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Probing the distribution of structural holes in statistical mechanical models of disordered systems

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Abstract. A statistical mechanical method is developed to probe the correlations between holes in the structure of a model for a disordered system. The probe is a fluid of point-like charges in varying concentration, which is allowed to permeate the disordered structure and to reach equilibrium with it without modifying it. The correlations of the probing particles with the 'quenched' matrix and their mutual correlations are evaluated by means of integral equations combining the Ornstein–Zernike relations for a partly quenched disordered system with the hypernetted-chain closure. The correlations between successive shells of structural holes in the matrix are displayed as the concentration of the probing charges is decreased, on account of their mutual Coulomb repulsions. As the simplest example of its application, the method is used to probe the holes in the structure of the one-component classical plasma under strong coupling.

1. Introduction

A recent development in the statistical mechanics of disordered systems has been the evaluation of the equilibrium structure of a dense fluid inside a quenched disordered matrix. It was first shown by Madden and Glandt [1], through an analysis of the cluster expansion for a partly quenched system consisting of a classical mixture of annealed and quenched particles, that the problem can be mapped onto the limiting case of a fully annealed multicomponent system. Given and Stell [2, 3] subsequently developed a suitable version of the replica method [4] to derive the full set of Ornstein–Zernike relations for a partly quenched system. Their theory has also been re-formulated within a density-functional frame [5]. Related numerical studies of the structure of fluids adsorbed in a quenched microporous matrix have been carried out for a variety of model systems [6–9].

It is evident that the annealed particles in these models occupy the available holes in the frozen structure of the host matrix. It is thus possible to probe for different types of hole (such as tetrahedral-like against octahedral-like holes) inside a given disordered structure by adopting suitable models for the interactions between the permeating fluid and the host [10].

It is also evident that the pair distribution function of the permeating fluid carries information on the spatial correlations between such structural holes. We present below a method allowing these hole–hole correlations to be analysed in detail. The method uses a fluid of point-like charges as a probe and varies its density to display the successive shells of structural holes surrounding an average preferred structural hole.

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2. The method

The system with which we are dealing consists of two components, one of which has been quenched into some disordered structure while the other is allowed to equilibrate with this fixed structure. We adopt the convention of labelling the matrix of quenched particles with the suffix $i = 1$ and the fluid of annealed particles with the suffix $i = 2$. We introduce the partial number densities n_i, the direct correlation functions $c_{ij}(r)$, the radial distribution functions $g_{ij}(r)$ and the total correlation functions $h_{ij}(r) = g_{ij}(r) - 1$.

In the replica method [2, 3] the partly quenched two-component system is mapped into a fully annealed three-component system by breaking $h_{22}(r)$ and $c_{22}(r)$ into the sums of 'blocked' and 'connected' contributions, $h_{22}(r) = h_b(r) + h_c(r)$ and $c_{22}(r) = c_b(r) + c_c(r)$. The blocked contribution $h_b(r)$ accounts for correlations between annealed particles separated from each other by quenched particles, whereas $h_c(r)$ accounts for correlations between a pair of annealed particles which are transmitted through successive layers of annealed particles. The following set of Ornstein–Zernike relations is obtained for the Fourier transforms of the direct and total correlation functions:

$$h_{11}(k) = c_{11}(k) + n_1 c_{11}(k) h_{11}(k) \tag{1}$$

$$h_{12}(k) = c_{12}(k) + n_1 c_{11}(k) h_{12}(k) + n_2 c_{12}(k) h_c(k) \tag{2}$$

$$h_{22}(k) = c_{22}(k) + n_1 c_{12}(k) h_{12}(k) + n_2 c_c(k) h_{22}(k) + n_2 c_b(k) h_c(k) \tag{3}$$

$$h_c(k) = c_c(k) + n_2 c_c(k) h_c(k) \tag{4}$$

$h_{11}(k)$ being the independently fixed pair structure of the disordered matrix. The symmetry relations $h_{12}(k) = h_{21}(k)$ and $c_{12}(k) = c_{21}(k)$ hold. The function $c_b(k)$ is set equal to zero in the set of Ornstein–Zernike relations proposed earlier by Madden and Glandt [1, 11].

