

# Nonsphericalized Free Volumes for Hole Theories of Liquids

Mariana Weissmann

Citation: *The Journal of Chemical Physics* **40**, 175 (1964); doi: 10.1063/1.1724856

View online: <https://doi.org/10.1063/1.1724856>

View Table of Contents: <http://aip.scitation.org/toc/jcp/40/1>

Published by the *American Institute of Physics*

---

---

**PHYSICS TODAY**

WHITEPAPERS

## ADVANCED LIGHT CURE ADHESIVES

Take a closer look at what these environmentally friendly adhesive systems can do

READ NOW

PRESENTED BY  
 **MASTERBOND**  
ADHESIVES | SEALANTS | COATINGS

## Nonsphericalized Free Volumes for Hole Theories of Liquids

MARIANA WEISSMANN

*Facultad de Ciencias Exactas y Naturales, Departamento de Meteorología, Peru 272, Buenos Aires, Argentina*

(Received 29 July 1963)

Free-volume integrals for hole theories of liquids were calculated for some special cases by Monte Carlo numerical integration. The dependence of the free volume on the number of nearest neighbors is thus obtained. Only molecules interacting with a Lennard-Jones potential and a temperature near the critical one have been considered. The results differ considerably from those of earlier theories, where spherical symmetry was assumed. However, the introduction of vacant cells (holes) does not improve the thermodynamic functions obtained with the cell theory of Lennard-Jones and Devonshire.

### INTRODUCTION

SEVERAL approximations to hole theory of liquids have been reviewed by Rowlinson and Curtiss.<sup>1</sup> All of them, and also later works,<sup>2-4</sup> calculate the free-volume integrals by means of a sphericalization process. They assume that the potential energy of a molecule in its cell depends only on the number of neighbors but not on their location, and that it is spherically symmetric.

In this paper we evaluate the integrals without such an approximation by using a Monte Carlo numerical integration. Our main object is a critical discussion of this approximation.

In order to overcome the effects of sphericalization, a linear dependence of the free volume on the number of nearest neighbors was proposed.<sup>5,6</sup> The computed values will also indicate if such dependence is adequate.

Particles interacting with a Lennard-Jones (6-12) potential were located in cells in a face-centered cubic lattice. Only one temperature and 14 of the 144 different arrangements of neighbors were considered. The number of cells, a parameter in the theory, was obtained by minimization of the free energy.

### THEORY

The classical partition function for  $N$  molecules is

$$Z_N = \lambda^{-3N} Q_N = \frac{\lambda^{-3N}}{N!} \int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 \cdots \int_V d\mathbf{r}_N \times \exp\left[\frac{-U(\mathbf{r}_1 \cdots \mathbf{r}_N)}{kT}\right], \quad (1)$$

where  $\lambda^2 = h^2/2\pi mkT$  and the integrations are performed over the entire volume  $V$  of the vessel.  $U(\mathbf{r}_1 \cdots \mathbf{r}_N)$  is the potential energy of the system of  $N$  particles.

The volume  $V$  is divided into  $L$  cells ( $L \geq N$ ); the

cell size being  $q = V/L$  and the volume per molecule  $v = V/N$ . The fraction of vacant nearest-neighbor sites of the  $i$ th molecule is  $w_i$ , and

$$\Omega = \sum_{i=1}^N w_i.$$

If each particle is located at a lattice point (center of a cell), the potential energy of the system is

$$U_0 = z/2(N - \Omega)\phi(a),$$

where  $z$  is the number of nearest neighbors in the lattice (for a face-centered cubic lattice  $z=12$ ).  $\phi(a)$  is the potential energy of interaction of a pair of nearest neighbor molecules at a distance  $a$ .

$$U(\mathbf{r}_1 \cdots \mathbf{r}_N) = U_0 + \sum_{i=1}^N \sum_{j=1}^{z(1-w_i)} [\phi(r_{ij}) - \phi(a)]. \quad (2)$$

Each term of the sum in this equation considers Particle  $i$  as a wanderer in its cell and all neighbors  $j$  as fixed to their lattice points. This procedure was shown by Kirkwood<sup>7</sup> to be an approximation of the general case. The effect of nonnearest neighbors, being a small correction, was neglected in the calculations. It was only included in  $U_0$  as a correction factor.

