

**Attachment 1 to DOE F241.1**  
**Final Technical Report - DE FG02-88ER-13825**

**Abstract**

This is an application of techniques of molecular theory to the study of nanostructures build on planar substrates and the face of membranes, with the ultimate goal of modifying their equilibrium and transport behavior. The work is focused on the mechanism for adsorption or deposition and how various regimes can be achieved by changing the rate of adsorption relative to characteristic diffusion and reaction time scales.

The first results are concerned with a discrimination of the full taxonomy of deposition regimes. The bulk of the work deals with sequential quenching,, a model for slow irreversible deposition. In this case, each new particle is allowed to equilibrate within the disordered matrix formed by all previous particles before it is quenched in place. This situation is a signature of a separation in characteristic times, such that diffusion is much faster than quenching, which itself is much faster than particle addition. Sequential quenching is considered here as an instance of quasi-thermodynamics because although the whole built-up structure is not strictly in equilibrium, each of its component particles was itself in equilibrium at one time. Thus, the problem is amenable to a treatment via Replica Ornstein-Zernike integral equations.

For structural problems, we applied both a polydisperse treatment, where we regard each particle as a different species, and a binary-mixture approximation, where all quenched particles are regarded as equivalent. The latter treatment was also used in the development of an integral-equation theory for connectedness. We applied the theory to a system of hard spheres, whose sequential quenching is equivalent to Random Sequential Adsorption (RSA). Simple short-range potentials such as the square-well and triangular-well models were introduced to study the effect of attractive forces. These forces lead to a clustering of the particles and raised the percolation thresholds and the jamming limits above those for RSA. We obtained the first percolation-and-packing phase diagram for these systems. Monte Carlo simulations were used to verify the theory and also to study systems at high densities and low temperatures, for which integral equations did not converge.

Sequential quenching deposition under the effect of attractive interparticle forces leads to the formation of growing surface clusters and, eventually, to a continuous film. We studied the evolution of the average cluster size and to determine the percolation threshold. We also applied the theory of continuum percolation to the sequential quenching problem, also using a square-well potential in the calculations. The calculated pair connectedness functions and cluster sizes compare well with Monte Carlo simulations.

We also studied the sub-monolayer growth of a system of triangular-well particles and observed a crossover from nucleation to growth. The ultimate structures exhibit a continuously varying degree of ordering with varying temperature, ranging from a virtually perfect triangular crystal in the low temperature limit to a disordered network in the opposite limit. The deposition of ellipsoidal particles leads to interesting modes of clustering, which are strongly dependent on the ratio of side-by-side to end-to-end attractive energies. We proposed an intermolecular potential that allowed us to explore this effect systematically.

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**Access in Nanoporous Solids**

**Final Report**

**for the period June 30, 1997 - May 31, 2000**

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**Submitted to the**

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## 1. Control and Optimization of Particle Deposition

The adsorption of molecular entities on solid surfaces is an important physical process with applications ranging from the formation of films and coatings to nanostructures of potential value in the fabrication of useful electronic, chemical, or mechanical devices. These microprocesses are not controlled directly but rather through operating conditions such as deposition rate and temperature, which are specified at much larger length and time scales. There are two challenges in the optimization of deposition: the multiscale nature of the problem, which ranges from the atomic to the mesoscopic to the continuum scales, and the large number of degrees of freedom in the chemistries of the substrate and particles and in the protocol for the deposition itself.

The goal of this work was to investigate modes for controlling and optimizing deposition, with the goals of producing spatially structured configurations or maximal density for potential application in device fabrication, which requires uniformity and optimal chemical reactivity. The adsorption of large molecules such as proteins and colloids on solid surfaces is generally a non-equilibrium process. The extent to which partial equilibrium is attained depends both on the processing conditions as well as the intrinsic properties of the substrate and adsorbed materials.

Three limiting deposition regimes were "unified" by considering three fundamental time-scales for the adsorption process. The rate of arrival  $R$  is determined by a molecular beam or evaporation source or by the concentration of solutes from solution. The deposition timescale,

$\tau_{arr}$ , is the average time between arrivals on a unit area. The diffusion timescale,  $\tau_{dif}$ , is given by  $d^2/D$ , where  $d$  is the molecular characteristic length scale and  $D$  is the surface diffusion

coefficient. The diffusivity, and hence  $\tau_{dif}$ , change over the deposition process. Finally, a

reaction timescale,  $\tau_{reac}$ , characterize the reaction rate of a molecule with the surface and with other molecules and aggregates. Other processes and timescales can be identified, such as molecular desorption, generally slow for large-molecule deposition, was neglected here.

