Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 1993, **3(4)**, 136–139
Mendeleev Communications

The Pressure Tensor and Local Density Profiles of Computer-simulated Water Clusters

Elena N. Brodskaya,[*a] Jan C. Eriksson,[*b] Aatto Laaksonen[c] and Anatoly I. Rusanov[d]

[a] *Department of Chemistry, St. Petersburg University, 199034 St. Petersburg, Russian Federation and Department of Physical Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden.*
[b] *Department of Physical Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden.*
[c] *Department of Physical Chemistry, Arrhenius Laboratory, University of Stockholm, S-10691 Stockholm, Sweden.*
[d] *Department of Chemistry, St. Petersburg University, 199034 St. Petersburg, Russian Federation. Fax +7 812 218 1346*

For small clusters composed of 125 or more water molecules there is an inner range where the local energy is approximately constant and equal to the bulk phase value whereas the pressure tensor remains anisotropic and has position-dependent components, even for clusters of 256 water molecules.

The properties of liquid clusters are of crucial importance for nucleation processes and for the formation of microemulsions. The detailed molecular packing of a cluster together with its thermodynamic parameters, in particular the surface tension γ, are of great interest. At present, this kind of direct information can be obtained only by means of computer simulations. We have studied water clusters of different sizes employing the molecular dynamics (MD) method. Special attention has been paid to the mechanical state as given by the pressure tensor profile which by proper integration yields the work of cluster formation from the vapour in equilibrium with the cluster. Water clusters have been investigated by computer simulations in earlier work.[1–9] However, the relation between the mechanical state and the local structure has not yet been studied in full detail.

The present communication is in continuation of our previous work[7] where relatively small clusters were investigated by MD simulations. Now, somewhat larger clusters composed of 64, 94, 125, 190 and 256 molecules have been modelled likewise by MD simulations. Such simulations entail numerical solution of the classical equation of motion for each of the molecules of the system at fixed initial and boundary conditions.

Our clusters were contained in a large sphere of radius R_s. This sphere generates a central, short-ranged $[\sim(R_s-r)^{-12}]$ repulsive interaction field, and the value of R_s was chosen to be large enough (*ca.* 6 Å outside the equimolecular dividing surface) so as not to influence the local properties of the system as judged from the appearance of the local density profiles. For the water we have used the well-known empirical ST2 model[10] which, in some respects at least, describes liquid water reasonably well. Although this model gives rise to a somewhat more structured liquid than real water it yields a correct value for the molecular energy and a surface tension value of the flat interface, $\gamma_\infty = 97 \pm 6$ mN m^{-1} at $T = 298$ K,[11] which is definitely too large but which is still closer to the experimental value than that obtained for other models. More complex and, supposedly, more realistic (flexible or polarizable) models are too computer time-demanding for this kind of problem. The details of the algorithm and the intermolecular potentials employed are given in ref. 7.

The temperature T of the system was defined on the basis of the average kinetic energy E_k by means of the formula (1),

$$T = E_k/3Nk \quad (1)$$

where N is the number of molecules in the system and k the Boltzmann constant. The values of T are given in Table 1 where the radii of the equimolecular dividing surfaces R_e are also shown. R_e is given by the relation (2),

$$R_e = (3N/4\pi\rho^\alpha)^{1/3} \quad (2)$$

ρ^α being the bulk liquid density (the vapour density is approximated to zero).

In our present investigation the interest was focused on the radial profiles of local properties, *i.e.* on how the local properties depend on the distance r from the centre of mass of the system. We have calculated the profiles of the local density of oxygen atoms, $\rho_O(r)$, hydrogen atoms, $\rho_H(r)$, the total energy per molecule $e(r)$, and the normal and tangential components of the pressure tensor $P_N(r)$ and $P_T(r)$, respectively. Before discussing the results we emphasize that one should not pay much attention to the central region of the clusters with $r \leqslant 1.5$ Å because of the comparatively large fluctuations there.

Fig. 1 displays the density profiles, $\rho_O(r)$, of the five clusters where $\rho_O(r)$ is equal to an average number of molecules per unit volume inside a spherical layer between r and $r+0.25$ Å. The profiles oscillate about the bulk density ρ^α in the inner part and decrease monotonously when approaching the vapour phase. The thickness of the interfacial layer is always *ca.* two molecular diameters. There is no visible influence on density profile due to the surrounding external shell as can be seen from Fig. 1.

