An investigation of the effects of the structure of gel materials on their adsorptive properties using a simple lattice-gas model

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We have used a simple lattice–gas model solved in the mean-field approximation to study the effects of material structure on adsorption and desorption isotherms in simple models of silica aerogels and xerogels. We have varied independently the gel particle radius, the density, the surface wettability and the degree of long-range structural correlation in the gel, and in each case obtained adsorption and desorption data at a series of temperatures. These data are discussed in the context of standard adsorption theories and classifications. Kelvin-like behaviour is observed over the entire range of models studied, for both randomly generated gel structures and diffusion-limited aggregates. The shape of the hysteresis loops in these systems appears to vary smoothly with gel structure and is principally determined by the gel density and gel particle size. We have also measured the structure factor at each pressure along each isotherm, for which we discuss data in developing a microscopic understanding of adsorption in these systems. The relative merits of small-angle scattering data and geometrically defined pore size distributions for understanding adsorptive behaviour are discussed. For the material models considered here, a geometric measure of pore size distribution appears to be the best predictor of adsorptive behaviour.

1. Introduction

The objective of this paper is to investigate the degree to which spatial correlations in the structure of porous gel materials influence their adsorption of simple liquids. Analysis of the adsorption isotherms of simple liquids such as argon and nitrogen remains the most commonly used method to obtain from experiments, the porosity, surface area and pore size distribution of microporous and mesoporous materials [1, 2]. Methods for gas adsorption analysis involve fitting (either implicitly or explicitly) the morphological properties of an idealized model of the material (for instance, a collection of cylinders of varying size) to the measured adsorption data, and then reporting the fitted quantities [3, 4]. All such methods are therefore model-dependent in the sense that the definition of the model is a physically motivated but ultimately arbitrary choice on the part of the experimenter which necessarily influences the fitted data. For microporous and mesoporous materials with regular (and morphologically simple) pore structures, the choice of such a model is straightforward and the results obtained are quite reliable; this is particularly true for templated materials such as MCM-41 and MCM-48 and their derivatives [5, 6], which exhibit very regular pore structures. However, most porous materials have no (pseudo)-crystalline order and tend instead to display a wide range of pore sizes and shapes connected in a ‘tortuous’ network topology which cannot reasonably be described using simple models as described above. One of the simplest such types of material are phase-separated glasses [7, 8], which have been intensely studied in efforts to understand adsorption phenomena [3, 4, 9–15]; the relatively well-behaved structure of these materials arises from the spinodal decomposition processes used to create them [16, 17].

Another class of materials for which the growth process is well understood are gels. Gels are highly branched system-spanning polymer networks that are produced by the aggregation of polyfunctional monomer species in solution. Of particular interest here are silicate materials prepared through sol–gel processing [18], in which small silica particles (the ‘sol’) aggregate into gels which are then dried. These aggregation processes can be studied using simple aggregation models, including diffusion-limited aggregation (DLA), reaction-limited aggregation (RLA), diffusion-limited cluster aggregation (DLCA), and others [18–20]. When a wet silica gel is dried under supercritical conditions the resultant material is called an aerogel, which has quite...
low density and morphological properties very much like the wet gel. If the gel is dried under subcritical conditions it tends to collapse due to tension in the desorbing liquid. The resulting xerogel is substantially denser, though still porous, and its morphological properties are changed substantially from the wet gel precursor; a complete understanding of this process remains to be developed. Xerogels are often further densified by heating; this process is commonly used to prepare both nanoscale thin films of silica and other glasses and materials for fibre optic applications. Aerogel structures, in particular, are known to have mass and surface distributions which are fractal over certain length scales, although the materials are homogeneous at sufficiently long length scales [21–23]. The properties of a fractal object can be extracted from small-angle scattering experiments, which have become a popular method for the investigation of gel-derived materials and the adsorption of gases on them.

In this work we focus on the structure imparted on a simple model gel precursor by the DLCA process and its effects on the adsorptive properties of the gel. We are especially interested in how the correlations as measured by small-angle scattering may be compared with more conventional measures of pore size distribution. We also obtain and discuss fluid–fluid and fluid–gel (cross) correlations functions and structure factors at different points along each isotherm. We have simulated gas adsorption and desorption using two different system scales. To generate a NOUR structure we randomly place particles in the simulation cell; if each new particle does not overlap any of the previously placed particles the new particle is accepted; else a new position is chosen at random with probability $p_n$ according to [28]:

$$p_n = \frac{\eta^f_i}{\sum_i \eta^f_i},$$

$$\sum_{i=1}^{N_{agg}} n_i = N_p,$$
with $a$ a parameter describing the effect of a cluster’s size on its diffusion constant. A spatial direction is chosen from a uniform distribution on a sphere, and the cluster moved a fixed distance $\delta l$ in that direction. If the cluster does not collide with any other cluster the algorithm continues by choosing another cluster at random and moving it. If a collision occurs, the moving cluster is backed off until the point of contact and the two clusters are merged. The process is repeated until only a single cluster remains. The fractal dimension in this model turns out to be independent of $a$ and has been previously computed \[28\] approximately as $D_F = 1.78$. We have chosen $a = -1 / D_F = -0.55$ so that the effective cluster diffusion coefficients vary as the inverse of the cluster radius \[28\]. Example NOUR and DLCA structures of gel density 3% (porosity 97%) prepared according to these procedures are shown in figure 1.