The equilibrium deposition regime (EQ) corresponds to  $\tau_{dif} \ll \tau_{arr} \ll \tau_{reac}$ . In this case, there is no binding with the surface and the particles reach instantaneous equilibrium between successive additions. A second limiting case is random sequential adsorption (RSA), characterized by instantaneous surface binding of adsorbed molecules with no surface diffusion, i.e.  $\tau_{reac} \ll \tau_{arr} \ll \tau_{dif}$ . Interparticle forces other than steric exclusion become irrelevant in this well-studied limit, in which there is equilibration. Sequential or differential quenching (SQ) is the important third limit, characterized by the condition  $\tau_{dif} \ll \tau_{reac} \ll \tau_{arr}$ , so that both surface reaction and surface diffusion processes are active when the process is analyzed over the arrival time scale. Each newly adsorbed particle has time to diffuse and equilibrate before it becomes quenched in place. This is a single-molecule equilibrium, as the unquenched molecule moves within the quenched pattern or structure formed by all the previous arrivals.

These three regimes constitute extreme behaviors, other cases falling in between, depending on the relative values of the characteristic molecular times. The triangular diagram shown as Figure 1 summarizes the classification of all possible intermediate regimes. An interesting and well-studied case akin to sequential quenching is that of diffusion-limited aggregation (DLA),  $\tau_{reac} \ll \tau_{dif} \ll \tau_{arr}$ , which occurs in the case of strong interparticle attractions. The different situations in this taxonomy of regimes lead to a range of cluster morphologies, which can be

controlled by varying the deposition conditions and the binding thermodynamics of the deposited species.

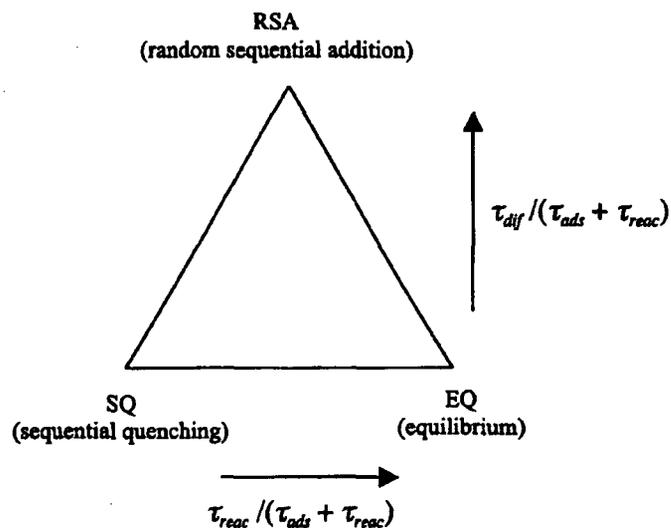


Figure 1. A "taxonomy" of deposition regimes.

## 2. A Theory of Sequential Quenching

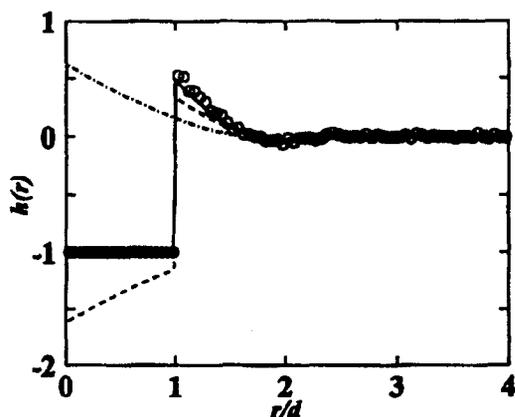
We have studied the structure of monolayers generated through sequential quenching of spherical particles. We used the genealogy of SQ to develop a polydisperse treatment because it treats each added particle as a different species. We obtained a set of two modified Ornstein-Zernike integral equations as well as diagrammatic expansion and closures. We have also presented a simple approximation to the theory, based on considering the system as a binary mixture. In graphical form, the two terms of the total correlation function were shown to be:

$$\begin{array}{c} h_1 \\ \circ \rightarrow \circ \\ \hline = \\ \circ \rightarrow \circ + \circ \rightarrow \bullet \rightarrow \circ \\ \rho \end{array}$$

and

$$\begin{array}{c} h_2 \\ \circ \leftrightarrow \circ \\ \hline = \\ \circ \leftrightarrow \circ + \circ \leftarrow \bullet \rightarrow \circ + \circ \rightarrow \bullet \rightarrow \circ + \circ \leftarrow \bullet \leftarrow \circ \\ \rho \quad \rho \quad \rho \\ \hline + \\ \circ \leftarrow \bullet \rightarrow \bullet \rightarrow \circ \\ \rho \quad \rho \end{array}$$

The results using a Percus-Yevick closure are shown in Figure 2.