It is worth mentioning that the local *kinetic* energy $e_k(r)$ per molecule is practically constant inside the clusters. This indicates that the molecular systems investigated have reached thermal equilibrium. We assume that this condition in conjunction with attaining stable normal pressure profiles (see below) are sufficient criteria for judging whether internal equilibrium has been reached in the clusters. So far it is impossible to calculate the local chemical potential in water systems, the constancy of which would constitute an even better equilibrium criterion. In addition, we assume that a

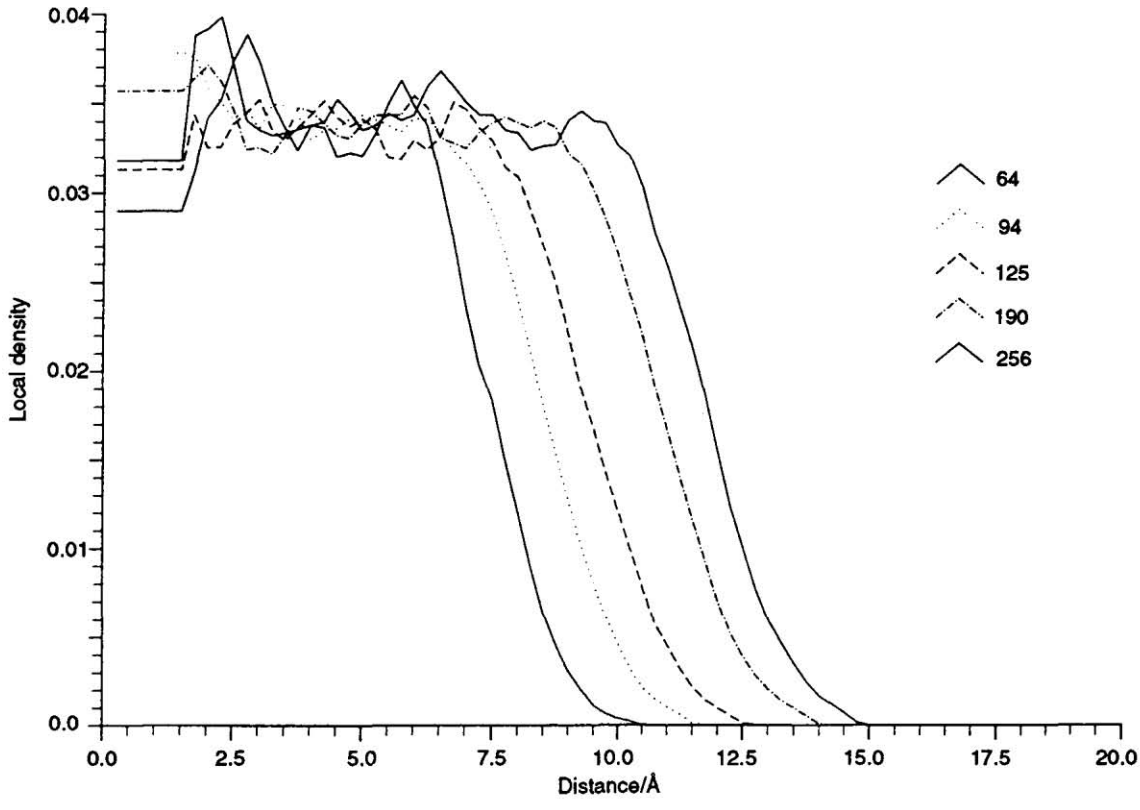

Fig. 1 Oxygen density profiles for $N=64$, 94, 125, 190 and 256. The oxygen density ρ_0 is given in $Å^{-3}$ and the radial distance r in Å. 1 kg m^{-3} corresponds to 0.03346 $Å^{-3}$.