Note that the definition of density used in this work is not the number density of gel particles, but instead the fraction of gel-occupied lattice sites; likewise, all other morphological quantities are measured from the lattice projection of the gel structure.

The thermodynamic behaviour of the fluid confined in such a model gel is given by the solution of the fluid model equation (1) in the grand canonical ensemble. The solution could in principle be obtained through Monte Carlo simulation, but this would be prohibitively expensive. Instead, at conditions far from critical a mean-field approximation has been shown to be sufficient for describing many properties \[29\].

In the mean field one obtains the following expression for the grand potential:

$$
\Omega = -w_{ff} \sum_{\langle ij \rangle} \rho_i \rho_j - w_{mf} \sum_{\langle i \rangle} \left[ \rho_i (1 - \eta_i) + \rho_j (1 - \eta_j) \right] + \frac{1}{\beta} \sum_i \left[ \rho_i \log \rho_i + (\eta_i - \rho_i) \log (\eta_i - \rho_i) \right] - \mu \sum_i \rho_i \ ,
$$

where $\rho_i$ denotes the average fluid densities $\langle \tau_i, \eta_i \rangle$. This expression can be arrived at by several routes, ranging from application of the Bragg–Williams approximation to the model Hamiltonian \[30, 31\] to a recasting of the entire problem as a coarse-grained version of classical fluid density functional theory \[25\]. By applying the variational condition $\partial \Omega / \partial \rho_i = 0$, a set of coupled equations is obtained

$$
\rho_i = \frac{1 + \exp \left( \frac{\eta_i}{\beta \left( \mu + \sum_{\langle j \rangle} \left[ w_{ff} \rho_j + w_{mf} (1 - \eta_j) \right] \right) \right)}{1 + \exp \left( \frac{-\beta \left( \mu + \sum_{\langle j \rangle} \left[ w_{ff} \rho_j + w_{mf} (1 - \eta_j) \right] \right) \right)} \ ,
$$

which can be solved iteratively.

In experimental studies of the phase behaviour of fluids adsorbed on porous materials the usual quantity reported is the Gibbs excess adsorption, the excess coverage of liquid on the internal surface of the gel, as a function of the external gas pressure at constant temperature. The Gibbs excess is measured both at increasing pressure (adsorption branch) and decreasing pressure (desorption branch). Porous materials with characteristic void sizes in the range of approximately 2 nm up to a few hundred nanometres almost all exhibit
hysteresis between these two branches at sufficiently low temperatures. In theoretical models and Monte Carlo simulations it is more convenient to use the chemical potential $\mu$ as a control variable, although of course the bulk gas pressure is easily related to $\mu$. Likewise, in simulation studies the absolute isotherm is generally reported, which differs from the excess isotherm only by the system volume multiplied by the density of the bulk gas, which changes little over the pressure ranges generally investigated.

It has been shown [32] in similar systems that the usual periodic boundary conditions are not acceptable for the simulation of desorption isotherms, as they suppress nucleation of the low-density phase and therefore often display greatly exaggerated hysteresis. Instead, we need to connect at least one surface of the simulated system to a reservoir of bulk vapour. We implement the ‘free surface boundary condition’ (FBC) in the $z$ direction and periodic boundaries in $x$ and $y$. In order to introduce free surfaces but still retain an ‘interior’ structure comparable with a PBC-bound model, we first duplicate the original PBC system in the $z$ direction, to have dimensions $L_x \times L_y \times 2L_z$. To simulate the gas-phase reservoir in contact with the surfaces, we add an extra cavity in the $z$ direction of size $L_x \times L_y \times 50$. The central part (10 lattice spacings) of this reservoir is kept in the gas phase by requiring $\rho_i < 0.5$ during the iteration of equation (5). The complete FBC system has dimensions $L_x \times L_y \times (2L_z + 50)$ and contains planar layers of gel material and bulk vapour reservoir (see figure 8, section 3.5). It is simulated using normal periodic boundary conditions.

In obtaining adsorption isotherms, structure factors and other data, we only analyse data from the ‘interior box’ $L_x \times L_y \times [L_z/2 : 3L_z/2]$; this volume is identical to the original PBC system and ‘far’ from the free surfaces. As described below, we find that the choice of free-surface or periodic boundary conditions has no effect whatsoever on the adsorption isotherms, but has a dramatic effect on desorption.

As the slope of the isotherms can change rapidly, rather than use equally sized steps in $\mu$ we attempt to choose $\mu$ intervals to yield a constant contour length along the isotherm. We calculate the absolute adsorption isotherm

$$\rho_i(\mu, T) = 1/N \sum_i \rho_i$$

by varying the chemical potential $\mu_i$ to $\mu_{i+1} = \mu_i + \delta_i$ according to [33]:

$$\delta_i = \delta^0 \frac{\delta_i^{-1}}{[(\mu_i - \mu_i^{-1})^2 + (\rho_i - \rho_i^{-1})^2]^2}^{1/2},$$

where $\gamma$ is a scale control parameter and $\delta^0$ is the target contour length. This generally produces quite smooth isotherms, although in systems with sharp steps in the isotherm the method fails and in the region of the step defaults to a very small constant $\delta_i$.