Substituting Eq. (2) into (1) we obtain

$$Z_N = \lambda^{-3N} \exp\left[\frac{-Nz\phi(a)}{2kT}\right] \sum \exp\left[\frac{\Omega z\phi(a)}{2kT}\right] \prod_{i=1}^N j(w_i), \quad (3)$$

in which

$$j(w_i) = \int_q d\mathbf{r}_i \exp\left[\frac{-1}{kT} \sum_{j=1}^{z(1-w_i)} \{\phi(r_{ij}) - \phi(a)\}\right]. \quad (4)$$

The sum in Eq. (3) corresponds to all arrangements of the  $N$  molecules in  $L$  cells, which differ by more than a permutation of the molecules. Only one molecule per cell is considered, and therefore it is implied that cells are small enough to prevent double occupancy.

The function  $j(w)$  is a generalized free volume, as

<sup>1</sup> J. S. Rowlinson and C. F. Curtiss, *J. Chem. Phys.* **19**, 1519 (1951).

<sup>2</sup> J. Grindlay, *Proc. Phys. Soc. (London)* **77**, 1001 (1961).

<sup>3</sup> G. E. Blomgren, *J. Chem. Phys.* **34**, 1307 (1961).

<sup>4</sup> S. Ono, *Nuovo Cimento, Suppl.* **9**, 166 (1958).

<sup>5</sup> D. Henderson, *J. Chem. Phys.* **37**, 631 (1962).

<sup>6</sup> G. E. Blomgren, *J. Chem. Phys.* **38**, 1714 (1963).

<sup>7</sup> J. G. Kirkwood, *J. Chem. Phys.* **18**, 380 (1950).

TABLE I. Computed values of  $j(w)$  for  $q^*=1.185$  and different curve fittings given by Eqs. (8), (9), and (10) in the text. When two calculated values are given for the same  $w$ , they correspond to different (extreme) configurations.

$w$	Calculated	Spheri- calized	Linear	Log	$a+bm^w$
0	0.019±0.005	0.0195	0.018	0.018	0.018
1/12	0.021±0.005	0.0208	0.115	0.025	0.020
2/12	$\begin{cases} 0.031±0.005 \\ 0.022±0.005 \end{cases}$	0.0232	0.213	0.036	0.024
3/12	$\begin{cases} 0.039±0.005 \\ 0.025±0.005 \end{cases}$	0.0253	0.310	0.051	0.028
6/12	$\begin{cases} 0.073±0.008 \\ 0.040±0.007 \end{cases}$	0.0366	0.602	0.146	0.077
9/12	$\begin{cases} 0.216±0.013 \\ 0.415±0.014 \end{cases}$	0.0640	0.893	0.415	0.286
10/12	$\begin{cases} 0.278±0.015 \\ 0.538±0.018 \end{cases}$	0.0860	0.991	0.590	0.456
11/12	0.730±0.017	0.1360	1.088	0.835	0.732
1	1.185	1.185	1.185	1.185	1.185

it differs from the usual free volume of cell theory in the number of neighbors considered. However, the sphericalization process must lead to a worse approximation in this case, because it prevents the free volume from expanding in the direction of vacant neighboring cells.

The summation in (3) has to be evaluated with the methods used in order-disorder problems. A very simple one is the Bragg-Williams approximation, that gives all terms in the sum equal probability

$$Z_N(B-W) = \lambda^{-3N} \frac{L!}{N!(L-N)!} [j(\bar{w})]^N \times \exp \left[ -\frac{(N-\Omega)z\phi(a)}{2kT} \right];$$

$$\Omega = N\bar{w}, \quad \bar{w} = 1 - N/L = 1 - q/v. \quad (5)$$

A more refined approximation is given by the quasi-chemical method, as used in Ref. 2.

#### CALCULATIONS

The Monte Carlo method of independent samples was described by Kahn<sup>8</sup> and used for free-volume cal-

culations in a previous paper.<sup>9</sup> The basic formulas are:

$$\bar{g} = \int_V f(\mathbf{r}) g(\mathbf{r}) d\mathbf{r} \cong \frac{1}{n} \sum_{k=1}^n g(\mathbf{r}_k), \quad (6)$$

where  $f(\mathbf{r})$  is a probability distribution function and therefore satisfies both conditions

$$f(\mathbf{r}) \geq 0 \text{ in } V; \quad \int_V f(\mathbf{r}) d\mathbf{r} = 1.$$

The points labeled  $\mathbf{r}_k$  are picked at random in volume  $V$  according to the probability density  $f(\mathbf{r})$ .

Our particular choice of  $f(\mathbf{r})$  was a constant and the points  $\mathbf{r}_k$  are then obtained by means of the pseudo-random numbers generated by a computer. This work was performed on the Mercury Ferranti digital computer at the Instituto del Cálculo of the University of Buenos Aires.