In the calculations reported below we adopt the hypernetted-chain (HNC) closure [7] to relate the radial distribution functions to pair potentials $\Phi_{ij}(r)$,

$$g_{ij}(r) = \exp\left[-\beta\Phi_{ij}(r) + h_{ij}(r) - c_{ij}(r)\right] \tag{5}$$

$$h_b(r) = \exp\left[h_b(r) - c_b(r)\right] - 1. \tag{6}$$

The use of equation (5) for the case $i = j = 1$ implies that the quenched structure is that of an internally equilibrated one-component fluid of particles interacting with each other via the pair potential $\Phi_{11}(r)$. Of course, other types of construction for the pair structure of the matrix are possible for input into equation (1).

As indicated in section 1 we propose to probe the distribution of structural holes in the matrix by taking $\Phi_{22}(r) = e^2/r$. Namely, the annealed component permeating the matrix is a classical plasma (OCP) of point-like charges neutralized by a uniform background at density n_2 (for reviews of earlier studies of the OCP see Baus and Hansen [12] and Ichimaru [13]). The pair potential $\Phi_{12}(r)$ may then be chosen so as to select a given type of hole in the matrix preferentially.

3. The application to the one-component plasma

For illustrative purposes we shall make the simplest possible choice for the pair potentials $\Phi_{12}(r)$ and $\Phi_{11}(r)$ in the calculations reported below; that is, we shall take $\Phi_{12}(r) = e^2/r$ and $\Phi_{11}(r) = e^2/r$. Namely, we shall be using an OCP at variable density n_2 to probe the structural holes in an OCP at given density n_1. Such a partly quenched OCP is fully described by the plasma coupling parameter $\Gamma = e^2/(ak_BT)$ and by the concentration $x_2 = n_2/n$, with $n = n_1 + n_2$ and $a = (\frac{3}{4}\pi n)^{1/3}$.

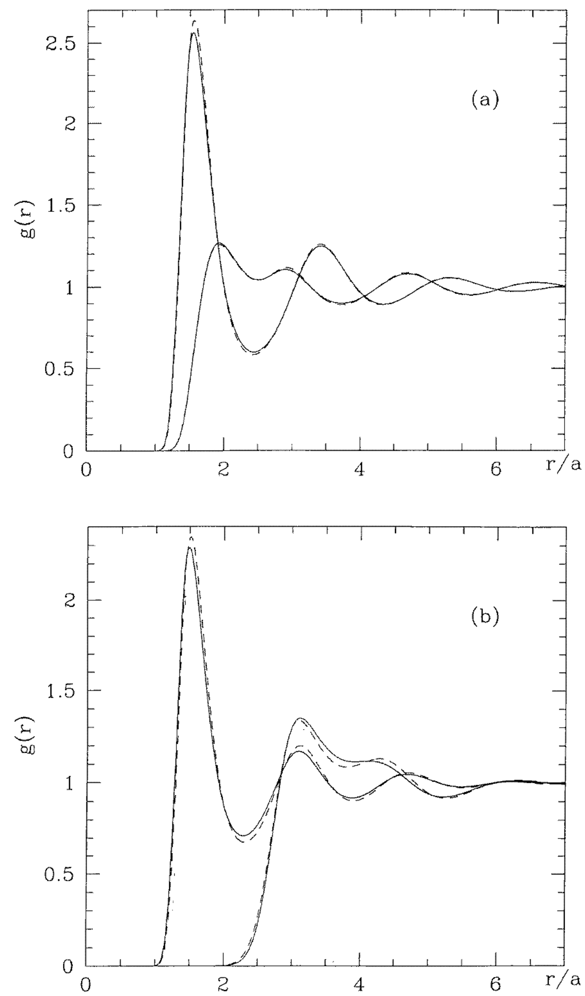

Figure 1. Pair distribution functions $g_{12}(r)$ (peaking at $r \simeq 1.5a$) and $g_{22}(r)$ in the partly quenched OCP at $\Gamma = 100$ versus the reduced interparticle separation r/a, for the cases (a) $x_2 = 0.5$ and (b) $x_2 = 0.1$. The full curves were obtained by numerical solution of equations (1)–(6); the broken curves were obtained by setting $c_b(r) = 0$ in equations (3) and (6).

