26 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (1), 26—28 (1975) [Vol. 48, No. 1

Investigation of the Concept of Free Volume by Means of a Correlation Function Method

Kiyoshi ARAKAWA and Kazumitsu KOJIMA
Research Institute of Applied Electricity, Hokkaido University, Sapporo 060

(Received March 6, 1974)

An investigation of the validity of the free volume theory of liquid has been undertaken on the basis of the theory of correlation functions. A formula for free volume without use of a geometrical model has been proposed and discussed. The magnitude of equivalent free volumes obtained from the formula has been found to be nearly equal to that calculated from the entropy of vaporization by means of the free volume theory. The results give support to the physical reality of the concept of free volumes. The communal entropy deduced agrees with that obtained by an expansion formula to the first order of density. A formula for compressibility has also been derived, which gives satisfactory results in comparison with observed data.

The Lennard-Jones and Devonshire (LJD) theory and the Yvon-Born-Green-Kirkwood (YBGK) theory were the starting points of extensive researches in the field of the theory of liquids.[1] The free volume theory originated from the LJD theory has been applied extensively to liquids[2] and solutions[3,4] as an approximate representation of their thermodynamic properties.

On the semi-emprical basis of the free volume theory, several critical studies have been carried out, among which those by Kirkwood[5] and by Hildebrand[6] are the most important. Concerning Kirkwood's critique (1950) with respect to the formulation of the theory, several improvements have been made.[7–9] The problem of communal entropy was also investigated by Hoover and Ree[10] and others by means of the Monte Carlo method.

Hildebrand proposed a serious question on the physical reality of the concept of free volume from results showing that free volumes calculated from identical thermodynamical data showed a marked discrepancy among the models adopted.[6] Thus it seems worth-while to attempt to place the concept of free volume on a sounder theoretical basis and to give a difinite explanation.

Since the proposition of Percus-Yevick and H N C equations in 1958—1960, development in the equilibrium theory of liquids using correlation functions is remarkable.[11–16] Some noticeable results from model experiments by Bernal and King[17] have been obtained, as well as those from computer experiments[18] by means of the Monte Carlo method and molecular dynamics.

At present, the application of these new theories to real liquids is limited except for that to liquid argon and liquid metals, model theories such as the free volume theory of liquids still playing an important role for the explanation of various properties of fluids.

We have examined the theoretical basis of the free volume theory according to recent liquid theories using correlation functions, with the purpose of elucidating the physical meaning of the concept of free volume.

Theoretical

Theoretical Consideration on the Nature of Free Volume. The Percus-Yevick integral equation is expressed as follows.[11–16]

$$h(r) = c(r) + \rho\int c(|\boldsymbol{r}-\boldsymbol{r}'|)h(|\boldsymbol{r}'|)\mathrm{d}\boldsymbol{r}' \qquad (1)$$

$$c(r) = g(r)\exp(u(r)/kT)[\exp(-u(r)/kT)-1], \qquad (2)$$

where $c(r)$ is the direct correlation function, $h(r)=g(r)-1$ the total correlation function, $g(r)$ the radial distribution function, and $u(r)$ the two body potential.

The equation has been solved analytically by Wertheim[19] and Thiele[20] for the fluid of hard spheres. The equation of state obtained has been found to be identical with that deduced from the scaled particle theory by Reiss *et al.*,[21] which is expressed as

$$p = \rho kT(1+y+y^2)/(1-y)^3, \quad y = \pi\rho a^3/6, \qquad (3)$$

where ρ is the number density, a the diameter of a hard sphere and y the volume fraction of hard sphere molecules.