In order to improve the convergence of the iterative solution of equations (5), we use a scheme different to that proposed in [27], which we have found to be faster in most cases. Each iteration of equations (5) involves a loop over the full set of $N$ lattice sites. However many sites converge very quickly and continuing to iterate them is wasteful. We tabulate active sites, $N_a$, defined by $\rho_i^{-1} - \rho_i > \epsilon_1$, and make iterations only in active sites. Because inactive sites may later become active, we periodically iterate over the whole system (every 15 cycles, in this work) to allow sites to ‘re-activate’. This approach requires performing more site updates than the method proposed in [27], but involves less storage and computational overhead and is faster, at least on our computer systems. The procedure is stopped when a cycle over all sites satisfies $(1/N_a) \sum_i [\rho_i^{-1} - \rho_i] < \epsilon_2$. We have used in this work $\epsilon_1 = 10^{-10}$ and $\epsilon_2 = 10^{-12}$.

2.1. Structural analyses

In fully periodic systems (PBC) we compute correlation functions for the fluid and gel, represented here by three-dimensional data $\rho_f$ and $\eta_i$ where the lattice site index runs over $i = 1, \ldots, L_x \times L_y \times L_z$. In the FBC case, the correlation functions are calculated only in the central box, $L_x \times L_y \times [L_z/2 : 3L_z/2]$; this approximates the interior behaviour of a much larger sample of porous material, avoiding inhomogeneity due to the surface. The 3D correlation function $g_{i,B}$ is computed by multiplying the Fourier transform of $A$ by the complex conjugate of the Fourier transform of $B$, which gives the Fourier transform of their correlation:

$$F[g_{i,B}] = F[A]F[B].$$

In order to compute the two-site correlation function $g(r)$ we take radial averages of $g_i$,

$$g(r) = \frac{\sum_i g_i \delta(r_i - r)}{\sum_i \delta(r_i - r)},$$

where $r_i$ is the minimum image distance between the lattice site $i$ and the coordinate origin, taking into account the periodic boundary conditions. Finally we compute the structure factor by the integral:

$$S(k) = 1 + 4\pi \rho \int r^2 [g(r) - 1] \frac{\sin (kr)}{kr} \, dr.$$
This approach to the calculation of structure factors and radial distribution functions is substantially less computationally expensive than the more common real-space route, which would require $O(N^2)$ work in these systems in order to obtain the lowest-\(k\) parts of the structure factor. The use of fast Fourier transforms brings this down to $O(N \ln N)$ which for our grids (see below) corresponds to a reduction of approximately seven orders of magnitude. In practice, this analysis requires significantly less computer time than the self-consistent iteration procedure described above.

An unambiguous geometric definition of pore size distribution (PSD) has been demonstrated by ourselves [4] and others [34]. Let $V_p(r)$ be the volume of the void space ‘coverable’ by spheres of radius $r$ or smaller; a lattice site $x$ contributes to $V_p(r)$ if and only if one can construct a sphere of radius $r$ that overlaps $x$ but does not overlap any matrix lattice sites. $V_p(r)$ is a monotonically decreasing function of $r$, and the derivative $-dV_p(r)/dr$ is the fraction of the void volume characterized by a certain radius $r$ (e.g. coverable by spheres of that radius but not larger spheres) and is a robust definition of a pore size distribution. For regular pore structures, such as a collection of spherical or cylindrical voids, this definition will simply regenerate the distribution of sphere (or cylinder) radii. The computation of this function using the lattice representation of the model is conducted as follows. First, the distance $r_i$ from each void site to the nearest matrix site is determined, producing what we have previously called an ‘accessible volume map’ [4]. Second, centred at each void site a sphere of radius $r_i$ is drawn in which every void site is labelled by $r_i$ or its current value, whichever is higher. At the end of this loop the second map contains points labelled by their coverable volume and a histogram is used to collect them into $V_p(r)$. Note that this procedure is an $O(N^2)$ operation and is therefore quite expensive on the large lattices used here, though when the maximum pore size is substantially smaller than the simulation cell a truncation can be used and the cost reduced to $O(N)$. This analysis trivially produces the same results when applied to the interior box of a FBC system and the PBC system from which it is derived.

3. Results

3.1. Systems studied

We have obtained a series of isotherms at different temperatures and values of $y$ in 26 different NOUR and 26 different DLCA model gel samples, with densities of 2.5\%, 5\%, 10\%, 15\%, 20\%, 30\% to 40\% (gel density) and gel particle radii of $r_m = 2, 4, 6$ and 10 lattice spacings. The (40\%, $r = 2$) and (2.5\%, $r = 10$) cases were not considered as the first required too many gel particles and the second required an unmanageably large system in order to provide acceptable statistics. For modelling adsorption of a simple liquid such as nitrogen or argon, the lattice spacing in this model should be taken at approximately 4 Å; the gel particles used in this model are therefore between 1.6 and 8 nm in diameter, which more than spans the range observed in base-catalysed and two-step acid–base-catalysed colloidal gel materials [18]. Periodic gel structures were generated in systems of size $L_x = L_y = L_z = 256$ lattice spacings (a volume of approximate $100^3$ nm$^3$); as explained above our FBC calculations require actually simulating a system of size $L_x \times L_y \times 2L_z + 50$ to obtain data in the $L_x = L_y = L_z = 256$ model.

