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Percolation thresholds of simple fluids

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Abstract. The percolation characteristics of hard-sphere (HS) and Lennard-Jones (LJ) fluids are determined by molecular dynamics computer simulations. The LJ percolation threshold is raised in the hard-core limit and lowered in the soft-core limit when compared with the equivalent hard-sphere fluid, using a temperature-dependent effective hard-sphere diameter. This difference in the soft-core limit increases as $T \to T_c$. The values for two percolation exponents are close to the values for random static percolation.

1. Introduction

Molecular fluids and colloidal suspensions interacting via continuous potentials can be approximated by a hard-sphere (HS) core, of diameter σ_{HS}, and a 'soft' outer penetrable shell, of thickness $\delta\sigma_{HS}$. We call $\delta \to 0$ the hard-core limit and $\delta \to \infty$ the soft-core limit. The transport coefficients, thermodynamic properties, electrical conductivity and mechanical parameters are examples of quantities that can be effectively interpreted on the basis of the degree of overlap of the soft shells (e.g. Seaton and Glandt 1987a). A change in slope of the density dependence of these quantities has been observed to occur at a density corresponding to the formation of infinitely spanning ('percolating') clusters formed from particles separated by a characteristic local interaction distance for the physical observable (Heyes and Melrose 1988). The *percolation transition* (PT) is defined as follows. Starting on an arbitrary molecule in the cluster one can step to another neighbour in the cluster if their centre-centre separations are within the distance $\sigma_S = (1+\delta)\sigma_{HS}$. If this procedure can continue, still remaining in the same cluster, so that at least one path with an arbitrarily large distance from the starting point can be traced, then the cluster is said to *percolate*.

The PT characteristics of idealised systems such as particles on lattices (Stauffer and Coniglio 1987), non-attractive hard-core-based continuum fluids (Balberg and Binenbaum 1987, Sevick *et al* 1988) and hard cores with attractive terms such as the square-well fluid (Bug *et al* 1985) have been considered. A MC continuum study of the PT of model colloidal suspensions (Seaton and Glandt 1987b) has been made using an 'adhesive' sphere potential. We continue this development towards more realistic systems, by investigating the PT of a model molecular fluid, represented by the Lennard-Jones (LJ) potential, which has a continuous repulsive and attractive component. We present a molecular dynamics analysis of the PT of the HS and LJ fluids in three

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dimensions, to assess the effect of a soft repulsive and attractive interaction potential on the percolation thresholds.

2. Simulation details

The details of the MD technique used for particles interacting via the LJ potential, $\phi(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ have been described recently (Heyes 1987). The MD simulations were performed on cubic unit cells of volume V containing $N = 32$, 108, 256, 500 and 864 particles for both HS and LJ fluids. In the LJ simulations the Verlet algorithm was used to increment the positions of the molecules. The temperature was fixed by half-timestep velocity rescaling. The LJ timestep was 0.01 at $T = 1.456$ and 0.005 at $T = 6.0$. The HS MD was performed as described by Allen and Tildesley (1987).

The cluster-search routine has been given elsewhere (Heyes and Melrose 1988). The scheme selects the percolating clusters that span all (periodic) space, not just those that span the MD cell also. For finite-N periodic systems, the infinite-N or 'true' percolation transition density is best estimated as the density when the probability of discovering a percolating cluster in a timestep, the percolation fraction, P, equals 0.5. This is because the density at which $P = 0.5$ shows the least system size dependence. The FORTRAN programs were optimised for a Cray-1S computer at the University of London Computer Centre. The programs automatically searched for the density at which $P = 0.5$, in the vicinity of $P = 0.5$, by linear regression. Such sub-average simulations were from 5000 timesteps at $N = 108$ to 1000 timesteps at $N = 500$. The statistics were *generally* not good enough to establish accurate finite-scaling scaling corrections but test simulations on $N = 32$, 108, 256, 500 and 864, revealed that changes in the PT density above $N = 256$ PT densities were not resolvable on the figures presented below.