We have solved equations (1)–(6) numerically for the structure of the partly quenched OCP by the iteration method described by Høye *et al* [14, 15] with a suitable extension of the cut-off procedure proposed by Springer *et al* [16] and Ng [17] to handle the numerical problems arising from the long-range nature of the Coulomb potential. Fourier transforms were taken on a discrete mesh consisting of 2048 points spaced $0.01a$ apart.

Our numerical results for the pair distribution functions $g_{12}(r)$ and $g_{22}(r)$ in the partly quenched OCP are presented in figures 1–3. We anticipate that the results obtained by setting $c_b(r) = 0$ in equations (3) and (6) (shown by the broken curves in figure 1) are very close to those obtained from the complete set of equations (full curves). As discussed by Given and Stell [2], this approximation is consistent with the Percus–Yevick closure but is in principle not correct when the HNC closure is adopted. In fact, we find that setting

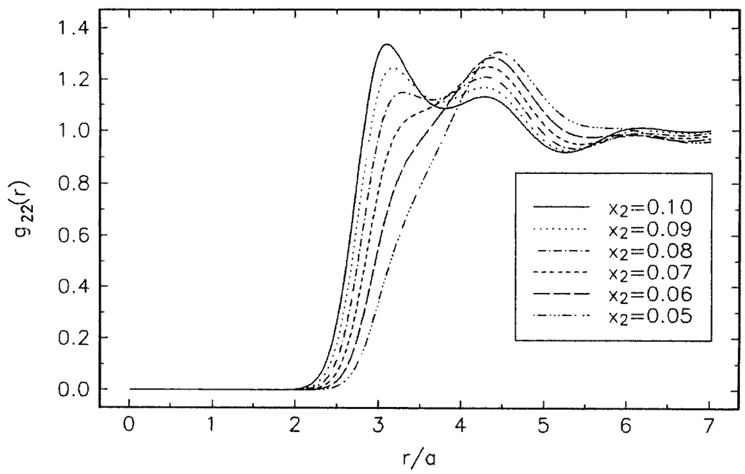

Figure 2. The pair distribution function $g_{22}(r)$ in the partly quenched OCP at $\Gamma = 100$ for various values of x_2 approaching very high dilution of annealed particles.

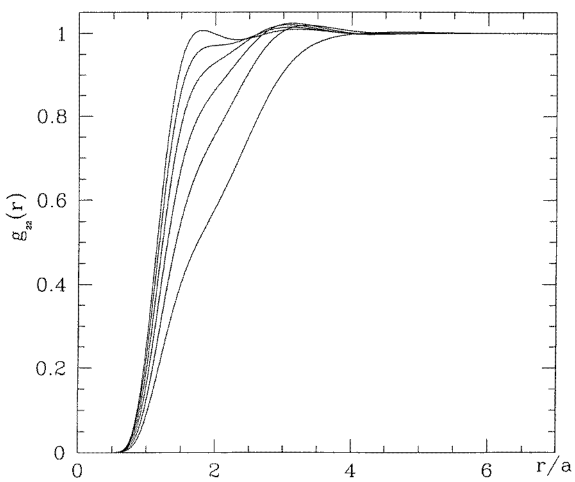

Figure 3. The pair distribution function $g_{22}(r)$ in the partly quenched OCP at $\Gamma = 10$ for various values of x_2 ($x_2 = 0.6$, 0.5, 0.4, 0.3, 0.2 and 0.1 from left to right).