The number of gel particles used varied from 200 to 150 240 in order to satisfy the different density constraints above. Adsorption values were obtained in each model with values of $y$ of 1.5, 2.0 and 3.0, and at temperatures of 0.8, 1.0, 1.1, 1.15, 1.2, 1.25, 1.3, 1.4 and 1.5, measured in units of $w_{li}/k_B$. In these units, the mean-field model has $T_c = 1.5$ and $\mu_c = \mu_{cex} = -3.0$. If not otherwise specified, results described below are those for $y = 1.5$.

With the adaptive $\mu$-sampling procedure, the iterative scheme described above, OpenMP parallelization and the FFTW libraries [35], the calculation of a complete isotherm containing approximately 100 different points and all associated correlation functions required in the order of 1–2 days on a dual-processor Athlon MP2200 computer; approximately 750 such isotherms have been obtained. We note here that prior studies using similar models have often used substantially smaller grids but then averaged over a very large number of realizations of the gel matrix in order to obtain a good description of the adsorption thermodynamics. We have not followed this approach because we are principally focused on the analysis of the adsorption isotherms as might be done in experiments and in the qualitative comparison of adsorption data with other characterizations, for which such precision is likely unnecessary. The large system sizes we have used do provide good statistics on the structure factors, smooth adsorption data and smooth pore size distributions in most of the systems studied; the $r_m = 10$ cases at low density are of course the poorest in this respect, since they contain only a few hundred gel particles.

3.2. Characterization of gel structures

In figure 2 we present the structure factors and geometrically measured pore size distributions for 5\% gel density systems with $r_m = 2$ in order to illustrate the different types of structural information contained in the two measures. In the structure factor plot, the DLCA structure clearly shows the expected behaviour for scattering from a fractal object at low $k$; a long linear
part corresponding to the mass fractal regime [36–38] and a shorter, steeper line at higher \( k \) corresponding to the surface fractal regime. The NOUR structure, however, gives nearly flat scattering at all low \( k \) values, in accord with the Guinier approximation for scattering from a dilute random assemblage. At high \( k \) (which is not clearly visible on this scale) both systems exhibit oscillatory behaviour due to short-ranged positional correlations resulting from the non-overlapping condition.

In the pore size distribution plots, however, the story is somewhat different. The NOUR and DLCA pore size distributions (PSDs) actually have nearly identical shapes, with the only difference being the scale; in the inset figure one of the curves is arbitrarily scaled in order to superimpose it on the other. Clearly, long-range correlations in the gel structure do not qualitatively affect the shape of the PSD for low-density materials, at least within the resolution of this study. We note that one may, at least in this case, distinguish between the two material structures based on a known porosity; assuming a random dispersion of spheres one may calculate the mean distance between neighbours, which should be comparable with the maximum in the pore size distribution.

The \( S(k) \) and PSD data, therefore, illustrate different aspects of the material structure. The important issue for the interpretation of adsorption data is which of these measures can be most effectively correlated with the characteristics of adsorption isotherms and therefore what information can be effectively extracted in adsorption experiments.
The geometric pore size distributions from a series of materials with \( r_m = 2 \) and differing gel densities are shown in figure 3. In this series of materials the NOUR and DLCA pore size distributions are quite similar at high gel densities, in which most of the void volume is the space between the closely packed gel particles. Even at 30% (and also 40%, not shown) density, though, the DLCA process does introduce larger voids due to the aggregation of gel particles, which is reflected in the somewhat higher values of the DLCA PSD at 3 and 5 lattice spacings. As the gel density is decreased, the curves change smoothly from this shape to that described above, and the quantitative difference between DLCA and NOUR pore size distributions becomes much more substantial.

3.3. Characterization of adsorption in different models: NOUR versus DLCA systems

In figure 4 we present a selection of adsorption and desorption isotherms using FBCs (free surface boundary conditions) as described in section 2. Additionally, and only in this figure, we include the isotherms obtained using fully periodic boundary conditions (PBC). We show in figure 4 sixteen of the NOUR and DLCA simulated structures at the moderate temperature of \( T = 1.0 \). The adsorption data obtained using PBC and FBC systems are in all cases identical, while the presence of the free surface clearly influences the desorption branch of the isotherm in all but the upper-rightmost system. Contact with the vapour phase reservoir (which is usually the case in experimental studies of gas desorption) greatly facilitates nucleation of the low-density phase so that desorption occurs at much higher pressures. Desorption in most of the PBC systems occurs at a low pressure largely independent of the material structure that is instead determined by the tensile strength of the desorbing fluid [1]. Since this is not physical and since the adsorption-branch data are the same for the two boundary conditions, in the rest of the paper and figures we will only show and discuss the FBC data.