The partition function Z for a hard sphere fluid is derived from Eq. (3) to be

$$Z = \left[\frac{V}{N}(1-y)\exp\left(1-\frac{3y(2-y)}{2(1-y)^2}\right)\right]^N\left(\frac{2\pi mkT}{h^2}\right)^{3/2N}. \qquad (4)$$

For a hard sphere fluid with an internal potential V_N, it is expressed as

$$Z = \left[\frac{V}{N}(1-y)\exp\left(1-\frac{3y(2-y)}{2(1-y)^2}\right)\right]^N\left(\frac{2\pi mkT}{h^2}\right)^{3/2N} \times \exp(-\langle V_N\rangle_{\mathrm{av.}}/kT). \qquad (5)$$

A formula similar to this expression was first introduced by Longuet-Higgins and Widom[22] and also given by Miller.[23] We have given an explanation of its theoretical basis in connection with the mean spherical model (MSM) approximation proposed by Lebowitz *et al.*[24] (see Appendix).

The free volume fraction f is defined as follows.

$$f \equiv (1-y)\exp\left(-\frac{3y(2-y)}{2(1-y)^2}\right). \qquad (6)$$

From Eq. (5), we then have

$$Z = \left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \mathrm{e}fv\right]^N \exp(-\langle V_N\rangle_{\mathrm{av.}}), \qquad (7)$$

where $v=V/N$ is the volume per molecule in liquid.

According to the free volume theory of liquid,[5] the partition function is expressed as a function of free volume, independent of the above theory as follows.

$$Z = \left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \mathrm{e}v_{\mathrm{f}}\right]^N \exp(-\langle V_N\rangle_{\mathrm{av.}}/kT) \qquad (8)$$

where $v_f = V_f/N$ is the free volume (fluctuational volume[25]) per molecule.

Equating Eqs. (7) and (8), we have

$$f = v_f/v \quad \text{or} \quad f = V_f/V \tag{9}$$

from which the nomenclature of f comes.

From Eqs. (6) and (7) we can calculate the values of V_f. Values of the free volume fraction f as a function of y, together with the values of V_f calculated for two liquids CCl_4, c-$C_6F_{11}CF_3$ are given in Table 1.

TABLE 1. FREE VOLUME FRACTION AND FREE VOLUME

y	0.50	0.51	0.52	0.54	0.60	0.64
$f \times 10^3$	5.55	4.25	3.20	1.72	0.152	0.0152
V(cm^3/mol) CCl_4	0.54	0.41	0.31	0.17	0.015	0.0015
c-$C_6F_{11}CF_3$	1.09	0.83	0.63	0.34	0.030	0.0030

Determination of the Equilibrium Values of Volume Fraction y and Free Volume V_f in Liquids. In the case of the face-centered cubic packing of hard sphere molecules, where all molecules are in contact with each other, the magnitude of y is $\sqrt{2}\pi/6 = 0.74$, which is the maximum value of y.

Bernal and King proposed the "random network model" for the structure of liquid state on the basis of a series of model experiments,[17] giving the magnitude of y to be 0.64 for the liquid state at its triple point.

For determination of the equilibrium values of y, the equation of state derived from Eq. (5) is used.

$$pV = NkT\left(\frac{1+y+y^2}{(1-y)^3}\right) - V\frac{\partial \langle V_N \rangle_{\text{av.}}}{\partial V} \tag{10}$$

When $\langle V_N \rangle_{\text{av.}}$ is taken to be propotional to the n-th power of volume V as usual, we have

$$pV = NkT\left(\frac{1+y+y^2}{(1-y)^3}\right) + n\langle V_N \rangle_{\text{av.}}. \tag{11}$$

For the determination of y the equation of state at vanishing pressure,[4,26] which is obtained by equating the right-hand side of Eq. (11) to zero, is used, together with the relation $-\langle V_N \rangle_{\text{av.}} = \Delta H_{\text{vap.}} - RT$ ($\Delta H_{\text{vap.}}$; the heat of vaporization). Thus, we get

$$RT\left(\frac{1+y+y^2}{(1-y)^3}\right) = n(\Delta H_{\text{vap.}} - RT). \tag{12}$$

The equilibrium values of y thus determined using the experimental data[27] of n and $\Delta H_{\text{vap.}}$ for CCl_4 and c-$C_6F_{11}CF_3$ are 0.50 and 0.54 at 25 °C, respectively. In the case of CCl_4 the magnitude of y determined by the consideration of compressibility is 0.51, in line with that determined by Eq. (12).