3. Results and discussion

In figure 1 we show percolation lines (PL) for a wide range of search diameters (σ_S, in LJ distance units, σ) placed on the LJ phase diagram, $k_B T/\varepsilon \rightarrow T$ against number density, $\rho = N\sigma^3/V$. The PL indicate that the soft interactions lower the percolation threshold for $\sigma_S \geqslant 1.2\sigma$ but increase it for smaller σ_S. (The distance 1.2σ approximately corresponds to the end of the first coordination shell.) This implies that there is an enhancement of local structure between the first and second coordination shells but a depletion in the inside of the first coordination shell as temperature decreases. To compare with the square-well work of Bug *et al* (1985) it is convenient to re-plot these data, in figure 2, in terms of the effective hard-sphere density. This is obtained from $\rho_{HS} = \rho(\sigma_{HS}/\sigma)^3$, where $\sigma_{HS}/\sigma = 1.0217(1 - 0.0178/T^{1.256})/T^{1/12}$, obtained by matching LJ and HS (MD-modified Enskog) shear viscosities (Hammonds and Heyes 1988). On decreasing the temperature, as $T \rightarrow T_c$, the critical temperature, the equivalent HS diameter of the LJ particles increases so that for a constant σ_S in LJ σ units, the LJ particle becomes less like a soft core and more like a hard core. The HS percolation density therefore increases rapidly as $T \rightarrow T_c$ for small σ_S.

It is not (yet) possible to determine where the PL terminates on the co-existence line because MD or Metropolis Monte Carlo are subject to pronounced N dependencies in the critical region.

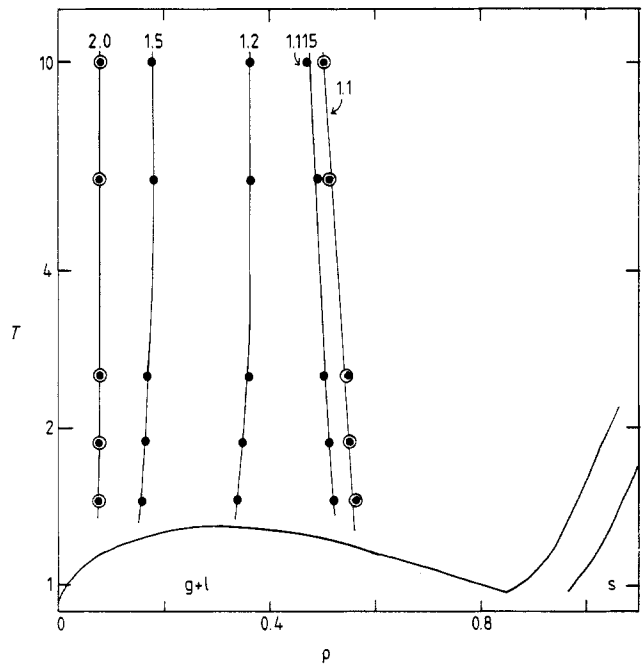

Figure 1. The percolation thresholds for the LJ fluid superposed on its phase diagram. The lines denote boundaries between non-percolating states (to the left) and percolating states (to the right) of the line. Each line corresponds to, and is annotated by, a particular search diameter σ_S in LJ units. The • points are for $N = 108$ and the ◉ points are for $N = 500$.

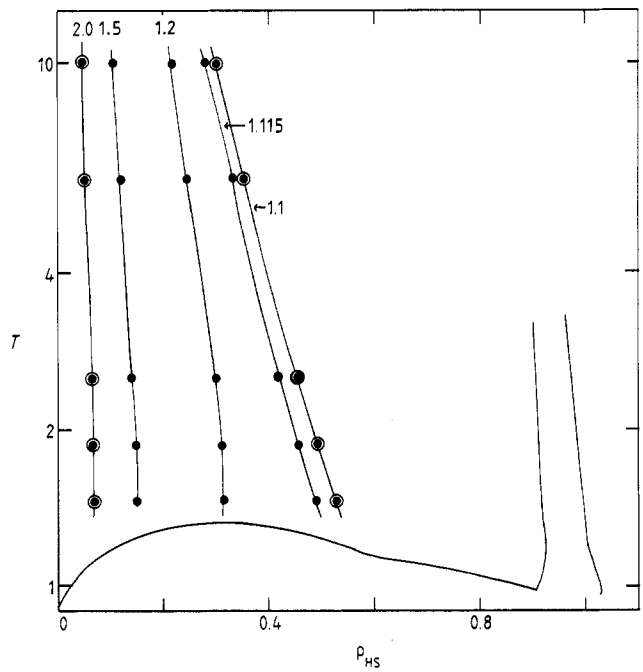

Figure 2. As for figure 1, except that the LJ densities are converted to their equivalent HS values (temperature dependent).