As is clear from the figure, both the sphere size \( r_m \) and the gel density qualitatively affect the shape of the hysteresis loop in these systems, although in a ‘coupled’ way such that the two are not simple to separate. Furthermore, we see that NOUR and DLCA structures differ in their adsorptive and desorptive properties most dramatically in the small-\( r_m \) materials.

A convincing treatment of the systems shown in the bottom and left of figure 4 (large particle radius and low density) is difficult as it would require using much larger systems than we are able in order to include a statistically significant number of particles. Multiple realizations of small systems would not be sufficient, as these systems also have quite large correlation lengths. We therefore show the results for system size \( N = 256^3 \) only to complete the figure; adsorption and desorption in the lower left corner of the figure are of much poorer quality than the rest of the data. Nonetheless, the trends observed in the rest of figure 4 do continue even into this region without visible deviation, which is encouraging.
In order to determine whether the sharp jumps in the adsorption isotherms are genuine capillary transitions or simply near-coexistence wetting behaviour, we plot the location (in $\mu$) of each of these jumps against the inverse mean pore size, in the spirit of the Kelvin equation for capillary condensation in macroscopic systems [1, 2],

$$\ln \left( \frac{P}{P_0} \right) = -\frac{2\gamma v_l}{r_K RT},$$

where the relative vapour pressure $P/P_0$ is related to the chemical potential used in the calculation by $\mu - \mu^0 \propto \ln (P/P_0)$, $\gamma$ is the surface tension and $v_l$ is the molar volume of the liquid. The Kelvin radius $r_K$ measures the average radius of curvature of the liquid–gas interface. In figure 5 we plot $\mu$ versus $1/r_K$ for all the systems studied in this paper, including both DLCA and NOUR structures. We take $r_K$ as the average size [1] from the pore size distributions, and the chemical potentials $\mu$ from the intersection of the $T = 1.0$, $y = 1.5$ adsorption isotherms with a horizontal line at $\rho_l = 0.5$. An excellent linear relationship is found, suggesting that for all of the systems studied here we are indeed observing capillary condensation and not other phenomena. We note here that in some systems, especially low-density NOUR structures with large gel particles, we observe condensation only at chemical potentials greater than $\mu_{\text{coex}}$, which of course is not physically realistic; this must be due to incomplete convergence of the iterative procedure (even though the high tolerances described above were satisfied). Likewise, the best-fit line through our data should intersect the $1/r_K = 0$ axis at $\mu_{\text{coex}}$, but does not; this is due to a combination of scatter in the data, the incomplete convergence just described and the inadequacy of the Kelvin equation for quantitative work in microscopic systems [4]. However, from the slope of the fitting line in figure 5, $-0.809976$, we can estimate the value of the liquid–gas surface tension in equation (11). At $T = 1.0$ the bulk liquid density at coexistence is $\rho_l = 0.929280$ and $v_l = \rho_l^{-1}$. The estimated value for $\gamma$ is $0.376347$. Because of the underlying lattice, the surface tension in this model varies with the orientation of the surface with respect to the lattice vectors. A direct calculation of the liquid–gas surface tension in the principal lattice planes gives us: $\gamma_{(100)} = 0.269323$, $\gamma_{(110)} = 0.398520$, $\gamma_{(111)} = 0.492066$, which average to $0.386636$, quite close to the estimation from the Kelvin equation.

Two clearly defined ‘extreme’ shapes of the hysteresis loop are displayed in these systems. Along the leftmost
column we see IUPAC ‘Type IVa’ isotherms displaying
type ‘H1’ hysteresis loops [2], where the capillary rise
and desorption drop are nearly vertical and parallel. In
such systems the nearly vertical capillary rise is referred
to as delayed adsorption. The upper right plot is
classified as an IUPAC ‘Type IVb’ isotherm, displaying
a characteristic triangular type ‘H2’ hysteresis loop; in
IVb systems the position of the sharp desorption branch
is thought to be dependent on network-percolation
effects, at least in some cases [27, 39]. What is perhaps
remarkable about this series of plots is that they clearly
show that these two classes of isotherm, at least within
the constraints of the model used, appear to be limiting
behaviour of a continuously variable range. That is, by
appropriate choice of gel particle size and system
density, the shape of the hysteresis loop can be varied
smoothly between type H1 and type H2, without
changing the qualitative structure of the material.

The differences between NOUR and DLCA isotherms
appear to be explained by recourse to the geometrical
pore size distributions. In all of the $r_m = 2$ systems the
NOUR data are quite similar to the DLCA data, just
shifted to lower chemical potentials; this is in keeping
with the smaller mean pore size in the NOUR systems.
This is generally true for systems in the upper diagonal
of figure 4; only in the lower left corner (and the $r_m = 4,$
5% system) do we see the NOUR models display
broader hysteresis loops than the DLCA ones. We
hypothesize that condensation in the DLCA models
can occur slightly before condensation in the NOUR
models because short-ranged correlations in the DLCA
structure (principally that every gel particle must be in
contact with at least one other) provide an opportunity
for somewhat greater adsorption in the multilayer
regime (at chemical potentials somewhat short of the
capillary rise, where a thick fluid layer wets the gel
surface) just short of capillary condensation, which in
turn slightly reduces the barrier to the condensation
event which then occurs at a lower pressure. However,
this phenomenon is observed principally in the systems
for which our statistical confidence is lowest and so may
be spurious.

