# Cavity size distribution in lattice liquids

C. Anteneodo[1] and F. M. C. Vieira[2]
[1]*Centro Brasileiro de Pesquisas Físicas/Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) Rua Dr. Xavier Sigaud 150, Rio de Janeiro RJ, 22290-110, Brazil*
[2]*Instituto de Biofísica, Universidade Federal de Rio de Janeiro, Ilha do Fundão, Rio de Janeiro RJ, 21949-900, Brazil*
(Received 11 May 1995)

We investigate a lattice model for liquids. The average cavity size dependence on the molecular size is analyzed. Our results confirm the idea that larger molecules lead to greater average cavity size. This feature of liquids has been recently interpreted as the reason for solubility differences between water and other liquids. We also study the percolation problem for empty sites. Critical densities and the critical exponents of correlation length and average cavity size are estimated.

PACS number(s): 05.70.Jk, 61.20.Gy, 05.50.+q

The study of the assembly of structures in solvents is relevant to understanding processes such as the formation of micelles and membranes and the folding or association of proteins. Among the noncovalent interactions responsible for these processes, the so-called "hydrophobic" ones are predominant.

Hydrocarbon molecules are more soluble in organic solvents than in water, i.e., the chemical potential of the solution is greater in the case of water and the difference of chemical potentials is proportional to the area of hydrophobic solute in contact with water. It is commonly accepted [1–3] that the structure of the aqueous medium surrounding the hydrocarbon molecule is altered by interruption of the lattice of hydrogen bonds between water molecules. It is supposed that water molecules form a cagelike structure around the solute. However, recent studies on the solubilities of inert gases [4–6] and organic compounds [7] in liquids have led to the suggestion that the characteristic differences between nonaqueous solvents and liquid water are not due to the hydrogen bonding organization in water. Instead, those differences would be mainly due to the comparatively small size of the water molecule, leading to cavities of smaller size in water, which would be finally reflected in a greater chemical potential of the solution.

Many calculations have been done based on a statistical mechanics model for liquids [5,7], the so-called "scaled particle theory" [8]. This theory has been developed to analyze a hard sphere model of liquids, which has a natural counterpart in a lattice model. To consider some features of this lattice model is the aim of the present paper.

Here, we employ a simple two-dimensional (2D) lattice model to investigate the cavity size distribution for arrangements of linear $n$-mers, with $n=1-10$. Only excluded volume effects are considered, which means that the $n$-mers are impenetrable and immobile, and geometrical restriction is the only source of interaction among them.

We consider a square lattice of $L\times L$ sites in which each site may be either empty or occupied by a monomer belonging to a linear polymer of size $n$. We use periodic boundary conditions. The density $\rho$ is defined as the fraction of occupied sites. For $n=1$ the sites are occupied randomly. For $n>1$ polymers correspond to random self-avoiding walks: we choose a random site that will correspond to one end of the polymer; then we choose (randomly) an empty first neighbor of the last chosen monomer. If the polymer is not complete and all first neighbors of the last chosen monomer are full, then this incomplete polymer is discarded. Figures 1(a) and 1(b) show typical configurations for $n=1$ and 10, respectively.

We define a cavity as a cluster of empty sites that can be reached by nearest neighbor steps from one site to another. As we will see, larger cavities are more probably found for increasing values of $n$. Let $p_{i,n}$ be the probability that a given empty site belongs to a cavity of size $i$ when the lattice is filled by polymers of size $n$. The average cavity size for a lattice filled with polymers of size $n$, $S_n$, is defined as [9,10]