It is informative to determine more specifically the effect of the hard core on the percolation density of the assembly of soft-shell spheres. Following Bug *et al* (1985), this is well represented by $\tilde{\phi}_{HS} = \phi_{HS}(1+\delta)^3$ and $\phi_{HS} = (\pi/6)\rho_{HS}$. Note that *any* LJ state can be compared with a nearest 'equivalent' HS fluid by making the identity, $\rho_{HS} = \rho_{LJ}(\sigma_{HS}/\sigma)^3$. Figure 3 shows the variation of $\tilde{\phi}_{HS}$ *at percolation* with δ, both dimensionless quantities, for the LJ fluids and HS fluids. The percolation threshold is raised in the hard-core limit and lowered in the soft-core limit when compared with the equivalent hard-sphere fluid, using a temperature-dependent effective hard-sphere diameter. The soft-core trend is in agreement with the results of Bug *et al* (1985) on the square-well fluids. In order to interpret this behaviour it is worth noting that, for each δ value on figure 3, we are principally interested in local structure at that pair separation.

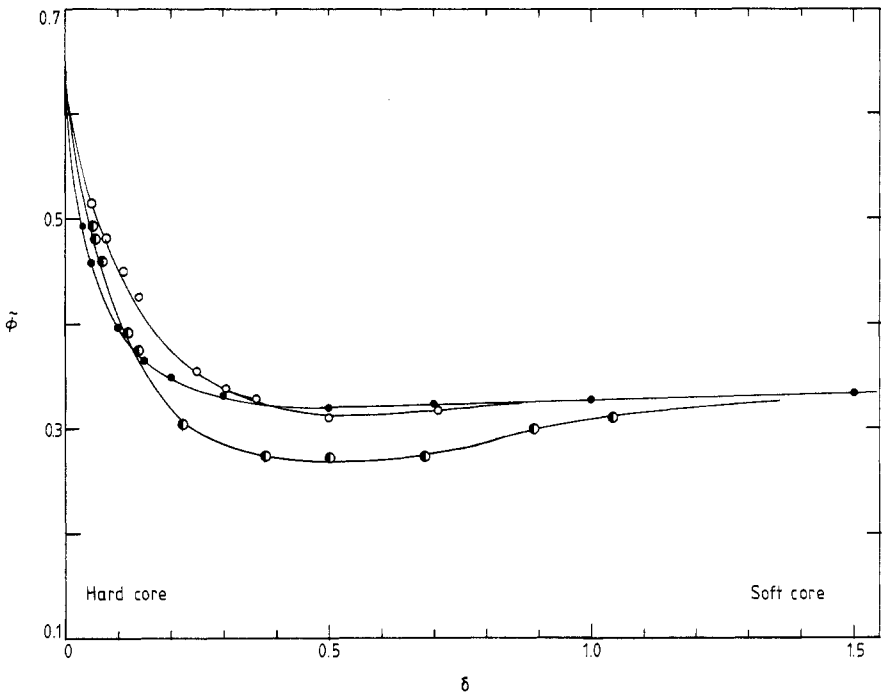

Figure 3. A plot of $\tilde{\phi}_{HS}$ against δ for the HS fluid (●) and the LJ fluids at $T = 1.456$ (◐) and $T = 6.0$ (○).