$c_b(r) = 0$ is generally a very good approximation even in the case of the HNC closure.

Figure 1 reports the pair distribution functions $g_{12}(r)$ and $g_{22}(r)$ at $\Gamma = 100$ for two values of the concentration of annealed particles, $x_2 = 0.5$ and 0.1. It should be first recalled that, in the OCP at full equilibrium, we would by definition have $g_{11}(r) = g_{12}(r) = g_{22}(r) = g_{eq}(r)$, say. The distribution $g_{12}(r)$ in figure 1 for the partly quenched OCP shows a very sharp first peak—indeed, an appreciably sharper one than the main peak in $g_{eq}(r)$. Furthermore, $g_{12}(r)$ is very similar in the two cases shown in figures 1(a) and (b): evidently, even at very different concentrations, the annealed particles occupy essentially the same set of holes inside the quenched structure, which is the same in the two cases. From these sites they see a strongly peaked first coordination shell of quenched particles located at $r/a \cong 1.5$, followed by at least two further shells of quenched particles. The rather broad peaks in the second and third shells are located at $r/a \cong 3.5$ and 5.3 for $x_2 = 0.5$ and move inwards somewhat as x_2 is reduced to $x_2 = 0.1$.

Turning to the distribution $g_{22}(r)$ at $x_2 = 0.5$ in figure 1(a), its superposition upon $g_{12}(r)$ shows a state of overall order at short range from alternation of annealed and quenched particles in space. At least three shells of annealed particles around a given annealed particle can be discerned. These are located at $r/a \cong 2.0$, 2.9 and 4.7. From the interpretation given above for $g_{12}(r)$ we may interpret this result as showing that the annealed particles are probing the correlations between holes in the quenched structure over a range of at least three shells of holes around a given 'average' hole.

It is seen next from $g_{22}(r)$ in figure 1(b) that, on reducing the concentration of annealed particles to $x_2 = 0.1$, the first shell of annealed particles around an annealed particle is emptied. Correlations build up in the former second shell, whose peak is shifted outwards somewhat (from $r/a \cong 2.9$ to $r/a \cong 3.1$). The occupation of the former third shell is also relatively increased, with some shift inwards of its peak (to $r/a \cong 4.4$) and increased overlap with the inner shell.

Figure 2 shows in detail how the second shell empties and the third shell is filled up on further decreasing the concentration of annealed particles from $x_2 = 0.1$ to $x_2 = 0.05$, still at coupling parameter $\Gamma = 100$. A full visualization of the distribution of third-neighbour holes in the quenched structure is obtained near the lowest value of x_1 in this range.

Finally, figure 3 stresses that strong coupling between the probing charges is crucial for the type of structural analysis that we have presented above. It reports the evolution of $g_{22}(r)$ at $\Gamma = 10$ on decreasing the concentration of annealed particles from $x_2 = 0.6$ to $x_2 = 0.1$. The emptying of the first shell and even that of the second shell are still seen to occur at this moderate value of the coupling strength, but the resolution that is being achieved in the structural analysis is quite poor.

4. Concluding remarks

We have presented a method in which a strongly coupled classical plasma of point charges is used to probe the spatial correlations which exist between holes inside a disordered structure. Up to three shells of holes can be revealed and their occupation examined in detail by varying the relative number of particles in the plasma.

We have illustrated the usefulness of the method by applying it to analyse the distribution of structural holes in the strongly coupled fluid OCP at internal equilibrium. However, we wish to emphasize again in closing that (i) the pair distribution function of the matrix may be chosen at will, thus replacing equation (5) for $i = j = 1$ by the desired pair structure for input into equations (1)–(4); and (ii) suitable modelling of the potential $\Phi_{12}(r)$ of interaction between quenched and annealed particles will allow some selectivity in the types of structural hole whose correlations one may wish to examine.

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