanics (John Wiley & Sons, Inc., New York, 1940), pp. 195–199.

[11] F. F. Abraham and G. M. Pound, J. Chem. Phys. 48, 732 (1968).

[12] R. Meyer and H. Günthard, J. Chem. Phys. 49, 1510 (1968).

[13] A. Messiah, Quantum Mechanics (North-Holland Publishing Co., Inc., Amsterdam, 1966), Chap. XVIII.

[14] T. L. Hill, An Introduction to Statistical Thermodynamics (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1960), p. 76.

[15] Actually we have implicitly introduced an ensemble already, because the behavior of the supersaturated vapor, in which sizes of clusters keep changing by attachment or evaporation of monomers, is represented by an ensemble of systems which have definite distributions of clusters of various sizes. Thus, the present ensemble is an ensemble within another ensemble.

[16] This point was suggested by Professor J. P. Hirth.

[17] S. Kunii and K. Senda, Rikigaku (Maruzen, Tokyo, 1958), Vol. II.

[18] H. Goldstein, Classical Mechanics (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1950).

[19] R. C. Tolman, The Principles of Statistical Mechanics (Oxford University Press, London, 1938), pp. 1–98.

[20] H. Ludloff, Z. Physik 57, 227 (1929).

[21] J. E. Mayer, S. Brunauer, and M. G. Mayer, J. Am. Chem. Soc. 55, 37 (1933).

[22] P. Ehrenfest and V. Trkal, Proc. Sec. Sci. Amsterdam 23, 162 (1920).

[23] K. Nishioka and G. M. Pound, Am. J. Phys. (to be published).