**Figure 2.** Total correlation function for random sequential adsorption at a reduced density of  $\rho = 0.4$ . The bold line represents the total correlation function and the dashed and dot-dashed lines its components. The circles are simulation results.

We have shown that the structures emerging from adding and then quenching sequential fractions of fluid can also be described as a quasi-binary. When the equilibrium fraction is eventually quenched, the overall structure is simply a linear mix of those of the two fractions. If a fresh fraction is then added, the problem remains binary, only that the concentration of the quenched component is now larger. When the amount added at a time is infinitesimal, one has the case of sequential quenching. It can be described rather accurately by the ROZ equations, but generalized to a polydisperse case, since one now has an infinite number of fractions, i.e. an infinite number of components.

### 3. Connectedness and Percolation

We have investigated the connectedness behavior of structures generated by sequential quenching and developed an integral-equation formalism for percolation, complementary to the one for structure. We carried out both numerical integrations and simulations. The first system considered was of three-dimensional randomly centered spheres, whose equilibrium- and sequential-quenching-percolation problems are identical. We also applied the theory to two-dimensional square-well fluids. Figure 3 is an example of the comparisons between the theoretical and simulation results.

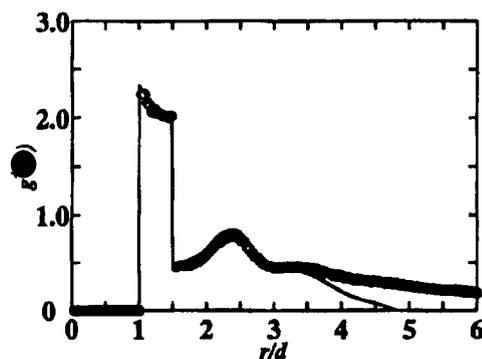


Figure 3. Connectedness functions for a two-dimensional square-well fluid with a well width of  $0.5d$  at a temperature  $T^* = 1.0$ . The bold line is the result from the numerical integration of theory and the circles are the simulation results for  $\rho^* = 0.3$ .

#### 4. Submonolayer Growth

We have used Monte Carlo simulations of triangular-well particles to study the stages in the preparation of a sub-monolayer film by sequential deposition from very low to very high temperatures, a limit at which the system becomes equivalent to RSA. We were concerned with cluster growth and in results regarding ordering within the structures. Special simulation methods needed to be developed for this study, especially for systems at low temperatures. At early times (low coverages) a deposited "seed" particle is quenched by itself, i.e. far from other particles or clusters of particles, thus constituting the nucleus for the growth of a new cluster. We studied the probability that an arriving particle may become a seed.

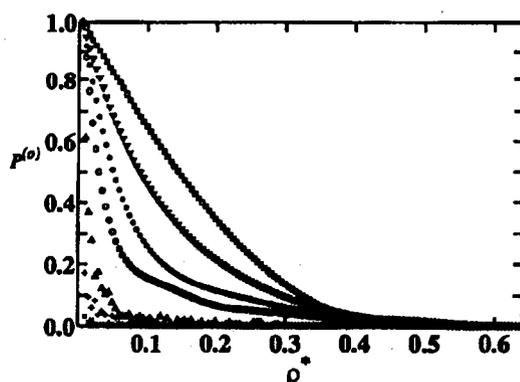


Figure 4. Probability of inserting a nucleus at (from bottom to top)  $T^* = 0.01, 0.1, 0.2, 0.3, 0.4, 1.0,$  and RSA.

As the number of nuclei and clusters grows, later arrivals join existing clusters and we found a crossover from a nucleation stage to a growth stage. We also report results on seed fractions and number of monomers on the surfaces. The percolation threshold and the jamming limit are two interesting features of the late stages of growth (high coverages).