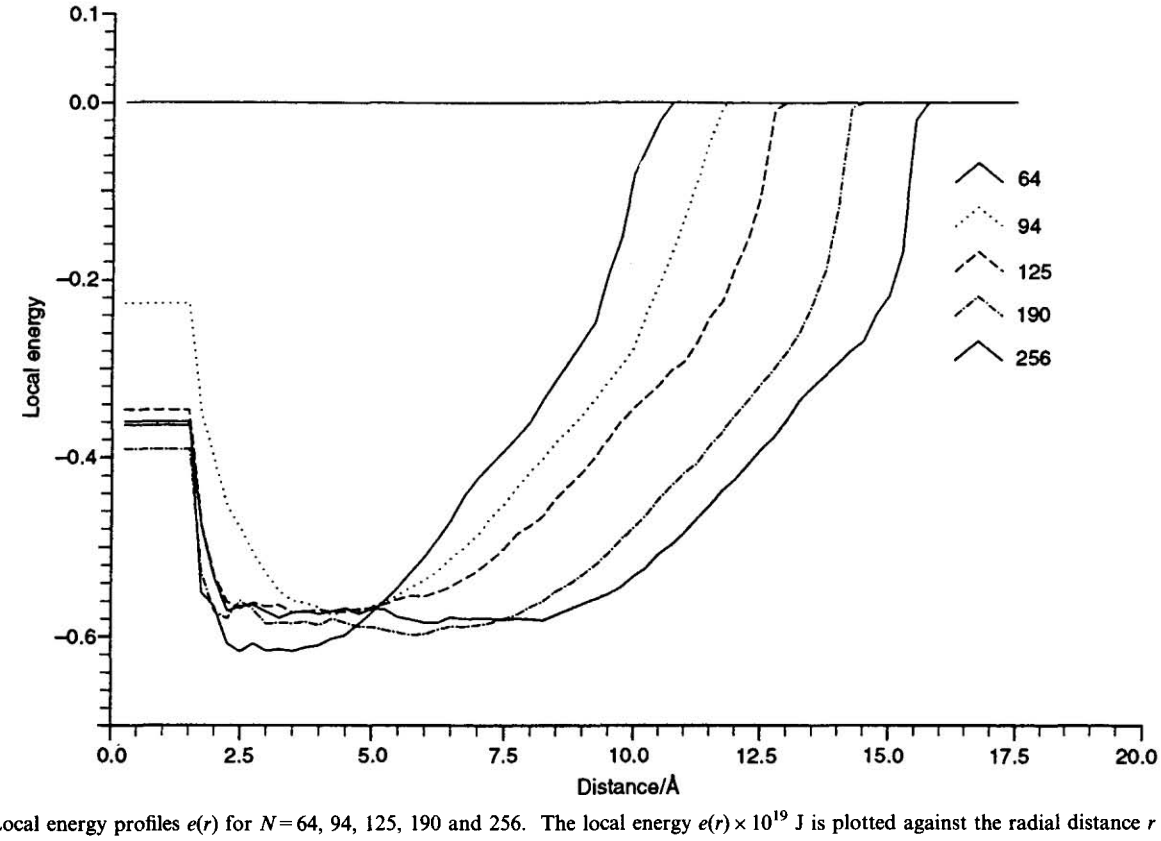

Fig. 2 Local energy profiles $e(r)$ for $N=64$, 94, 125, 190 and 256. The local energy $e(r)\times 10^{19}$ J is plotted against the radial distance r in Å.

poor cluster-vapour equilibrization does not appreciably influence our cluster data since the vapour density is very low.

The profiles of the *total* energy $e(r)$ per molecule are shown in Fig. 2. We observe that it is only for clusters with $N\geqslant 125$ that there is a range of a few molecular diameters inside the cluster where the local energy $e(r)$ approaches the bulk liquid value e^{α}. Essentially the same conclusion was reached by Jeong Yun Yu and Mu Shik Jhon[9] in their recent MD simulation study of water clusters. Hence, the overall course of an e-profile may be rather remotely related to the corresponding local density profile. Another difference between the $e(r)$ and $\rho_0(r)$ functions is that the oscillations of $e(r)$ about e^{α} are much less pronounced than those of $\rho_0(r)$ about ρ^{α}.

Table 1 Energetic properties of water clusters[a]

N	R_e	T	E	E/N	e_s	W	$3W/4\pi R_e^2$	t
64	7.70	304	−30.44	−0.476	0.081±0.008	1.20±0.06	48.0±2.0	800
94	8.75	308	−43.96	−0.468	0.100±0.010	2.40±0.12	75.0±4.0	200
125	9.63	308	−58.50	−0.470	0.107±0.010	3.30±0.15	85.0±4.0	235
190	11.10	283	−97.52	−0.513	0.092±0.009	6.20±0.60	120.0±12.0	170
256	12.22	300	−129.18	−0.504	0.097±0.010	8.10±1.20	130.0±20.0	90

[a] N is the number of molecules, R^e is the radius of the equimolecular dividing surface in Å, T is the tempeature in K, E is the total energy of the system and E/N is the average molecular energy in 10^{-19} J, e_s is the surface energy in J m^{-2}, W is the work of cluster formation in 10^{-19} J, $3W/4\pi R_e^2 = \gamma_e - R_e d\gamma_e/dR_e$ is the effective surface tension in mN m^{-1}, t is the calculation time in ps.