The values of V_f for CCl_4 and c-$C_6F_{11}CF_3$ at 25 °C are thus determined to be 0.41 and 0.34 cm^3/mol, respectively, from the values of y given in Table 1. The values are nearly equal to those for "$\Delta S_{\text{vap.}}$" given by Hildebrand (Table 2). This shows that the values of V_f obtained directly from $\Delta S_{\text{vap.}}$ by means of the free volume theory are consistent with those of the "equivalent free volume" determined here as a statistical average by use of correlation functions (Eqs. (6), (9), and (12)).

TABLE 2. FREE VOLUMES AT 25 °C (cm^3/mol)[a]

	V	V_f				
		van der Waals[b]	$\Delta S_{\text{vap.}}$[c]	Cage[d]	Cubic[e]	This work
CCl_4	96	7.7	0.24	0.042	0.34	0.41
c-$C_6F_{11}CF_3$	196	10.9	0.36	0.034	0.27	0.34

a) The values of V_f for models b)—e) are cited from Table 1 in the note by Hildebrand.[6] They were calculated from identical data[27] on the basis of the relation $\partial S/\partial V = R(\partial \ln V_f/\partial V)$. The difference between the values is ascribed to the geometrical feature of each model.[6] b) Calculated from the definition $V_f = V - b$. c) Calculated from $\Delta S_{\text{vap.}}$ using the relation $\Delta S_{\text{vap.}} = R \ln(V_g/V_f)$, where V_g is the volume of gaseous state in equilibrium. d) The fluctuational volume for a cage model; $(V_f)_{cage} = [R/V^{2/3}(\partial S/\partial V)]^3$. e) The fluctuational volume for simple cubic packing.

For deriving Eqs. (1)—(9) (except Eq. (8)), no approximation based on a geometrical model was introduced. The free volume fraction defined by Eq. (6) consists of a factor $1-y$ and an exponential factor $\exp(-3y(2-y)/2(1-y)^2)$. The former factor is equal to the fraction of void space for the total volume V, and the latter is supposed to come from the volume exclusion effect of hard sphere molecules in their thermal motions. The free volume V_f is thus regarded as a statistical average of fluctuational void space. This brings the free volume fraction f as a function of y only. Agreement of the values of V_f for $\Delta S_{\text{vap.}}$ with those determined through f (Eq. (6)) gives a comfirmative support of the concept of free volume calculated from $\Delta S_{\text{vap.}}$ as a thermodynamic parameter.

Communal Entropy. The communal entropy ΔS is obtained as

$$\Delta S = k \ln (ef)^N. \tag{13}$$

Inserting Eq. (6) into Eq. (13), we get

$$\Delta S = Nk\left[1 + \ln(1-y) - \frac{3y(2-y)}{2(1-y)^2}\right]. \tag{14}$$

The volume fraction y is expressed by (ρ/ρ_0), where ρ_0 is the closest number density at face-centerd cubic packing.

$$\rho_0 = \sqrt{2}/a^3$$

and

$$y = \frac{\pi}{6}\rho a^3 = \frac{\sqrt{2}\pi}{6}\left(\frac{\rho}{\rho_0}\right) = 0.740475\left(\frac{\rho}{\rho_0}\right).$$

Thus the communal entropy ΔS is expressed by the power of (ρ/ρ_0) as follows.

$$\Delta S/Nk = 1 - 2.9619(\rho/\rho_0) - 2.741515(\rho/\rho_0)^2 \tag{15}$$

The expansion of $\Delta S/Nk$ by (ρ/ρ_0) agrees to the first order term with the formula obtained by Hoover and Ree[28] by means of the Mayer f function expansion. The linear dependence of the communal entropy at small density has been confirmed by means of a Monte Carlo calculation.[10]

