CORRELATION BETWEEN THE SIGNIFICANT LIQUID STRUCTURE THEORY AND THE CELL THEORY

BY TEREESA S. REE, TAIKYUE REE, AND HENRY EYRING

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF UTAH, SALT LAKE CITY

Communicated December 16, 1963

In 1937 Lennard-Jones and Devonshire¹ (hereafter denoted as L-J & D) proposed the so-called cell theory on a quantitative basis by introducing certain assumptions. The main idea of the assumptions is that an atom in a dense gas is to be regarded as confined for most of its time to a cell whose volume is \( V/N \), where \( V \) is the molar volume of the gas and \( N \) is the number of atoms, and that its average environment is something like that of an atom in a liquid or a crystal. This picture can only be accepted as a rough first approximation, for it neglects the possibility of the migration or diffusion of atoms from one cell to another. This restriction of ignoring interchange of molecules between cells introduces an error in the entropy of the system, which is usually corrected by arbitrarily adding what is known as the communal entropy factor, \( e^N \). The cell theory has been investigated by several authors²–⁷ by introducing holes in the lattice. This procedure eliminated the necessity of introducing the factor \( e^N \). However, none of these procedures shows much improvement over the original cell theory in calculating the compressibility factors, vapor pressures, and various thermodynamic properties, even though theoretically they are an improvement.

In this paper, we introduce Eyring’s idea of the “degeneracy factor”⁸–¹¹, into the free volume term in Ono’s hole theory based on the earlier L-J & D procedures. In this way, we obtain a new partition function using the Bragg-William approximation and apply it to the equation of state and the thermodynamic properties of rigid sphere molecules. The results obtained are astonishingly good compared to the previous hole theories and to the L-J & D theory. Furthermore, it is shown that the significant liquid structure theory can be related to the L-J & D theory.

Theory.—The cell theory of L-J & D is derived from the classical partition function, \( Z_N \), for an assembly of \( N \) monatomic molecules:\¹²

\[
Z_N = \lambda^{-3N}Q_N. \tag{1}
\]

Here, \( \lambda^3 = \hbar^2/2\pi mkT \) and \( Q_N \) is the associated configurational integral defined as:
\[ Q_N = \frac{1}{N!} \int_V \ldots \int_V e^{-\phi'(r_N)/kT} \, dr_N, \quad (2) \]

the integration is over the configuration space, \( V \) is the volume, \( T \) the temperature, \( k \) the Boltzmann constant, \( \hbar \) Plank’s constant, \( \phi'(r_N) \) the potential of intermolecular force. If we divide the volume \( V \) into \( L \) cells, \( (\text{where } L \geq N), \) and the volume of the cells is \( \Delta_1, \Delta_2, \ldots, \Delta_L \), and express the integral of each molecule over \( V \) in the configuration space as a sum of integrals over the individual cells, the above configurational integral becomes

\[ Q_N = \frac{1}{N!} \sum_{i_1=1}^{L} \ldots \sum_{i_N=1}^{L} \int_{\Delta_{i_1}} \ldots \int_{\Delta_{i_N}} e^{-\phi'(r_N)/kT} \, dr_N. \quad (3) \]

The sum contains \( L^N \) terms corresponding to the \( L \) different cells to which the coordinates of each of the \( N \) different molecules may be restricted. Since here it has been assumed that each cell is sufficiently small so that there is only one molecule in one cell, and that the cell is sufficiently large so that the intermolecular forces do not extend beyond immediately adjacent cells, the above summation contains only \( L!/L^{N-N}! \) nonvanishing terms. Let us consider a lattice system in which any one lattice site has \( z \) nearest neighbors at a distance \( a \). Because of the presence of lightly held lattice sites located in the excess volume of the liquid over the solid, the coordination number of molecule \( i \), \( z_i \), will be decreased according to the equation:

\[ z_i = y_i \sigma, \quad (4) \]

where \( y_i \) is the fraction of nearest neighbor sites of the \( i \)th molecule which are occupied, and \( \sigma \) is the maximum number of the nearest neighbors. Then, \( \phi'(r_N) \) in equation (3) is written as follows:

\[ \phi'(r_N) = \sum_{i=1}^{N} \frac{z_i}{2} \phi(a) + \sum_{i=1}^{N} \frac{z_i}{2} [\phi(a + r_i, y_i) - \phi(a)]. \quad (5) \]

The first term on the right is the potential energy due to the molecules at the cell origin, and the second term is the potential energy due to the molecules being located away from the cell origin. According to Lennard-Jones, the energy of interaction of two molecules at a separation of \( r \) is given by:

\[ \phi(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} \right] - \left[ \left( \frac{\sigma}{r} \right)^{6} \right] \quad (6) \]

and

\[ \phi(a) = \epsilon \left[ 1.0109 \left( \frac{2^{1/6} \sigma}{a} \right)^{12} - 2.4090 \left( \frac{2^{1/6} \sigma}{a} \right)^{6} \right] = \epsilon \left[ 1.0109 \left( \frac{\sigma^2}{q} \right)^{4} - 2.4090 \left( \frac{\sigma^2}{q} \right)^{2} \right]. \quad (7) \]