The particles were supposed to interact with a Lennard-Jones (6-12) potential

$$\phi(r) = 4\epsilon \left[ (r_0/r)^{12} - (r_0/r)^6 \right], \quad (7)$$

and the notation  $r^* = r/r_0$ ,  $v^* = v/r_0^3$ ,  $T^* = kT/\epsilon$  was used.

Only one temperature  $T^* = 1.25$ , near the critical one, was used. The computed cell sizes were  $q^* = 1.185$ ,  $q^* = 1.56$ ,  $q^* = 2.00$ , and  $q^* = 2.52$ . In each case 13 dif-

TABLE II. Computed values of  $j(w)$  for  $q^* = 1.56$  and different curve fittings given by Eqs. (8), (9), and (10) in the text. When two calculated values are given for the same  $w$ , they correspond to different (extreme) configurations.

$w$	Calculated	Spheri- calized	Linear	Log	$a+bm^w$
0	0.129±0.020	0.128	0.124	0.124	0.124
1/12	0.145±0.022	0.133	0.243	0.153	0.137
2/12	$\begin{cases} 0.176±0.020 \\ 0.148±0.022 \end{cases}$	0.140	0.363	0.189	0.156
3/12	$\begin{cases} 0.185±0.022 \\ 0.159±0.022 \end{cases}$	0.146	0.482	0.234	0.180
6/12	$\begin{cases} 0.339±0.037 \\ 0.264±0.031 \end{cases}$	0.178	0.841	0.440	0.320
9/12	$\begin{cases} 0.605±0.037 \\ 0.941±0.028 \end{cases}$	0.246	1.199	0.827	0.670
10/12	$\begin{cases} 0.692±0.039 \\ 1.073±0.033 \end{cases}$	0.296	1.319	1.040	0.880
11/12	1.185±0.030	0.395	1.438	1.260	1.165
1	1.56	1.56	1.56	1.56	1.56

<sup>8</sup> H. Kahn, in *Symposium on Monte Carlo Methods*, edited by H. A. Meyer (John Wiley & Sons, Inc., New York, 1956); H. Kahn in *Mathematical Methods for Digital Computers*, edited by A. Ralston and H. S. Wilf (John Wiley & Sons, Inc., New York, 1960), p. 249.

<sup>9</sup> M. Weissmann and R. M. Mazo, *J. Chem. Phys.* **37**, 2930 (1962).

ferent integrals were obtained on the same run of the computer. They correspond to  $j(w)$  for 1, 2, 3, 6, 9, 10, 11, 12 nearest neighbors. In the cases where several orientations of the neighbors had to be considered, we computed only extreme situations, such as two vacant sites being in consecutive or in opposite places. No such local configuration may be repeated throughout the lattice due to geometric incompatibility, and some type of average must be made.

TABLE III. Computed values of  $j(w)$  for  $q^*=2$  and different curve fittings given by Eqs. (8), (9), and (10) in the text. When two calculated values are given for the same  $w$ , they correspond to different (extreme) configurations.

$w$	Calculated	Spheri- calized	Linear	Log	$a+bm^w$
0	0.60±0.04	0.540	0.600	0.600	0.600
1/12	0.64±0.04	0.538	0.716	0.662	0.666
2/12	{0.69±0.04 0.63±0.04}	0.538	0.833	0.732	0.738
3/12	{0.68±0.04 0.66±0.04}	0.540	0.850	0.810	0.816
6/12	{1.12±0.07 1.00±0.05}	0.565	1.300	1.120	1.104
9/12	{1.42±0.06 1.66±0.03}	0.650	1.350	1.480	1.486
10/12	{1.44±0.05 1.78±0.03}	0.722	1.766	1.632	1.644
11/12	1.79±0.03	0.870	1.883	1.805	1.814
1	2.00	2.00	2.00	2.00	2.00

The procedure used was very similar to that explained in Ref. 9. The results are shown in Column 2 of Tables I-IV and in Fig. 1. All quoted errors refer to the 95% confidence limits, defined as  $\pm 1.96\sigma/n^{1/2}$ , where  $\sigma$  is the standard deviation

$$\sigma^2 = n^{-1} \left[ n^{-1} \sum_{k=1}^n g^2(\mathbf{r}_k) - n^{-2} \left\{ \sum_{k=1}^n g(\mathbf{r}_k) \right\}^2 \right].$$

Column 3 of those tables gives the sphericalized values for the integrals.<sup>10</sup> They are obviously a poor approximation and give consistently lower values of  $j(w)$ . Column 4 gives the linear dependence of  $j(w)$ ,<sup>5,6</sup>

$$j(w) = (1-w)j(0) + wj(1). \quad (8)$$

It is also a very poor approximation, especially for small  $q^*$ . Column 5 gives the linear dependence of  $\log j(w)$ ,

$$\log j(w) = (1-w) \log j(0) + w \log j(1), \quad (9)$$

<sup>10</sup> R. H. Wenthorf, R. J. Buehler, J. O. Hirschfelder, and C. F. Curtiss, J. Chem. Phys. **18**, 1484 (1950).