We will first consider the soft-core limit. In order to understand this behaviour it is useful to examine the pair radial distribution function, $g(r)$. Figure 4 shows $g(r)$ for the low density $\rho = 0.193$ and near-critical temperature $T = 1.456$ LJ state. The separation, r, is scaled by the hard-sphere diameter and the $g(r)$ compared with the 'equivalent' hard-sphere $g(r)$ obtained by independent HS MD. It reveals that attractive interactions cause a clustering of LJ molecules at intermediate distances between $r = 1.0\sigma_{HS}$ and $1.5\sigma_{HS}$ in the first coordination shell. This is largely absent with the nearest equivalent hard-sphere fluid, being a consequence there of the excluded volume. Percolation occurs at lower densities (ϕ_{HS}) than the equivalent hard sphere fluid for σ_S in this range due to this increase in local density. Therefore $\tilde{\phi}_{HS}$ at percolation is lower for LJ than HS at the same δ. As the LJ temperature increases, this effect gradually

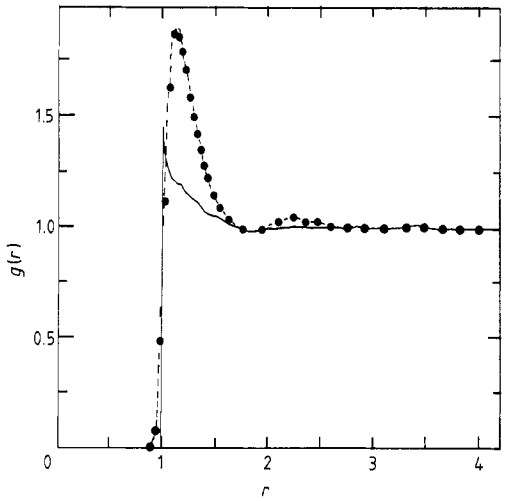

Figure 4. A comparison between $g(r)$ against r/σ_{HS} for the LJ state point, $\rho_{LJ} = 0.193$, $T = 1.456$ (●) and the HS state point $\rho_{HS} = 0.181$ ($T = 1.0$) (full curve); $N = 108$.

disappears and the LJ and HS curves come closer together. The LJ fluid becomes structurally identical with the equivalent HS fluid, at intermediate distances at least.

We will now consider the hard-core limit. The hard-core limit concerns high density fluids and small $\sigma_S \leqslant 1.1\sigma$. In this part of figure 3, the LJ percolation density *exceeds* that of the equivalent hard-sphere fluid. The LJ and HS $g(r)$ in this part of the phase diagram are shown in figure 5. In this distance range there are fewer particles for the LJ than the equivalent HS fluid. Consequently, percolation occurs at a higher ϕ_{HS} for LJ than HS systems at the same σ_S in HS units. This difference between HS and LJ behaviour does *not* disappear with increasing temperature, as does the above soft-core effect.

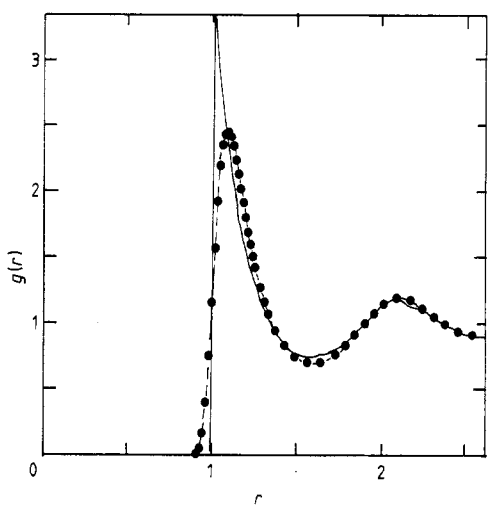

Figure 5. As for figure 4 except that the LJ state point is $\rho_{LJ} = 0.808$ ($T = 1.456$) and the HS state point is $\rho_{HS} = 0.758$ ($T = 1.0$).