Knowing e^α and employing the equimolecular dividing surface we can estimate the surface density of the excess energy, e_s, by means of the equation (3),

$$e_s = (E - e^\alpha N)/4\pi R_e^2 \quad (3)$$

where E is the total energy of the system. Values of E and e_s are listed in Table 1. e_s increases appreciably with cluster size below $N=125$. The upper limit of e_s is equal to 0.11 ± 0.01 J m^{-2} and is in fair agreement with the experimental value for the planar water/air interface (0.119 J m^{-2} at 308 K[12]). Consequently, we may claim that the ST2 model of water describes the energetic properties of water surfaces reasonably well. The overall relative error of the surface energy obtained is for each cluster size *ca* 10%.

The predominant source of error here is not related to our calculation of the total energy of the cluster as a whole but rather to our estimate of the molecular energy e^α. The energy e^α can be obtained in two ways, either from our own calculations for relatively large clusters or by interpolating the data of Rahman and Stillinger.[10] The deviation between our data for e^α and those of the above-mentioned authors is *ca.* 2% resulting in an estimated error in surface energy of *ca.* 10%.

As to the local pressure profiles the situation is more complex. The normal and tangential components of the pressure tensor, P_N and P_T, are shown in Figs. 3 and 4. The normal component of the Irving–Kirkwood pressure tensor was calculated using the definition relation (4),

$$P_N = kT\rho_0 - P_u \quad (4)$$

where $P_u(r)$ is the average of the radial components of pair intermolecular forces per unit area for a sphere of radius r when the vector of the intermolecular distance crosses this sphere and the acting molecule is located outside this sphere, ref. 7. The tangential component P_T was computed by means of the mechanical equilibrium condition (5)

$$P_T = d(r^2 P_N)/dr^2 \quad (5)$$

Further, we have used the stability of the profile of P_N as a criterion of mechanical equilibrium.

First of all we note that for none of the clusters studied is there an isotropic bulk liquid range where $P_N = P_T = P^\alpha$. Secondly, we observe that the values of P_N are larger than $kT\rho_0$ in the inner part of the surface zone. This means that P_u is negative there which might be related to the deformation or even the disruptiom of the hydrogen bonds in this region owing to the influence of the surface.[7] Upon approaching the cluster centre from the vapour side there is a substantial change of the stretched and squeezed regions both in the normal and tangential directions.This was observed neither for the case of Lennard–Jones clusters[13,14] nor for pure polar liquid clusters.[6]