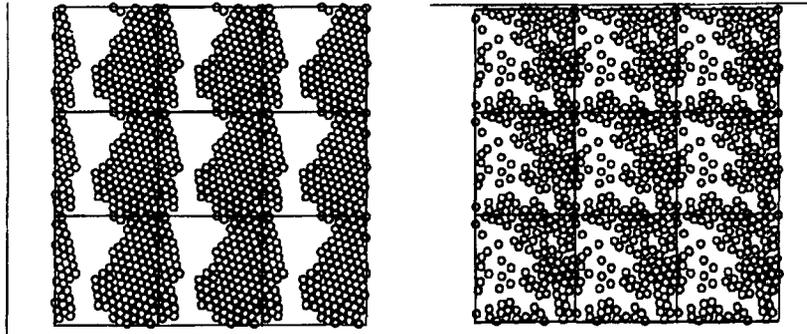


Figure 5. Percolating configurations for sequential quenching at (a)  $T^* = 0.01$ ,  $\rho^* = 0.69$  and (b)  $T^* = 0.3$ ,  $\rho^* = 0.52$ .

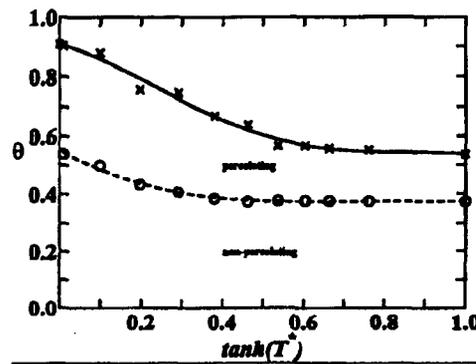


Figure 6. Phase Diagram: jamming limits (x) and percolation thresholds (o) for a system of triangular-well sequentially quenched particles at various temperatures.

### 5. Ordering in Sequential Deposition

Structures grown through sequential quenching at a low temperatures display high degrees of ordering; the same systems are disordered at a very high temperature, the limiting case rigorously

equivalent to RSA. We have studied the evolution of order between these two extremes, with particular interest in determining if there is an onset of order, a characteristic temperature equivalent to freezing, of whether the evolution between fluid-like and solid-like states is continuous, unlike what happens in equilibrium systems. The quantification of order required the definition of an order parameter. We used a special Monte Carlo method to study the onset of order in the sub-monolayer regime. The bond-orientation order parameter defined as

$$h_6 = \left\langle \cos \left[ 6(\theta_i(\mathbf{r}_i) - \theta_j(\mathbf{r}_j)) \right] \right\rangle$$

is presented in figure 7.

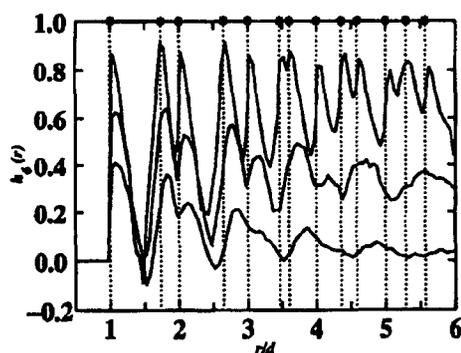


Figure 7. Bond-orientation correlation function at a density  $\rho^* = 0.65$  and at (from top to bottom)  $T^* = 0.01, 0.1$  and  $0.2$ .

The overall bond-order parameter for the same structures is shown in Figure 8.

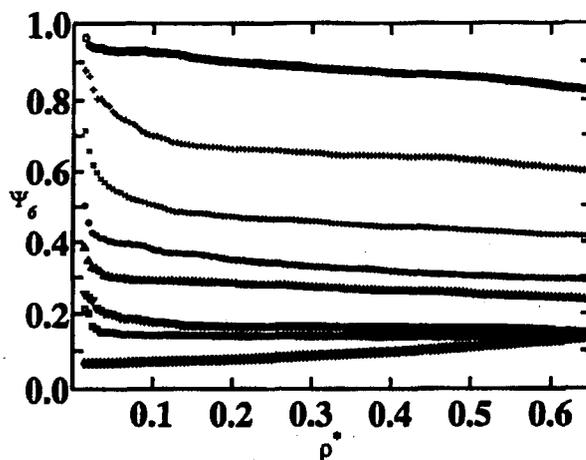


Figure 8. Bond-order parameter versus density for systems at (from top to bottom)  $0.01, 0.1, 0.2, 0.3, 0.4, 0.7, 1.0$ , and RSA.

Typical structures are shown in Figure 9; average coordination numbers in Figure 10.