Here \( \sigma \) and \( \epsilon \) are the distance and energy characteristic of the system, and the second equality in \( \phi(a) \) is true only for a hexagonally packed lattice; i.e., \( q = a^2/\sqrt{2} \) where \( q \) is the cell size. We should note here that in \( \phi(a) \) the nonnearest
neighbor interaction has also been taken into account. Hence, using equation (5), one obtains

$$\int_{\Delta n} dr_1 \int_{\Delta n} dr_2 \ldots \int_{\Delta N} dr_N \exp[-\phi'(r^N)/kT] = \prod_{i=1}^{N} [e^{-z\phi(a)/2kT}]^{y_i} (y_i)$$

(8)

where \(j(y_i)\) is a "generalized free volume," in that it accounts for neighboring lattice sites, some of which are vacant, and it is defined as:

$$j(y_i) = \int_{\Delta} \left\{ \exp \left[ -z y_i \phi(a + r, y_i) - \phi(a) \right] \right\} 4\pi r_i^2 dr_i.$$

(9)

If all the cells around the \(i\)th molecule are occupied, then \(y_i = 1\) and \(j(y_i)\) is identical with \(v_f\), tabulated by Wentorf et al.\(^{14}\). If all the surrounding cells are empty, the \(y_i = 0\), and \(j(0)\) becomes the volume of the cell. Equation (9) shows that \(j(y_i)\) does not depend on \(y_i\) in a simple way. However, the following linear dependency of \(j(y_i)\) has been assumed by various authors:

(a) Henderson:\(^a\)

$$j(y_i) = y_i v_f + (1 - y_i) q;$$

(10)

(b) Cernuschi and Eyring:\(^2\)

$$j(y_i) = v_f;$$

(11)

(c) Ono:\(^3\)

$$\ln j(y_i) = y_i \ln v_f + (1 - y_i) \ln q;$$

(12)

(d) Peek and Hill:\(^4\)

$$j(y_i) = j(\bar{y}) ;$$

where \(\bar{y}\) is the average nonempty site around any molecule.

(e) Rowlinson and Curtiss:\(^5\)

$$\ln j(y_i) = \ln j(\bar{y}) + (y_i - \bar{y}) \left[ \frac{\partial}{\partial y_i} \ln j(y_i) \right]_{y_i = \bar{y}} ;$$

(13)

(f) Present model:

$$\ln j(y_i) = y_i \ln v_f q_i + (1 - y_i) \ln q.$$ \hspace{1cm} (14)

The factor \(q_i\) in equation (14) is the Eyring degeneracy factor, and has been introduced by the authors for the following reason: it is natural to suppose that, of the possible positions available to a molecule on the average, some one is energetically favored over the others by the way the neighbors are organized around a molecule; this difference in energy between the best position and the neighboring available positions should be proportional to the interaction potential energy, \(z\phi(a)/2\) and inversely proportional to the number of holes, \(n_h = z(1 - \bar{y})\); thus, it should have the value \(a'\phi(a)/2(1 - \bar{y})\), where \(a'\) is a proportionality constant fixed at the melting point. Then the degeneracy due to the holes around a molecule is written as:

$$q_i = 1 + z(1 - \bar{y}) \exp[a'\phi(a)/2kT(1 - \bar{y})] ,$$ \hspace{1cm} (15)
where the unity in the first term on the right of equation (15) indicates the best available position.

By substituting equation (14) into (8), equation (3) is written as follows:

\[ Q_N = \frac{1}{N!} \sum_{<y_i>} \prod_{i=1}^{N} (v_f y_i)^{y_i} (1 - y_i) \exp \frac{-zy_{i} \phi(y_i)}{2kT}, \]  

(16)

where \( <y_i> \) indicates that the summation is taken over all possible values of \( y_i \) from 0 to 1. Equation (16) can be evaluated by means of the Bragg-Williams approximation\(^{1}\) as Hendon did in his hole theory.\(^9\) Accordingly, since \( q = V/L \) and \( v = V/N \), then

\[ \gamma_t = N/L = q/v. \]  

(17)

The partition function of the hole theory is thus written as:

\[ Z_N = \lambda^{-3N} \left\{ \exp \frac{-2\phi(a)}{2kT} \right\} \left[ 1 + z \frac{v - q}{v} \exp \frac{a' \phi(a)v}{2(v - q)kT} \right] \frac{v_{f}^{qN/\epsilon}}{q} q^{N}(L/N). \]  

(18)

or, by using Sterling’s approximation,

\[ Z_N = \lambda^{-3N} \left\{ \exp \frac{-2\phi(a)}{2kT} \right\} \left[ 1 + z \frac{v - q}{v} \exp \frac{a' \phi(a)v}{2(v - q)kT} \right] \frac{v_{f}^{qN/\epsilon}}{q} \times v^{N(1 - q/v)} (1 - v/q)^N. \]  

(19)

In the following, we obtain the equation of state and the entropy for the rigid sphere model using equation (19).