TABLE IV. Computed values of  $j(w)$  for  $q^*=2.52$  and different curve fittings given by Eqs. (8), (9), and (10) in the text. When two calculated values are given for the same  $w$ , they correspond to different (extreme) configurations.

$w$	Calculated	Spheri- calized	Linear	Log	$a+bm^w$
0	2.01±0.13	1.57	1.95	1.95	1.95
1/12	2.04±0.13	1.57	2.00	1.99	2.05
2/12	{1.92±0.10 1.96±0.12}	1.45	2.05	2.04	2.13
3/12	{1.87±0.11 1.99±0.12}	1.41	2.09	2.08	2.20
6/12	{2.71±0.19 2.42±0.13}	1.34	2.23	2.22	2.36
9/12	{2.73±0.14 2.49±0.04}	1.39	2.37	2.36	2.46
10/12	{2.59±0.11 2.61±0.05}	1.45	2.42	2.42	2.48
11/12	2.54±0.05	1.68	2.47	2.47	2.50
1	2.52	2.52	2.52	2.52	2.52

corresponding to the choice of parameters of Ono.<sup>1,4</sup> Column 6 gives another simple functional dependence which seems to be in better agreement with the calculated results for small  $q^*$ :

$$j(w) = a + bm^w, \\ \log m = 12.66 - 5.76q^*. \quad (10)$$

The coefficients  $a$  and  $b$  are functions of  $j(0)$  and  $j(1)$ . But  $j(1) = q^*$  and  $j(0)$  is a known function of  $q^*$ . In a previous paper,<sup>9</sup> a curve was fitted to the data of  $j(0)$ , and it is used again here. The sphericalized values of  $j(0)$  differ from the calculated ones for  $q^* > 2$ .

Equation (10) is a poor approximation for large  $q^*$  and possibly (8) or (9) may be used. However, one of the postulates of the theory is that  $q^*$  must be small.

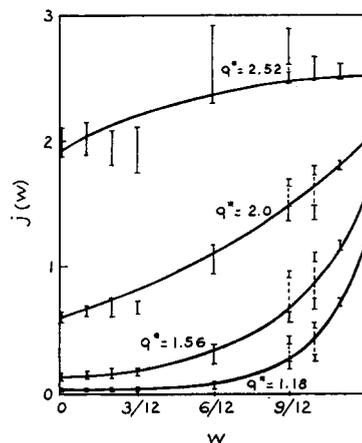


FIG. 1.  $j(w)$  vs  $w$ . Vertical lines are estimated errors. The curves are fitted by Eq. (10) in the text.

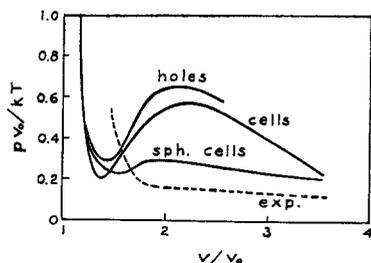


FIG. 2.  $p v_0 / k T$  vs  $v / v_0$ ,  $T^* = 1.25$ . "holes," calculated using Eq. (10); "cells," unspherulized cell theory<sup>9</sup>; "sph. cells," sphericalized cell theory<sup>10</sup>; "exp.," experimental results.<sup>11</sup>

From the Bragg-Williams partition function, the following equation of state is obtained:

$$\frac{pv}{kT} = \frac{q^*}{v^*} \left[ \frac{\partial \log j(w)}{\partial w} \right]_{q^*} + \frac{zq^*}{2T^*v^*} \left( \frac{1.011}{q^{*4}} - \frac{2.409}{q^{*2}} \right) - \frac{v^*}{q^*} \log \left( 1 - \frac{q^*}{v^*} \right). \quad (11)$$