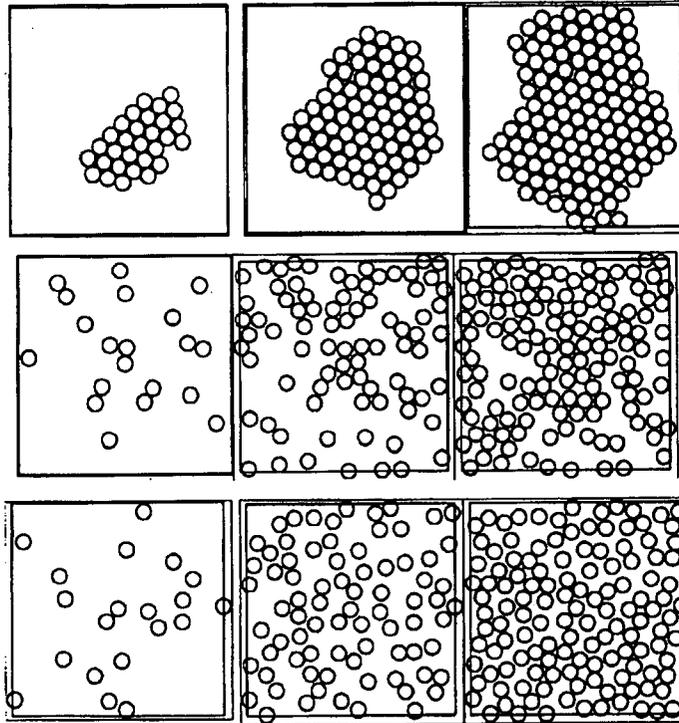


Figure 9. Configurations of systems grown through sequential quenching for  $\rho^* = 0.1$ , 0.4 and 0.65 at  $T^* = 0.01$  (top),  $T^* = 0.3$  (center) and RSA (bottom).

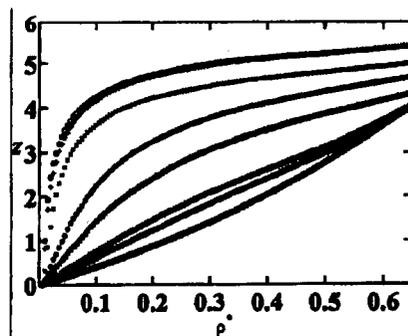


Figure 10. Average coordination numbers at (from top to bottom)  $T^* = 0.01$ , 0.1, 0.2, 0.3, 0.4, 0.7, 1.0 and RSA.

### 8. Deposition of nonspherical particles

In the last part of the study we introduced a degree of anisotropy in the interparticle potential and investigated the orientational order in monolayers of sequentially adsorbed particles. Many proteins are highly non-spherical, as can also be colloidal particles. For example, fibrinogen can be approximated by a rod of aspect ratio 5:1; BSA is considered a compact ellipsoid of aspect ratio 3.5:1; E. Coli bacteria have the shape of a prolate ellipsoid of aspect ratio of 2:1. The investigation of sequentially quenched monolayers requires the choice of an intermolecular potential. We have developed a suitable orientation-dependent pair potential appropriate for the study of sequential quenching of ellipses, which allows for a varying ratio of the end-to-end and side-by-side energies:

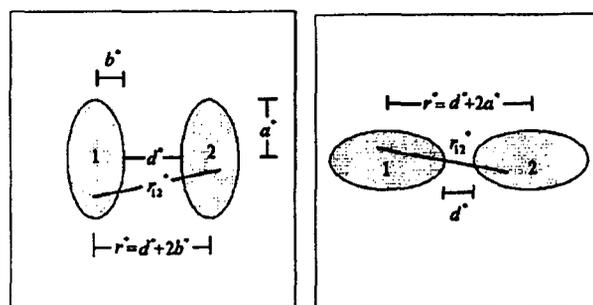
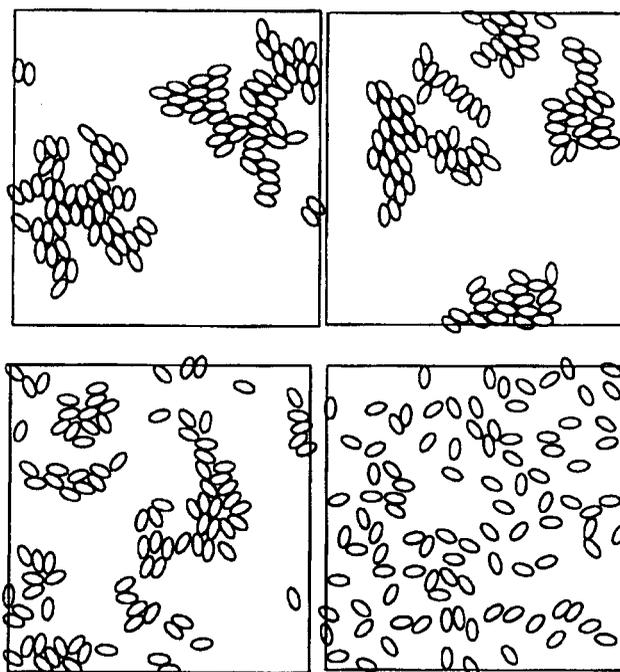