Calculations.—The following relations apply for the rigid sphere molecules:

\[ \phi(r) = 0 \quad \text{if} \quad r > d \]
\[ \quad = \infty \quad \text{if} \quad r < d. \]

(20)

where \( d \) is the diameter of the sphere and \( a > d \). Using the above relations, we obtain:

\[ \phi(a) = 0. \]

Thus, equation (19) becomes very simple for hard spheres, i.e.,

\[ Z_N = \lambda^{-3N} \left[ (13 - 12) \frac{v_f}{q} \right]^{qN/\epsilon} q^{N} v^{N(1 - q/v)} (1 - v/q)^N. \]  

(21)

where \( z \) has been taken as 12.

The Helmholtz free energy of a system \( A \) is related to \( Z_N \) by

\[ A = -kT \ln Z_N. \]

(22)

For carrying out numerical calculation, \( q = V_s/N \) is used\(^{18}\) where \( V_s \) is the molar solid volume at the melting point (Ono\(^4\) originally made an assumption, \( q = a^3 \)\). From the result of machine calculation by Alder and Wainwright,\(^{17},^{18}\) the phase transition from solid to liquid is observed at 1.5 \( V_o < V_s < 1.7 V_o \), where \( V_o \) is the closest packing volume, being equal to \( N d^3/\sqrt{2} \); therefore, the mean value \( V_s = 1.6 V_o \) is taken for our calculations. The value \( v_f/q \) for \( V_s = 1.6 V_o \) was obtained by interpolating the results obtained by Buehler et al.\(^{19}\)
The pressure is given by

\[ P = -(\partial A/\partial V)_T. \]  

Hence, the compressibility factor is given by

\[ \frac{PV}{NkT} = 2.298 \left( \frac{V_0}{V} \right) - 1.6 \frac{V_0}{V} \ln \left( 1 - 1.477 \frac{V_0}{V} \right) + \frac{2.363 (V_0/V)^2}{1 - 1.477 (V_0/V)} - \frac{V}{1.6 V_0} \ln \left( 1 - 1.6 \frac{V_0}{V} \right). \]  

Expanding equation (24) in powers of $b/v$, we obtain

\[ \frac{PV}{NkT} = 1 + 1.046 \left( \frac{b}{v} \right) + 0.636 \left( \frac{b}{v} \right)^2 + 0.242 \left( \frac{b}{v} \right)^3 + 0.106 \left( \frac{b}{v} \right)^4 + \frac{0.0494}{(b/v)^6} + \ldots \]  

where $b = (2/3) \pi d^3$.

Equation (25) is in good agreement with the correct virial expansion

\[ \frac{PV}{NkT} = 1 + \frac{b}{v} + 0.625 \left( \frac{b}{v} \right)^2 + 0.287 \left( \frac{b}{v} \right)^3 + 0.110 \left( \frac{b}{v} \right)^4 + 0.0386 \left( \frac{b}{v} \right)^5 + \ldots \]
It is interesting to note that all virial coefficients in equation (25) are positive. Indeed, the present theory is in better agreement with the correct virial expansion than is the result obtained by Henderson from the significant liquid structure theory; i.e.,

\[
\frac{PV}{NkT} = 1 + 1.296 \left( \frac{b}{v} \right) + 0.470 \left( \frac{b}{v} \right)^2 + 0.164 \left( \frac{b}{v} \right)^3 + 0.068 \left( \frac{b}{v} \right)^4 + \ldots \quad (27)
\]

In Figure 1, it is shown that for the compressibility factor the present theory agrees better with the machine calculation by Alder and Wainwright than the cell theory. It has also been found that our virial coefficients agree with those in equation (26) even better than those in the Percus-Yevick pressure equation.