$$S_n=\sum_{i=1}^{\infty} i p_{i,n} \ .$$

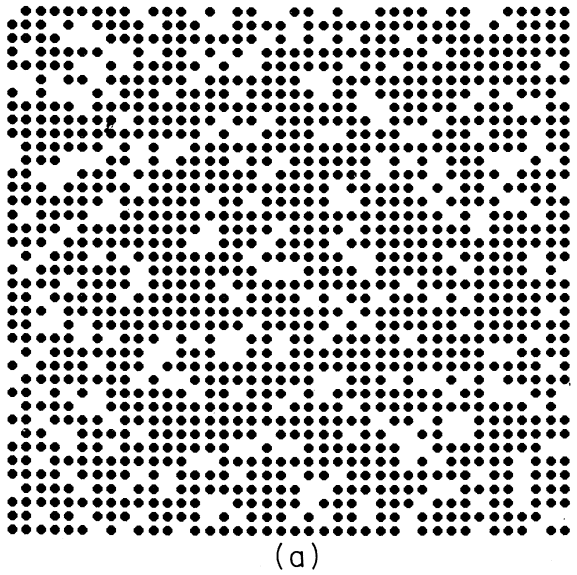
For high densities ($0.7\lesssim\rho\leq 1$) the cavity size distribution is not significantly dependent on the dimensions of the lattice, since now only finite cavities appear with high probability. Of course, one should take $n\ll L\times L$ to average among representative configurations of polymer arrangements. Size distributions were obtained by averaging over 500 configurations for each different condition. The average cavity size $S$ (from here on we omit the subscript $n$) is almost independent of lattice size if the density $\rho$ is much greater than $\rho_c$. For $\rho=0.7$ and $1\leq n\leq 10$ a limit value is reached for $L\sim 40$ within the 5% error range. For higher densities, this dependence on $L$ is expected to be even smaller. Furthermore, in this range of densities ($\rho>0.7$), the fraction of one-site cavities ($p_{1,n}$) is independent of the lattice size for $L\geq 10$.

Cavity size distributions for $n=1$ (i.e., $p_{i,1}$ vs $i$) and different values of $\rho$ are presented in Fig. 2(a). In the case of $n=1$ the size distribution may be obtained analytically. This is basically the well-known *lattice animals* and

*perimeter polynomials* calculation [11–13]. The first equations for $p_{1,n}$ are given in Table I. Values from simulations coincide with analytical values for $p_{i,1}$ within the standard deviation of the simulation values as shown in Fig. 2(a). It should be noted that the analytical calculation of $p_{i,n}$ for $n=2$ is related to the so-called complete dimer problem [14–16] which is still an open hard problem. This should also be the case for $n>2$.

Figure 2(b) shows size distributions for $n=10$ and the same values of $\rho$ as in Fig. 2(a), for comparison. It is already clear that with greater values of $n$ the probability of finding larger cavities increases.



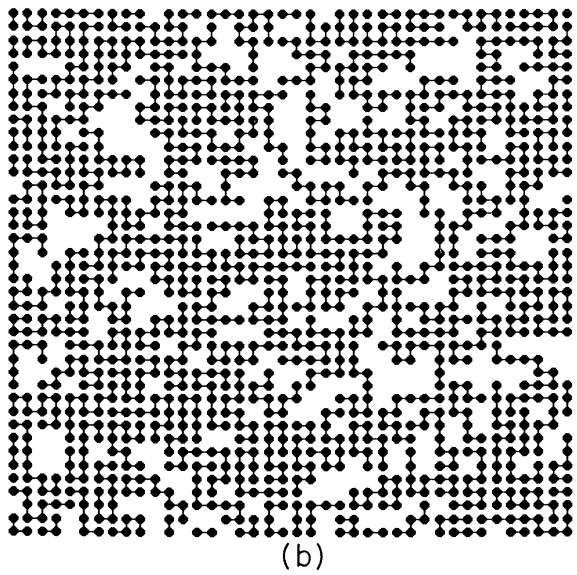
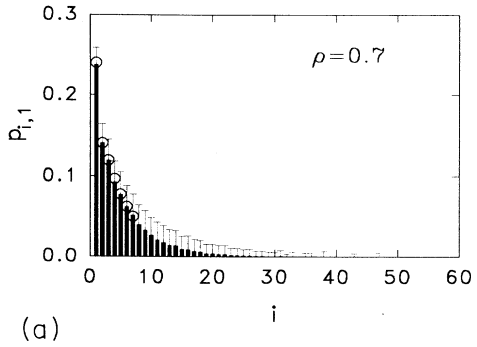
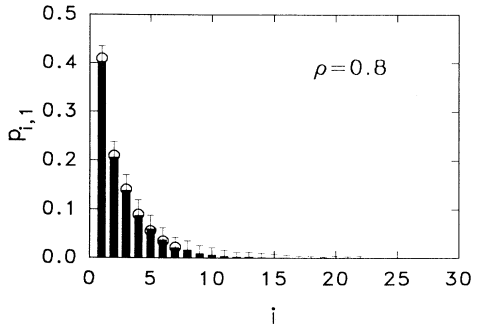
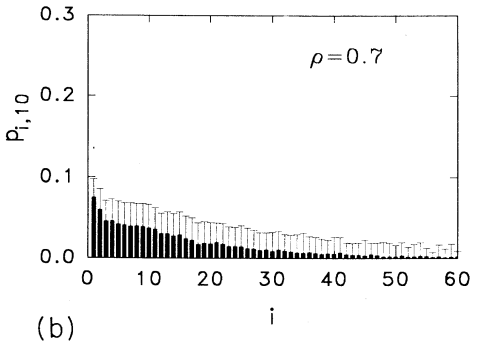