For each set ( $v^*$ ,  $T^*$ ), the best value of  $q^*$  is obtained minimizing the free energy. It must satisfy the equation

$$\left[ \frac{\partial \log j(w)}{\partial q^*} \right]_w - \frac{1}{v^*} \left[ \frac{\partial \log j(w)}{\partial v} \right]_{q^*} - \frac{z}{2T^*v^*} \left( \frac{2.409}{q^{*2}} - \frac{3.033}{q^{*4}} \right) + \frac{v^*}{q^*} \log \left( 1 - \frac{q^*}{v^*} \right) = 0. \quad (12)$$

Combining (11) and (12),

$$\frac{pv}{kT} = q^* \left[ \frac{\partial \log j(w)}{\partial q^*} \right]_w + \frac{2zq^*}{T^*v^*} \left( \frac{1.011}{q^{*4}} - \frac{1.2045}{q^{*2}} \right). \quad (13)$$

Equation (13) coincides with the equation of state given by the cell theory of Lennard-Jones and Devonshire if  $q^* = v^*$ .

The derivatives of  $j(w)$  were obtained from the approximating functions mentioned above, because graphical or numerical differentiation would be almost impossible with our data. This is easily seen in Fig. 1, where the estimated errors for each integral are shown as solid vertical lines. Two different extreme orientations of the nearest neighbors give different results for the integral (which are connected in the figure by dashed vertical lines), and there is no simple criterion to make the average between them. The absence of such criterion would make the computation of all 144 different configurations useless, but the conclusions of this paper would certainly not change if more calculations were made.

If the fitting is done with (10), the values of  $q_{\min}^*$  given by Eq. (12) follow approximately a linear relation in the studied range of  $v^*$ ,  $1.3 \leq v^* \leq 3.5$ :

$$\bar{w} = 1 - q^*/v^* = -0.104 + 0.087v^*. \quad (14)$$

Therefore,  $\bar{w}$  is always small in the liquid densities, and  $q_{\min}^*$  increases with  $v^*$ . Experimental results, based

on x-ray scattering measurements, indicate that  $\bar{w}$  should be 0.5 at the critical point ( $T^* \cong 1.3$ ,  $v^* \cong 3$ ). Equation (14) only gives 0.16 for  $\bar{w}$  in such conditions.

The results obtained for  $pv/kT$  are shown in Fig. 2.<sup>11</sup> The representation  $pv_0/kT (v_0 = r_0^3)$  was chosen for easier comparison with other theories. Values from Eqs. (11) or (13) are compared with those of cell theory and of sphericalized cell theory. No values are given for the entropy or other thermodynamic functions that require differentiation with respect to temperature, as only one temperature was used in computations.

The solution of Eq. (12) will evidently change with the functional dependence chosen for  $j(w)$ . We have used (10) as it fits our data particularly well. However, (9) also fits the data reasonably well and may be considered. This was done by Ono<sup>4</sup> with the sphericalized values for  $j(0)$ . He obtained a small  $q_{\min}^*$  always, and the values of  $\bar{w}$  were higher than those given by (14). But if nonsphericalized  $j(0)$  are used, a discontinuity appears in the values of  $q_{\min}^*$  as soon as the sphericalization is no longer a good approximation for  $j(0)$ :

$$\begin{aligned} v^* = 2.3, & \quad q_{\min}^* = 1.3, & \quad \bar{w} = 0.43, \\ v^* = 2.5, & \quad q_{\min}^* = 2.2, & \quad \bar{w} = 0.12. \end{aligned}$$

For  $v^* > 2.5$  the number of holes increases slowly, the same as for Eq. (14), and therefore the same conclusion will be valid. Since the difference between sphericalized and nonsphericalized  $j(0)$  grows continuously for increasing  $q^*$ , it can not be the only cause for a discontinuity. The other fact must be that Eq. (9) is a better approximation for large  $q^*$  than it is for small  $q^*$ .

The quasichemical method would require the solution of another equation, in order to obtain  $\bar{w}$ . It was used in some cases, but it showed no new features, as the errors in the curve-fitting approximations for  $j(w)$  are much larger than those of the different order disorder methods.

## CONCLUSIONS

These calculations, though restricted to very special cases, show that the introduction of holes does not significantly improve the equation of state predicted by cell theory, for  $T^* = 1.25$ . The successful results obtained with a linear dependence of  $j(w)$ ,<sup>5,6</sup> appear to be fortuitous, as the computed values of  $j(w)$  are certainly not linear for the small cell sizes required by the theory.

## ACKNOWLEDGMENTS

I wish to thank Dr. Robert M. Mazo of the University of Oregon and Dr. J. M. H. Sengers-Levelt of the University of Amsterdam for their helpful and encouraging correspondence regarding the present work.

<sup>11</sup> J. M. H. Levelt, *Physica* **26**, 361 (1960).