The entropy is obtained as follows:

\[
S = -\frac{\partial A}{\partial T}\rho. \quad (28)
\]

\(S_E\), the excess entropy at constant pressure over that of an ideal gas, is given as

\[
S_E = S + Nk \ln P - S^*(T) \quad (29)
\]

where \(S^*(T) = \lim_{P \to 0} (S + Nk \ln P)\). Hence, \(S_E\) is given by:

\[
\frac{S_E}{Nk} = 1.6 \frac{V_0}{V} \ln \left[ \left( 13 - 19.2 \frac{V_0}{V} \right) 0.0183 \right] +
\left( 1 - \frac{V}{1.6V_0} \right) \ln \left( 1 - \frac{1.6V_0}{V} \right) - 1 + \ln \left( \frac{PV}{RT} \right) \quad (30)
\]

The calculations are made with the use of equation (30), and the results are plotted in Figure 2. Excellent agreement with the machine calculation by Alder and Wainwright is obtained. It is obvious that the cell theory predicts higher \(-S_E\).
than the machine calculation. This is because the cell theory is really a theory for the superheated solid.

Discussion.—Henderson has obtained the following partition function for the rigid sphere molecules by using the significant liquid structure theory with the value \( V_s = 1.5 V_0 \):

\[
Z_N = \left( \frac{2\pi m k T}{h^2} \right)^{1/2} e^{N V / 2N} \left[ 0.00967 \left( 8 - 11 \frac{V_0}{V} \right) \right]^{V_s N V_s / V} \tag{31}
\]

where \( e = 2.718 \), while the present theory with \( V_s = 1.5 V_0 \) gives

\[
Z_N = \left( \frac{2\pi m k T}{h^2} \right)^{1/2} e^{N V / 2N} \left[ 0.0183 \left( 13 - 18 \frac{V_0}{V} \right) \right]^{V_s N V_s / V} \times \left( 1 - \frac{q}{v} \right)^{(1 - \nu / q) N} \tag{32}
\]

For large and small volumes, the following mathematical equality holds for the term \((1 - q/v)^{(1 - \nu / q)}\) in equation (32):

\[
\lim_{v \to \infty} \left( 1 - \frac{q}{v} \right)^{(1 - \nu / q)} = e \tag{33}
\]

and

\[
\lim_{v \to q} \left( 1 - \frac{q}{v} \right)^{(1 - \nu / q)} = 1. \tag{34}
\]

Hence, equation (32) at low and high densities yields the following equations, respectively:

\[
Z_N = \left( \frac{2\pi m k T}{h^2} \right)^{1/2} e^{N V / 2N} \left[ 0.0183 \left( 13 - 18 \frac{V_0}{V} \right) \right]^{V_s N V_s / V} \tag{35}
\]

and

\[
Z_N = \left( \frac{2\pi m k T}{h^2} \right)^{1/2} e^{N V / 2N} \left[ 0.00673 \left( 13 - 18 \frac{V_0}{V} \right) \right]^{V_s N V_s / V}. \tag{36}
\]

Equations (35) and (36) are nearly identical with (31), the partition function for the significant liquid structure theory.

Summary.—Eyring's idea of the so-called degeneracy factor in the significant liquid structure theory is introduced into the classical hole theories derived from Lennard-Jones and Devonshire's cell theory. The partition function thus obtained is applied to liquids and gases of rigid sphere molecules. The virial coefficients in our equation of state are very close to those obtained by the molecular dynamics method, while none of the earlier classical quasi-lattice theories predict good virial coefficients. Our theory is also used to obtain the entropies and compressibility factors of rigid sphere molecules in close agreement with the results of the machine calculations. We further show that the partition function from the improved hole theory is nearly equal to that from the significant liquid structure
theory in the regions of low and high densities. These facts indicate that the classical hole theories require a degeneracy factor of the sort introduced.

The authors wish to thank the National Science Foundation under grant GP-415, and the Atomic Energy Commission under grant AT(11-1)-1144 for financial support of this research. We also appreciate the valuable advice of Dr. Francis H. Ree of Lawrence Radiation Laboratory, and our stimulating discussions with him.

8 Ibid., 38, 1714 (1963).
10 Ibid., 39, 54 (1963).
12 Eyring, H., and T. Ree, these PROCEEDINGS, 47, 526 (1961).
18 Ibid., 33, 1439 (1960).

DNA CIRCULARITY AND THE MECHANISM OF STRAND SELECTION IN THE GENERATION OF GENETIC MESSAGES*

BY M. HAYASHI, M. N. HAYASHI, AND S. SPIEGELMAN

DEPARTMENT OF MICROBIOLOGY, UNIVERSITY OF ILLINOIS

Communicated by T. M. Sonneborn, December 9, 1963

A potentially informative paradox exists in the literature of genetic transcription. Experiments1-3 with preparations of purified DNA and transcribing enzyme (the DNA-dependent RNA polymerase, for brevity referred to as "transcriptase") have yielded RNA complementary to both strands of the DNA employed as a template. On the other hand, analyses4-6 of transcription in the intact cell revealed that primarily only one of the two complementary DNA strands generates RNA messages. Resolution of this riddle could conceivably illuminate the mechanism operating to restrict in vivo transcription to one of the two strands.

As a departure for a further analysis of the difference between the in vivo and in