FIG. 1. Typical configurations of polymers with length (a) $n=1$ and (b) $n=10$ in a $40\times40$ lattice with periodic boundary conditions. In both cases the polymer density is $\rho=0.8$.



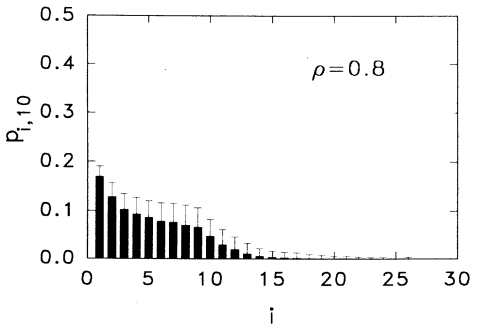




FIG. 2. Cavity size distributions for (a) monomers ($n=1$); open circles show analytical values (from Table I); (b) polymers of length $n=10$. In all cases data correspond to the average and error bars to the standard deviation of the values corresponding to 500 different configurations in $40\times40$ lattices. Densities are indicated in the figure.

TABLE I. Probability $p_{i,1}$ that a given empty site belongs to a cavity of size $i$ when the lattice is filled by monomers, with density $\rho$.

$p_{1,1}=\rho^4$
$p_{2,1}=4\rho^6(1-\rho)$
$p_{3,1}=6\rho^7(1-\rho)^2(2+\rho)$
$p_{4,1}=8\rho^8(1-\rho)^3(\frac{9}{2}+4\rho+\rho^2)$
$p_{5,1}=10\rho^8(1-\rho)^4(\frac{1}{2}+10\rho+14\rho^2+6\rho^3+\rho^4)$
$p_{6,1}=12\rho^9(1-\rho)^5(2+27\rho+40\rho^2+30\rho^3+8\rho^4+\rho^5)$
$p_{7,1}=14\rho^{10}(1-\rho)^6(11+68\rho+126\rho^2+114\rho^3+50\rho^4+10\rho^5+\rho^6)$

By representing $p_{1,n}$ as a function of $1/n$ for different values of $\rho$, straight lines can be fitted to the data corresponding to $n>2$ (inset of Fig. 3). From these fits we may conclude that in the limit $n\to\infty$ the probability of finding one-site cavities tends to a finite value $p_{1,\infty}$, which increases with increasing density. In Fig. 3, we show $p_{1,\infty}$ vs $\rho$ and, for comparison, also $p_{1,n}$ vs $\rho$ for $n=1,2,10$.

Below critical values of the occupied site density $\rho_c$ there is site percolation of unoccupied sites, which means that in the thermodynamic limit $L\to\infty$ there appear cavities of infinite size. For $\rho<\rho_c$ and in the neighborhood of $\rho_c$, the calculation of the cavity size distribution is greatly affected by the lattice size, and one should correct for the finite size effects to calculate any relevant feature of the model.