For type H2 loops observed in systems with small $r_m$
and higher gel densities, the DLCA and NOUR
adsorption data are again very similar, except for a
shift of the DLCA isotherms to higher chemical
potentials. As above, this is effectively explained by
recourse to the larger mean pore sizes of the DLCA
systems. Note that in the $(r_m = 2, 30\%$ gel density)
system (upper right), the choice of PBC or FBC
conditions does not affect the desorption branch data,
suggesting that a homogeneous nucleation mechanism is
at work during desorption, rather than a surface-
induced one.

### 3.4. Effects of temperature

All the data shown in figure 4 were taken at the same
temperature. In order to better understand the effects of
temperature on adsorption in these systems, and also to
further investigate the differences between adsorption in

![Figure 5. ‘Kelvin plot’ for 50 gel configurations, both DLCA (circles) and NOUR (squares), for sphere radii $r = 2, 4, 6$ and $10$
and gel densities $\rho_{gel} = 2.5\%, 5\%, 10\%, 15\%, 20\%$ and $30\%$. The chemical potential at condensation is taken as the intersection
of the adsorption isotherm with $\rho_c = 0.5$. The temperature $T = 1.0$ and $y = 1.5$. The Kelvin radius has been computed as the
average pore size from the PSD distributions. The line is a regression fit to all the data.](image-url)
NOUR and DLCA structures, we have repeated these calculations at several higher temperatures. Data from four representative systems are shown in figure 6. These models present clear examples of H1 and H2 hysteresis as well as two different ‘intermediate’ systems. All four systems exhibit the same general trend. The height and width of the hysteresis loop decrease with increasing temperature and eventually disappear, with the adsorption and desorption isotherms becoming reversible and identical. This type of behaviour is known from both experiments [9, 10, 40, 41] and theoretical work [42–44], and is the adsorbed-fluid analogue of the evolution of the van der Waals loop with increasing temperature in a bulk fluid. The temperature at which hysteresis disappears, $T_h$, is clearly a function of the material structure and can differ between DLCA and NOUR structures with the same $r_m$ and density.

In figure 6 (a) (upper left), the shift in the position of the capillary rise between the DLCA and NOUR structures eventually results in a $T_h$ for the NOUR structure between 1.3 and 1.4, while in the DLCA model hysteresis persists to at least 1.4; note that the critical temperature of this model solved in the mean-field approximation is 1.5. In system (b) (upper right), the stretched triangular shape of the hysteresis loops makes it difficult to determine $T_h$ without a higher-resolution study; in any case, the DLCA and NOUR adsorption data are remarkably similar except for a nearly constant shift of the DLCA curves to a higher chemical potential.

In system (c), corresponding to much larger gel particles, the DLCA and NOUR isotherms are essentially identical at all temperatures studied, and only small shifts are visible in the data from system (d); this is again consistent with the pore size distribution data and Kelvin equation analysis given earlier.

In figure 7 we consider the effects of the surface wettability $y$ on the isotherms in the same four systems as in the previous figure. It is clearly shown that, at least at this temperature, increasing the value of $y$ does not qualitatively change the adsorptive behaviour of the materials. The only real effect is that for systems with higher $y$ the adsorption in the multilayer regime is greater, which reduces the height of the hysteresis loops. There is no real change in the quantity of fluid present upon filling at high chemical potential. This is expected, because at this temperature the bulk liquid density is approximately 0.93, relatively close to its maximum value of 1.0, and so there is little room left to increase the fluid density near the surface. As $y$ is increased the difference between NOUR and DLCA isotherms becomes slightly greater. This is likely due to thickened multilayers causing capillary condensation to occur at somewhat lower chemical potentials in the NOUR system. The effect of multilayer thickness on the position of capillary condensation is qualitatively accounted for in the Barrett–Joyner–Halenda (BJH) [45] model, in which the multilayer thickness is subtracted from the void space diameter before application of the Kelvin equation. Although no longer
considered quantitatively accurate [4], the essentials of this model are sound and nicely explain the observed shift as follows. While the multilayer thickness is likely almost the same in NOUR and DLCA models with the same $y$, the NOUR models always have smaller pores, so that small changes in multilayer thickness will cause greater changes in the position of the capillary rise in NOUR models than in DLCA models, as observed.

3.5. Fluid structure during adsorption and desorption

In figure 8 we show sequences of $(x = L_x/2, y, z)$ sections of the fluid density field for both DLCA and NOUR structures with $r_m = 4$ and 10% gel density. We show in the pictures the complete simulated system; again, statistics are gathered only in the central box. The replication of the PBC structure to make a ‘slab’ geometry in the FBC calculations is clearly visible here. During adsorption, the fluid density field in the initial stages of capillary condensation (sections A and B in each sequence) also displays this translational symmetry, although later in the adsorption process (section C) the influence of the free surfaces is felt. Again, although the surface effect is clearly visible, the adsorption data measured in the interior of the slab are independent of the choice of PBC or FBC simulation conditions. Desorption is initiated at the free surfaces, and the progress of a vapour-phase front into the material is clearly visible in both systems. For the $r_m$ and porosity shown here, the NOUR model displays a more uniform desorption front (sections E and F) than does the DLCA model, which appears to display percolative behaviour.