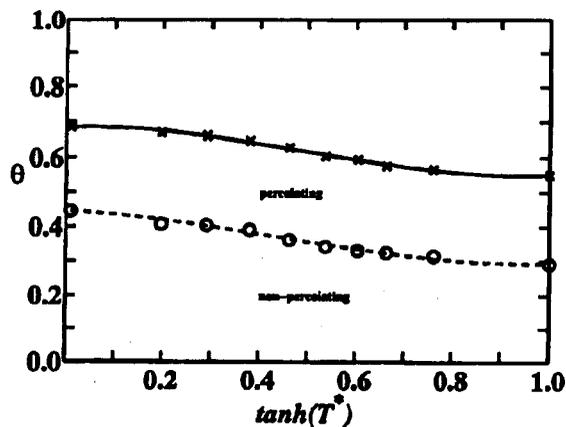
Figure 11. Examples of a side-by-side and an end-to-end configuration.

The effect of temperature on anisotropy on the alignment of particles in the clusters is quantified through the orientational correlation function, the average cluster size and the percolation thresholds and jamming limits. Figure 12 shows configurations of ellipses sequentially quenched at various temperatures,  $T^* = 0.01, 0.2, 0.6$  and  $\infty$  (the latter equivalent to the case of RSA) for a reduced number density  $\rho^* = 0.5$ . As expected, lowering the temperatures leads to clustering of the particles. Because in this example the side-by-side arrangement of two particles has a lower energy than any other configuration, at low temperatures the ellipses attach themselves side-by-side and form long ribbons, which are interrupted only sporadically.



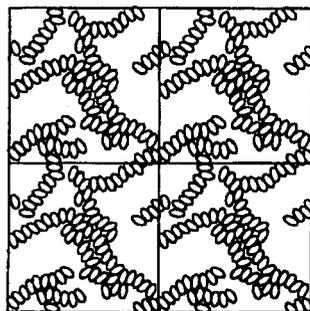
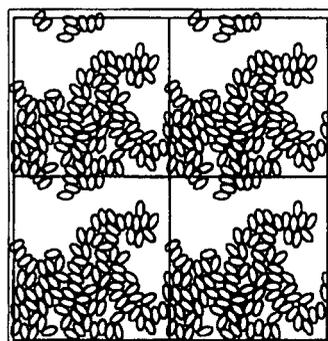
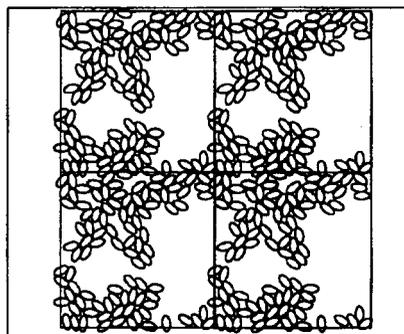
**Figure 12.** Configurations of sequentially quenched ellipses with an aspect ratio of 2:1. The results are for  $r^* = 0.5$  and for  $T^* = 0.01, 0.2, 0.6$  and  $\infty$ .

The jamming coverages are displayed in Figure 13, together with the percolation thresholds. Both the percolation thresholds and the jamming limits are understandably higher at lower temperatures, where the compactness and the smaller number of clusters leave more space for new particles. The lower limits for these two quantities are at RSA, the high temperature limit.



**Figure 13.** Phase diagram showing the percolation transitions and the jamming limits.

We have also studied the effect of the resulting structures, as illustrated below.



**Figure 14.** Configurations for a preferred end-to-end binary potential, a no-preference case and a preferred side-by-side binary potential at  $T^* = 0.3$ .

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