In order to investigate percolation of the empty sites close to the critical density $\rho_c$, we studied the behavior of the average cavity size $S$. To obtain estimates of $\rho_c$, curve fittings were carried out using the following expression for $dS/d\rho$ [9,17]:

$$\frac{dS}{d\rho}=k_1\exp\{-k_2[\rho-\rho_c(L)]^2\}\ ,$$

where $\rho_c(L)$ is the critical size as a function of $L$, and $k_1$ and $k_2$ are not dependent on $\rho$.

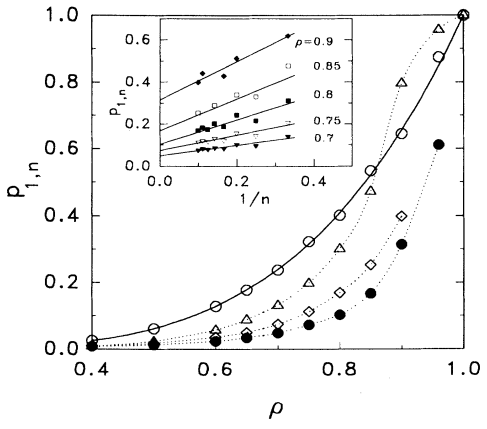



FIG. 3. Probability of finding one-site cavities $p_{1,n}$ vs polymer density $\rho$, for $n=1$ (○), 2 (△), 10 (◇), and $n\to\infty$ (●). Dotted lines are guides to the eyes. The full line corresponds to the function $p_{1,1}=\rho^4$. Inset: $p_{1,n}$ as a function of $1/n$ for different values of $\rho$. Full lines correspond to linear fittings.

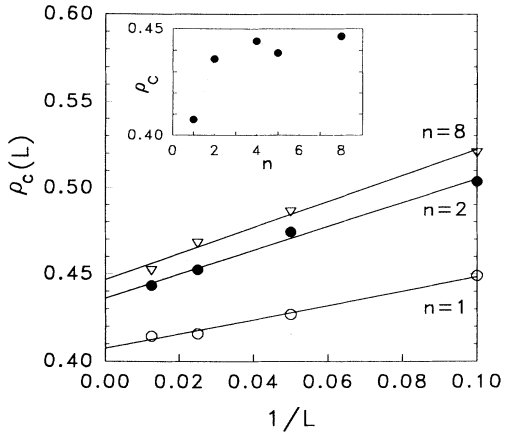



FIG. 4. Dependence of $\rho_c(L)$ on $L^{-1}$ for some values of $n$. The slope is related to exponent $\nu$. Inset: critical density $\rho_c$ [$\rho_c=\rho_c(\infty)$] vs $n$. The dotted line is a guide to the eyes.

Figure 4 shows $\rho_c(L)$ as a function of the lattice size $L$. For $n=1$ we obtained $\rho_c=0.407\pm0.005$. The best estimate for this density is $\rho_c=0.407\,254\,0\pm0.000\,000\,5$ [18]. We can also observe (see inset of Fig. 4) that the critical density seems to be slightly dependent on $n$.

The correlation length $\xi$ is related to the critical density through

$$\xi\propto(\rho-\rho_c)^{-\nu}\ .$$

When $\rho=\rho_c(L)$, the correlation length $\xi$ reaches the linear dimension $L$ of the lattice. In that case we have [17]

$$\rho_c(L)-\rho_c\propto L^{-1/\nu}\ .$$

The value of $\nu$ for $n=1$ is supposed to be $\frac{4}{3}$ according to conformal invariance calculations [19]. Our results in-

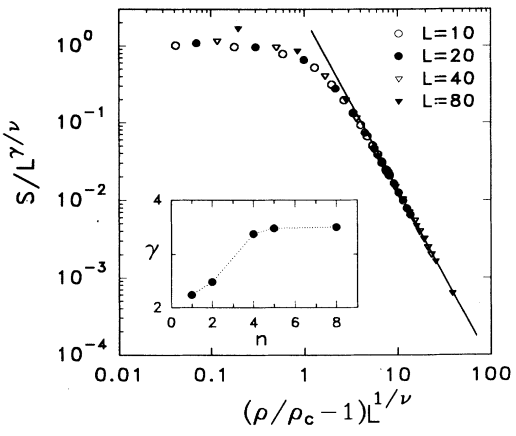



FIG. 5. Finite size scaling plot for $n=1$. The scaling is quite good, resulting in a value of $\gamma=2.24$, compared to the possibly exact value $\gamma=\frac{43}{18}$. Inset: values of $\gamma$ as a function of $n$ for the empty site percolation. Again, the dotted line is a guide to the eyes.

dicate that for increasing values of $n$ there is no significant departure from the critical exponent $\nu$ corresponding to $n=1$.