We have used Fourier transform methods to efficiently obtain the fluid–fluid, fluid–gel and gel–gel structure factors at every point along every isotherm generated, in order to better understand the effects of correlations in the gel structure (which are captured well by this analysis) on the adsorption of the fluid.

In figure 9 we show structure factor data along the adsorption and desorption branches for the $r_m = 2$, 10% gel density DLCA and NOUR materials. Starting with adsorption in the DLCA material (figure 9(a)), in the multilayer regime there is a single broad peak centred around $\ln k = -1.0$, which results from the underlying gel structure. As fluid condenses into the pore network the magnitude of $S(k)$ increases at low $k$ and a broad peak grows near $\ln k = -2.5$. However, as the last void spaces are filled at high chemical potential, this correlation largely disappears. The remaining low-$k$ correlations at pore filling are identical to the gel–gel correlation (also shown, but shifted vertically by a linear factor) as expected from Babinet’s Principle [37] that complementary structures must yield the same scattering. We have previously considered similar functions in a different material [14] and shown that the broad peak at low adsorption correlates roughly with the position of the maximum in the geometric pore size distribution, while the position of the lower-$k$ peak observed from scattering along the capillary rise is related to the mean separation between large void volumes. We also note that in the higher-$k$ region corresponding to correlations comparable with the gel particle size ($\ln k \approx 1$), oscillations are present at low adsorption but disappear.

Figure 7. DLCA (solid lines) and NOUR (dashed lines) adsorption and desorption isotherms. The coupling constant ratio is varied; from left to right in each plot $y = 3.0, 2.0$ and 1.5. In order to avoid overlap, data at different $y$ have been shifted to the left by $\Delta \mu = 0.8, 0.4$ and 0, respectively. Temperature $T = 1.0$. The four systems are (a) $r_m = 2$, 10% gel density, (b) $r_m = 2$, 30% gel density, (c) $r_m = 6$, 10% gel density and (d) $r_m = 6$, 30% gel density.
rapidly as the chemical potential is increased, signifying the growth of a smooth fluid multilayer with less structure than at lower pressures.

During desorption a very similar sequence of data is obtained, although the sharp desorption `shoulder' makes it difficult to obtain $S(k)$ data very near (but below) pore filling. This similarity is not surprising, given the great similarity between the shape of the capillary rise and desorption shoulder in the isotherms.

In the NOUR material, very similar behaviour is observed in both adsorption and desorption, with one important difference. In $S(k)$ data taken on the adsorption branch, a single large peak grows in and then disappears at a low $k$ (in fact, at the same $\ln k \approx -2.5$ position as in the DLCA structure), again due to pore–pore correlations, but there is no gel peak at $\ln k = -1.0$ due to the randomness of the NOUR structure.

This does not seem to affect the growth and disappearance of the low-$k$ peak. That the low-$k$ peak occurs at approximately the same position in the NOUR and DLCA models is particularly interesting since it suggests that the distribution of large voids throughout the two materials is comparable, even though the models

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Figure 8. Sequence of fluid density profiles (grey scale, light for gas phase and dark for liquid phase) within the gel structure (white spheres). These are two-dimensional $(y, z)$ slices through the density field at $x = Lx/2$. Gel models have $r_m = 4$, 10%, $T = 1.0$ and $y = 1.5$. Sections are shown for the DLCA structure at: $\mu = -3.0504, -3.0226, -3.0203, -3.0137, -3.0507, -3.0517, -3.0517$, and for the NOUR structure at: $\mu = -3.0293, -3.0254, -3.0249, -3.0074, -3.0507, -3.0730, -3.0731$, from top to bottom. Sections A–D are taken along the adsorption branch of the hysteresis loop and sections E–G from the desorption branch.
have clearly different pore size distributions. It is possible that more sophisticated analyses of the void space structure could directly address this distribution, e.g. the autocorrelation function of the coverable volume map described earlier, but we have not attempted such at this time. Finally, the desorption $S(k)$ data in the NOUR model are very much like those from the DLCA structure, except of course for the absence of the gel peak.

In figure 10 we show the cross-correlation functions between fluid and gel for the same systems at the same chemical potentials. These data are not plotted logarithmically, since many of them are negative. During adsorption in the DLCA model, a strong correlation at $k \approx 0.2$ grows along the capillary rise, and upon pore filling is replaced by a negative correlation. This is easily explained; when fluid completely fills the void space the fluid–gel and fluid–fluid functions must be complementary, and furthermore should sum to the structure factor of a homogeneous material, e.g. 1. The negative correlation is therefore nearly identical with $2 - S_{\text{gel–gel}}(k)$, again indicating that at pore filling the same information is contained in each of the three structure factors. Upon desorption, a similar path is followed in reverse.