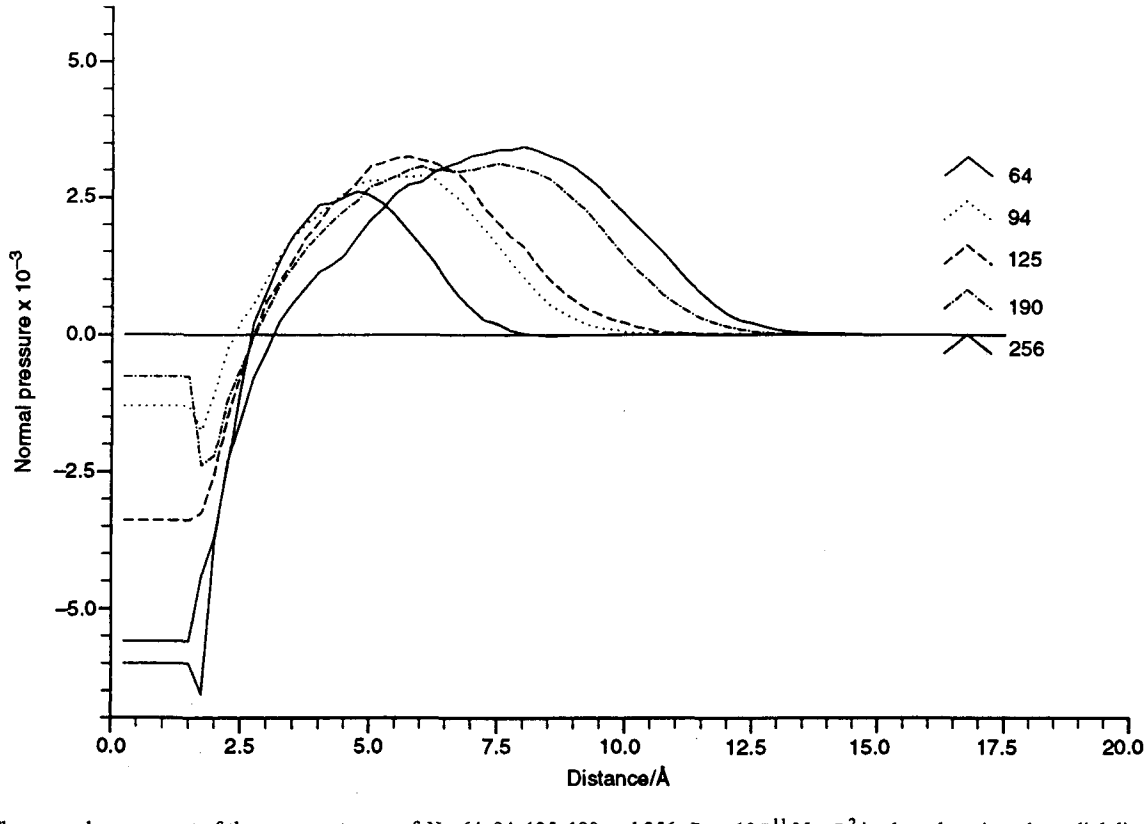

Fig. 3 The normal component of the pressure tensor of $N=64$, 94, 125, 190 and 256. $P_N \times 10^{-11}$ N m^{-2} is plotted against the radial distance r in Å.

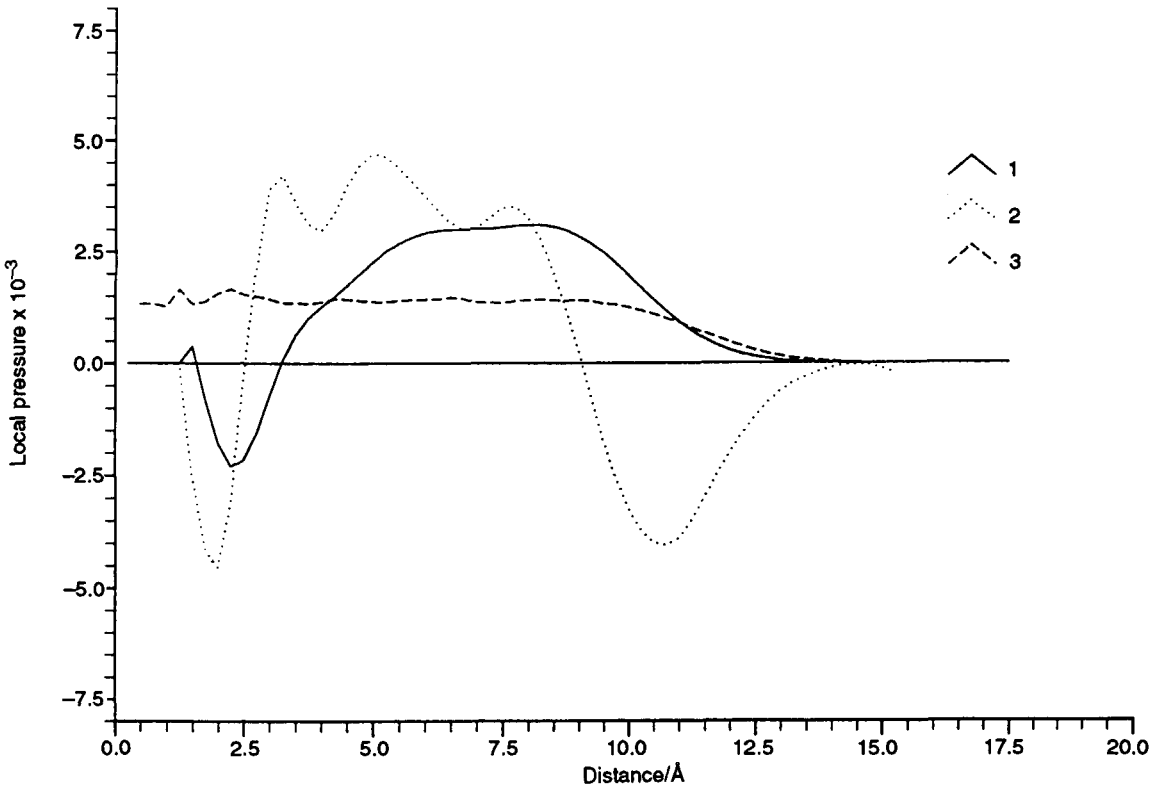

Fig. 4 The pressure components $P_N(1)$, $P_T(2)$ and $kT\rho_0(3)$ in N m^{-2} multiplied by 10^{-11} for $N=190$ are plotted against the radial distance r in Å.