According to scaling hypotheses, the average cavity size is related to the density through [9,10]

$$S \propto (\rho - \rho_c)^{-\gamma} .$$

To evaluate $\gamma$ we must take into account finite size effects. According to finite size scaling theory [9,20,21] we should obtain a straight line fitting for the log-log plot of

$$(S/L^{\gamma/\nu}) \times [\rho/\rho_c(L) - 1] L^{1/\nu} .$$

Figure 5 shows the finite size scaling plots for $n=1$. In the inset of Fig. 5 we show the values of $\gamma$ obtained for different $n$. We observe a significant increase of this value for greater values of $n$. The increase of $\gamma$ seems to be related to the increase in average cavity size for greater values of $n$.

Larger cavities are found with higher probabilities as $n$ increases. Thus assemblies of larger polymers are more able to accommodate a large structure than a water lattice is. This may be at least one of the ingredients responsible for hydrophobic solubilities. This agrees with the finding that the solubilities of inert gases are greater in organic solvents than in water [4]. Even when the fractional free volume is greater for water, i.e., if the organic solvent is denser than liquid water, the free volume is distributed in smaller packets in the latter case. Our simple model considering only geometric features with no reference to thermal effects allows an understanding of a general aspect of the hydrophobic effect.

The results obtained here for percolation of empty sites indicate no significant change of the critical density $\rho_c$ nor correlation length exponent $\nu$ as $n$ increases. On the other hand, the critical exponent for average cavity size $\gamma$ shows a significant increase with $n$. The relevance of percolation problems is well known. Nevertheless, the problems we treat here have not appeared in the literature before, as far as we know. It seems that a new class of percolation problems has been observed.

[1] S. J. Singer and G. L. Nicolson, Science **175**, 720 (1972).
[2] H. S. Frank and M. W. Evans, J. Chem. Phys. **13**, 507 (1945).
[3] F. H. Stillinger, Science **209**, 451 (1980).
[4] A. Pohorille and L. R. Pratt, J. Am. Chem. Soc. **112**, 5055 (1990).
[5] G. L. Pollack, Science **251**, 1323 (1991).
[6] L. R. Pratt and A. Pohorille, Proc. Natl. Acad. Sci. U.S.A. **89**, 2995 (1992).
[7] B. Lee, Biopolymers **31**, 993 (1991).
[8] H. Reiss, Adv. Chem. Phys. **9**, 1 (1966).
[9] D. Stauffer, *Introduction to Percolation Theory* (Taylor & Francis, London, 1985).
[10] M. F. Sykes and M. Glen, J. Phys. A **9**, 87 (1976).
[11] D. S. Gaunt, M. F. Sykes, and H. Ruskin, J. Phys. A **11**, 1899 (1976).
[12] D. Stauffer, Phys. Rep. **54**, 1 (1979).
[13] V. Privman and N. M. Švrakić, Phys. Rev. Lett. **60**, 1107 (1988).
[14] P. W. Kasteleyn, Physica **27**, 1209 (1961).
[15] M. E. Fisher, Phys. Rev. **124**, 1664 (1961).
[16] M. Jerrum, J. Stat. Phys. **48**, 121 (1987).
[17] F. Yonezawa and S. Sakamoto, Phys. Rev. B **40**, 636 (1989).
[18] R. M. Ziff, Phys. Rev. Lett. **69**, 2670 (1992).
[19] B. Nienhuis, J. Stat. Phys. **34**, 731 (1984).
[20] M. E. Fisher and A. E. Ferdinand, Phys. Rev. **185**, 832 (1969).
[21] D. P. Landau, Phys. Rev. B **14**, 255 (1976).