In the NOUR model, the cross-correlations follow a similar trend, except that the well-defined peak at $k \approx 0.2$ is replaced with a very broad curve, and the peak that appears during the capillary rise is at a lower $k$ than in the DLCA model. The broad peak is likely another manifestation of the Guinier approximation, since at pore filling it coincides well with a linear transformation of the gel–gel structure factor.

Finally, in figure 11 the fluid–fluid $S(k)$ data for adsorption and desorption in the $r_m = 2$, 30% gel density DLCA and NOUR models are presented. In the DLCA model the adsorption data are quite similar to those presented in figure 9, with the same dramatic growth of a peak at $\ln k \approx -2$ along the capillary rise, followed by its disappearance at pore filling. In the NOUR model, however, while the low-$k$ intensity grows in this region it is difficult to reliably identify a peak position (and thus to extract a pore–pore correlation length). Since the hysteresis loops in these systems are quite narrow and the desorption drops are not vertical, one would expect to see a similar (although reversed) process in the desorption data. This is indeed the case in the DLCA model and also true to a lesser extent in the NOUR model.

The most substantial difference between the data in the 30% gel density model and the 10% gel density model is the peak at $\ln k \approx 0.25$ present in both the high-density DLCA and NOUR gel–gel structure factors, and its behaviour during adsorption and
Figure 10. Fluid–gel ‘cross’ structure factor series along the isotherms, shown in the inset. Systems parameters are $r_m = 2$, 10% gel density. Temperature $T = 1.0$ and coupling constant ratio $y = 1.5$. The DLCA plots are on the left and NOUR plots on the right, with adsorption above and desorption below. The chemical potentials, etc., are the same as in figure 9. In each plot the heavy solid line is a linear transformation of the gel–gel structure factor. $k$ is in units of $(lattice\ spacing)^{-1}$.

Figure 11. Fluid structure factor series along the isotherms, shown in the inset. Systems parameters are $r_m = 2$, 30% gel density. Temperature $T = 1.0$ and coupling constant ratio $y = 1.5$. The DLCA plots are on the left and NOUR plots on the right, with adsorption above and desorption below. In plot (a) data are shown for $\mu = -2.90, -3.3660, -3.5125, -3.5423, -3.5980, -3.6875$ and $-4.0281$. In each plot the heavy solid line is a linear transformation of the gel–gel structure factor; see text. $k$ is in units of $(lattice\ spacing)^{-1}$. 
desorption in the fluid functions. Clearly the peak in the gel function is due to the large degree of short-range positional correlation between neighbouring spheres in the dense model; the location of this peak corresponds to a real-space distance of approximately 4.9 lattice spacings, quite close to the particle diameter. In the fluid functions, however, this peak is moved to somewhat higher $k$, which can only be due to correlations between adsorbed multilayers around neighbouring particles; as the adsorbed layers become thicker they move closer together, causing the correlation to move to higher $k$. Upon pore filling, or at least filling of the smaller voids between closely packed gel particles, this correlation disappears and the shape of the gel–gel structure factor is recovered, again due to complementarity.

4. Discussion

We have surveyed the adsorptive properties of DLCA and NOUR model gel structures and attempted to correlate the shape and position of various features in their adsorption isotherms with two different structural characterizations of the gel models. Despite the numerous approximations used and the simplicity of the model, adsorption data in these systems are in good qualitative agreement with experimental results on typical sol–gel materials [18] and a number of conclusions can be drawn that may be generally applicable within this class of systems.

The shape of the hysteresis loop is found to be strongly determined by the gel particle size and the gel density, but to not be strongly influenced by the temperature or the surface wettability, at least over the ranges studied here. Hysteresis loops are traditionally used to identify morphological characteristics of materials; we can confirm that they definitely reflect the density and ‘grain’ of this class of materials, but unfortunately do not seem to contain an appreciable amount of information about the gel structure.

The geometrically obtained pore size distribution appears to be an excellent predictor for adsorption behaviour as shown in the good correlation of this measure via the Kelvin equation plot. This is true for NOUR and DLCA models, suggesting that although these models have substantially different structures, only the mean pore size (and porosity and gel particle size, as above) of a model substantially influences its adsorptive behaviour, with ‘finer’ structural details not displayed in the adsorption isotherms.

The fluid structure factors and fluid–gel cross-correlation function are strongly influenced by the ‘dry’ gel structure factor, which itself unambiguously distinguishes the DLCA and NOUR models. The fluid structure factor measured along the capillary rise in DLCA models and some NOUR models shows a large peak at low $k$ which provides some information on pore–pore correlations not otherwise available to any of the other analyses used here; in other NOUR models it does not show a peak but instead shows a broad plateau at low-$k$, again suggesting a random structure.

We therefore conclude that relatively little morphological insight into the gel structure can be obtained from single adsorption isotherms in these systems, although pore size distribution information could certainly be extracted. Conversely, the structural information obtained from correlation functions (or experimentally, from small-angle scattering) does not appear to be particularly useful in predicting or explaining the adsorptive behaviour exhibited by each model. We project that a more complete understanding of the relationship between these types of material characterization could result from more sophisticated analyses of the structure factor of the adsorbing fluid, which will be the focus of a future study.

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