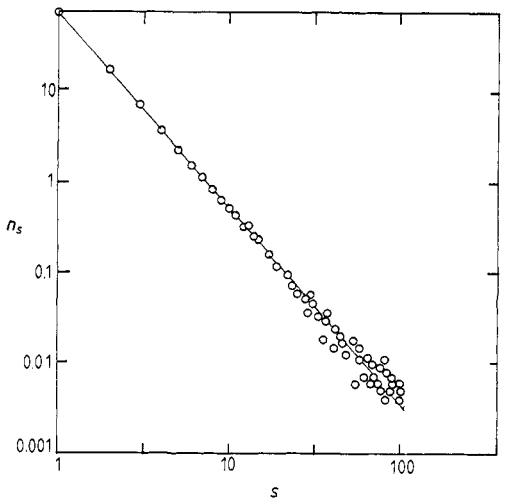

Figure 6. The cluster number distribution for non-percolating clusters, $n_s(s)$ for the LJ state point, $\rho_{LJ} = 0.566$, $T = 1.456$, $\sigma_S = 1.1\sigma$ and $N = 500$. This state point is at the percolation threshold. The exponent of $n_s \propto s^{-\tau}$ is $\tau = 2.1 \pm 0.1$.

We now consider some cluster statistics of the LJ system. In figure 6 we consider n_s, the average number of clusters of size s, at the PT for a $N = 500$ LJ fluid, $\rho = 0.566$, $T = 1.456$ and $\sigma_S = 1.1\sigma$. Considering only non-percolating clusters, n_s should obey the scaling law, $n_s \propto s^{-\tau}$, where the accepted value for static random percolation for τ is 2.2 (Stauffer 1986, Seaton and Glandt 1987b). We find $\tau = 2.10 \pm 0.05$ for the LJ fluid irrespective of temperature or whether one is the soft- or hard-core limit. We found the same value for the HS fluid.

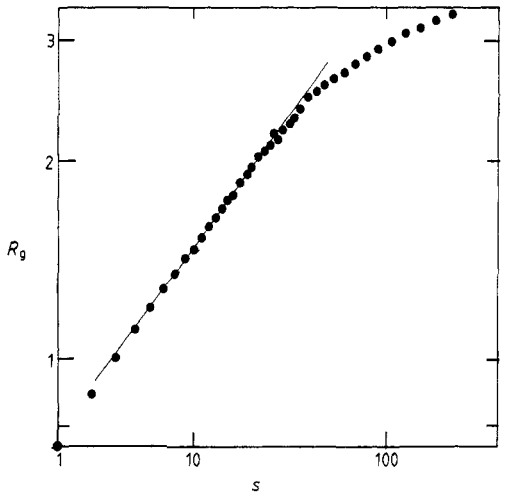

Figure 7. The s dependence of the radius of gyration, R_g, for the LJ state point, $\rho_{LJ} = 0.5120$, $T = 6.0$, $\sigma_S = 1.1\sigma$, $N = 500$. For $R_g \propto s^{1/D_f}$, then the line in the figure indicates $D_f = 2.3 \pm 0.1$. This state point is at the percolation threshold.

We now look at the tenuity of the clusters at the PT by considering the radius of gyration, R_g:

$$R_g = \tfrac{1}{2}\left\langle \sum_{i}^{S-1} \sum_{j=i}^{S} \boldsymbol{R}_{ij}^2 / S(S-1) \right\rangle^{1/2}$$

where $\boldsymbol{R}_{ij}$ is the vector separation between particles i and j. The scaling relationship here is $R_g \propto s^{1/D_f}$ as $r \to \infty$, and where D_f is the fractal or Hausdorff dimension (Herrmann 1986). Figure 7 gives a typical example, for the supercritical LJ state $\rho = 0.5120$ and $T = 6.0$ at the PT. There is an intermediate s regime where this scaling relationship is obeyed, with $D_f = 2.3 \pm 0.1$, slightly lower than the accepted value for 3D static random percolation, $D_f = 2.5$ (Stauffer 1986). As for n_s, the finite size of the MD cell leads to deviations from scaling laws in the $s \to N$ limit.

4. Conclusions

We have used, for the first time, a molecular dynamics computer simulation to determine the percolation characteristics of a model off-lattice fluid. The percolation characteristics of the Lennard-Jones molecular fluid cannot be mapped onto an equivalent hard-sphere fluid. This arises from the attractive interactions in the soft-core regime and soft-repulsion term to the potential in the hard-core regime. We therefore have demonstrated another consequence of molecular forces on the percolation threshold. However, the calculated values for the *exponents*, τ and D_f, suggest some extension of universality to the Gibbs-weighted interacting systems studied here.

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