For large enough clusters which have central parts with bulk phase properties we can expect the pressure inside the cluster to be higher than the external pressure according to the Laplace equation. Small clusters, however, are non-uniform everywhere and overlapping surface layers may give rise to a very complicated behaviour of the local pressure tensor components. Still, the Laplace equation is valid if the interior liquid phase is considered to be a hypothetical homogeneous phase with the same values of temperature and chemical potential as those in the actual system. This is in essence the Gibbs' approach for strongly non-uniform systems. The negative sign of P_T in the surface layer ultimately yields a positive value of the surface tension and, hence, cluster stability. The fine structure of P_T has no physical implications beause it is primarily related to the mode of making the P_N interpolation.

Knowing the P_N function one readily obtains the work of cluster formation W by computing the integral (6), where R_β is

$$W = 2\pi \int_0^{R_\beta} r^2 P_N dr \qquad (6)$$

located in the vapour part with a vapour pressure that is assumed to be equal to zero. This equation follows from the general expression[15] $W=(4\pi/3)\int_0^\infty (P_N-P_T)^2 r^2 dr$ and makes use of the condition (5). The values of W and the following, closely related interfacial tension quantity at the equimolecular dividing surface, $\gamma_e - R_e d\gamma_e/dR_e = 3W/(4\pi R_e^2)$, are given in Table 1 ($\gamma_e$ and $-d\gamma_e/dR_e$ are the surface tension and the curvature-related pressure at the equimolecular dividing surface[16]). $\gamma_e - R_e d\gamma_e/dR_e$ increases rapidly with the cluster size in the limited size range so far studied. This might indicate that the interfacial tension γ_e of the cluster is also increasing with cluster size in the size range investigated. However, in order to further elucidate this interesting question we first of all need to firmly establish that the $N=190$ and $N=256$ clusters have really reached internal equilibrium by extending the corresponding calculation times.

References

1 F. F. Abraham, *J. Chem. Phys.*, 1975, **61**, 1221.
2 C. L. Briant and J. J. Burton, *J. Chem. Phys.*, 1975, **63**, 3327.
3 M. R. Mruzik, *Chem. Phys. Lett.*, 1977, **48**, 171.
4 A. C. Belch and M. Berkowitz., *Chem. Phys. Lett.*, 1985, **113**, 278.
5 R. M. Townsend, J. Gryko and S. A. Rice, *J. Chem. Phys.*, 1985, **81**, 4391; 1991, **94**, 2207.
6 A. D. Shreve, J. P. R. B. Walton and K. E. Gubbins, *J. Chem. Phys.*, 1986, **85**, 2178.
7 E. N. Brodskaya and A. I. Rusanov, *Mol. Phys.*, 1987, **62**, 251.
8 M. Maroncelli and G. R. Fleming, *J. Chem. Phys.*, 1988, **89**, 5044.
9 Jeong Yun Yu and Mu Shik Jhon, *J. Colloid Interface Sci.*, 1991, **147**, 443.
10 F. H. Stillinger and A. Rahman, *J. Chem. Phys.*, 1974, **60**, 1545.
11 C. Y. Lee and H. L. Scott, *J. Chem. Phys.*, 1980, **73**, 4591.
12 R. Cini, G. Loglio, and A. Ficalbi, *J. Colloid Interface Sci.*, 1972, **41**, 287.
13 A. I. Rusanov and E. N. Brodskaya, *J. Colloid Interface Sci.*, 1977, **62**, 542.
14 S. M. Thompson, K. E. Gubbins, J. P. R. B. Walton, R. A. R. Chantry and J. S. Rowlinson, *J. Chem. Phys.*, 1984, **81**, 530.
15 J. C. Eriksson and S. Ljunggren, *J. Colloid Interface Sci.*, 1991, **145**, 224.
16 J. C. Eriksson, S. Ljunggren and U. Henriksson, *J. Chem. Soc., Faraday Trans. 2*, 1985, **81**, 833.

Received: Moscow, 10th March 1993
Cambridge, 1st April 1993; Com. 3/01501G