Compressibility. From Eqs. (6) and (10), we can derive the following formula for the isothermal compressibility κ_T of liquid, using the relation

$$\langle V_N \rangle_{\text{av.}} = \Delta H_{\text{vap.}} - RT = \frac{\text{Const.}}{V^n} \tag{16}$$

$$\kappa_{\mathrm{T}} = \left[\frac{1}{\kappa_0} - \frac{n(n+1)}{V}(\Delta H_{\mathrm{vap.}} - RT)\right]^{-1}, \tag{17}$$

where κ_0 is the isothermal compressibility for the fluid of hard spheres and expressed by

$$\kappa_0 = \left(\frac{V}{NkT}\right)\left[\frac{(1-y)^2}{(1+2y)}\right]^2. \tag{18}$$

The first term in $(\kappa_{\mathrm{T}})^{-1}$ in Eq. (17) comes from the repulsion of hard spheres in thermal motions and the second term from the attraction between molecules.

Using Eqs. (17) and (18), we have calculated the values of compressibility of various liquids and the results are given in Table 3. As the values of a we have used those estimated from the results of studies of X-ray diffraction,[29,30] second virial coefficient,[2] viscosity[2] and molecular structure theory,[31] noting that the estimated values of a should be consistent with the values of y determined through Eq. (12). The agreement between calculated and observed values is very good. Equations (17) and (18) could therefore be used for determination of the equivalent hard sphere diameter of molecules.

TABLE 3. COMPRESSIBILITY

	a	n	T	y	$\kappa_{\mathrm{obs.}}$	$\kappa_{\mathrm{calc.}}$
	(Å)		(K)		(10^{-12} dyn^{-1} cm^2)	
Ar	3.40	1.00	87.3	0.43	215.2	226.8
CCl_4	5.40	1.09	298	0.51	106.7	90.9
C_6H_6	5.20	1.05	293	0.50	101.5	101.1
C_6H_{12}	5.60	1.00	298	0.51	116.0	95.1

Appendix

A similar equation to Eq. (5) has been used by Longuet-Higgins and Widom[22] and also by Miller[23] for a discussion of thermodynamic properties of fluids. We have undertaken here to give a theoretical basis for the approximation.

Using the exact solution of Percus-Yevick equation for the fluid of hard spheres together with the mean spherical model (MSM) approximation,[24] we postulate as follows as regards the direct correlation function $c(r)$,

$$\begin{aligned} c(r) &= c_0(r) && \text{for } r \leq a \\ c(r) &= -u(r)/kT && \text{for } r > a, \end{aligned} \tag{A1}$$

where $c_0(r)$ is Wertheim-Thiele's analytical solution.

The MSM approximation assumes (1) the Ornstein-Zernike equation, (2) $g(r)=0$ for $r<a$ and (3) $c(r)=-u(r)/kT$ for $r>a$. When $u(r)\rightarrow 0$, the MSM approximation is reduced to the Percus-Yevick equation for the fluid of hard spheres with no attraction. Thus the direct introduction of Wertheim-Thiele's solution to MSM as in Eq. (A1) is reasonable as a zeroth order approximation, if $u(r)$ is not much larger than kT. In the approximation Eq. (A1), the change of $c(r)$ from $c_0(r)$ for $r \leq a$ which results from the presence of $u(r)$ for $r>a$ is ignored.

The compressibility equation is expressed as

$$\partial(p/kT)/\partial\rho = 1 - \rho\int c(\boldsymbol{r})\mathrm{d}\boldsymbol{r}. \tag{A2}$$

Inserting Eq. (A1) into Eq. (A2), we obtain

$$\begin{aligned} \partial(p/kT)/\partial\rho &= 1 - \rho\int_0^a c_0(r)4\pi r^2\mathrm{d}r + \frac{\rho}{kT}\int_a^\infty u(r)4\pi r^2\mathrm{d}r \\ &= \frac{(1+2y)^2}{(1-y)^4} + \frac{\rho}{kT}\int_a^\infty u(r)4\pi r^2\mathrm{d}r. \end{aligned} \tag{A3}$$

Integrating with respect to ρ, we have

$$p/\rho kT = \frac{1+y+y^2}{(1-y)^3} + \frac{2\pi\rho}{kT}\int_a^\infty u(r)4\pi r^2\mathrm{d}r. \tag{A3}$$

If we put $$(2\pi/kT)\int_a^\infty u(r)4\pi r^2\mathrm{d}r \equiv \text{const.}$$

Eq. (A4) becomes identical with that used by Longuet-Higgins & Widom, and also by Miller.

References

1) A. Harashima, "Theory of Liquids," Iwanami, Tokyo (1954); T. L. Hill, "Statistical Mechanics," McGraw-Hill, New York (1956).

2) J. O. Hirshfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York (1954).

3) I. Prigogine, A. Bellemans, and V. Mathot, "The Molecular Theory of Solutions," North Holland Pub., Amsterdam (1957).

4) K. Arakawa and O. Kiyohara, This Bulletin, **43**, 975 (1970).

5) J. G. Kirkwood, *J. Chem. Phys.*, **18**, 380 (1950).

6) J. H. Hildebrand, *ibid.*, **31**, 1423 (1959).

7) J. E. Mayer and G. Careri, *ibid.*, **20**, 1001 (1952).

8) J. S. Dahler and J. G. Hirshfelder, *ibid.*, **32**, 330 (1960); H. S. Chung and J. S. Dahler, *ibid.*, **40**, 2868 (1964).

9) J. Fisher, F. Kohler, and F. Weissenböck, *ibid.*, **53**, 2004 (1970).

10) W. G. Hoover and F. H. Ree, *ibid.*, **49**, 3609 (1968).

11) H. L. Frisch and J. L. Lebowitz, "The Equilibrium Theory of Classical Fluids," Benjamin, New York (1964).

12) S. A. Rice and P. Gray, "The Statistical Mechanics of Simple Liquids," Interscience, New York (1965).

13) H. L. Frisch and Z. W. Salsburg, "Simple Dense Fluids," Academic Press, New York (1968).

14) H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke, ed., "Physics of Simple Liquids," North-Holland, Amsterdam (1968).

15) J. S. Rowlinson, "Liquids and Liquid Mixtures," 2nd ed. Butterworth, London (1969).

16) K. Kojima and K. Arakawa, *Bull. Res. Inst. Appl. Elec.* (Hokkaido Univ.), **25**, 1 (1973).

17) J. D. Bernal and S. V. King, Ref. 14), chapt. 6.

18) W. W. Wood, Ref. 14), chapt. 5; L. Verlet, *Phys. Rev.*, **159**, 98 (1967), **165**, 201 (1968).

19) M. S. Wertheim, *Phys. Rev. Lett.*, **10**, 321 (1963); *J. Math. Phys.*, **5**, 643 (1964).

20) E. Thiele, *J. Chem. Phys.*, **39**, 474 (1963).

21) H. Reiss, H. L. Frish, and J. L. Lebowitz, *ibid.*, **31**, 369 (1956); H. Reiss, *Advan. Chem. Phys.*, **9**, 1 (1964).

22) H. C. Longuet-Higgins and B. Widom, *Mol. Phys.*, **8**, 549 (1964).

23) R. C. Miller, *J. Chem. Phys.*, **55**, 1613 (1971).

24) J. L. Lebowitz and J. K. Percus, *Phys. Rev.*, **144**, 251 (1966); M. S. Wertheim, *J. Chem. Phys.*, **55**, 4291 (1971); E. Waisman and J. L. Lebowitz, *ibid.*, **56**, 3086 (1972).

25) A. Bondi, *J. Phys. Chem.*, **58**, 929 (1954).

26) I. Prigogine and A. Bellemans, *Discuss. Faraday Soc.*, **15**, 80 (1953).

27) E. B. Smith and J. H. Hildebrand, *J. Chem. Phys.*, **31**, 145 (1959).

28) W. G. Hoover and F. H. Ree, *ibid.*, **47**, 4873 (1967).

29) P. G. Mikolaj and C. J. Pings, *ibid.*, **46**, 1401 (1967).

30) A. H. Narten, M. D. Danford, and H. A. Levy, *ibid.*, **46**, 4895 (1967).

31) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, New York (1960).