

## **SIMULATION OF SUB-MOLECULAR AND SUPRA-MOLECULAR FLUIDS**

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Computer simulations indicate that many forms of liquid crystalline order in lyotropic systems may be due to simple excluded volume effects. Yet, there is more to liquid crystalline ordering than simple hard-core repulsion. In order to understand liquid crystalline order in supra-molecular systems one must consider the effect of molecular flexibility. I shall discuss some recent developments that appear to open the way to a systematic study of the phase behavior of semi-flexible molecules.

### **1. Introduction**

One of the surprising findings of computer simulation studies of very simple model systems, is that a great variety of ordered or partially ordered phases can be induced by pure excluded volume effects. More than 30 years ago, Alder and Wainwright [1] showed that a system of hard spheres undergoes a first-order phase transition from the fluid to the crystalline solid phase. During the past few years, it has become apparent that hard-core interactions can also give rise to a number of liquid crystalline phases. In particular, the computer simulations by Frenkel and Mulder showed that a system of hard ellipsoids-of-revolution can form a nematic phase if the length-to-width ratio of the ellipsoids is larger than 2.5 or smaller than 0.4 [2]. Fig. 1 shows the phase diagram of hard ellipsoids-of-revolution, as obtained in the computer simulations of ref. [2]. Although the determination of the range of stability of hard-core nematics is of considerable interest, the finding *as such* that hard ellipsoids form a nematic phase was not surprising. In contrast, the observation of hard-core *smectics* was a surprise. Smectic phases that are stabilized by excluded volume effects alone, were first found by Stroobants et al. in a system of hard parallel spherocylinders [3]. Subsequently, it was found that a stable smectic phase also occurs in a less artificial model system, namely a system of freely rotating, hard spherocylinders [4]. Fig. 2 shows part of the phase diagram of hard spherocylinders. Finally, it is even possible to prepare hard-core columnar phases. Although the first observation of a hard-core

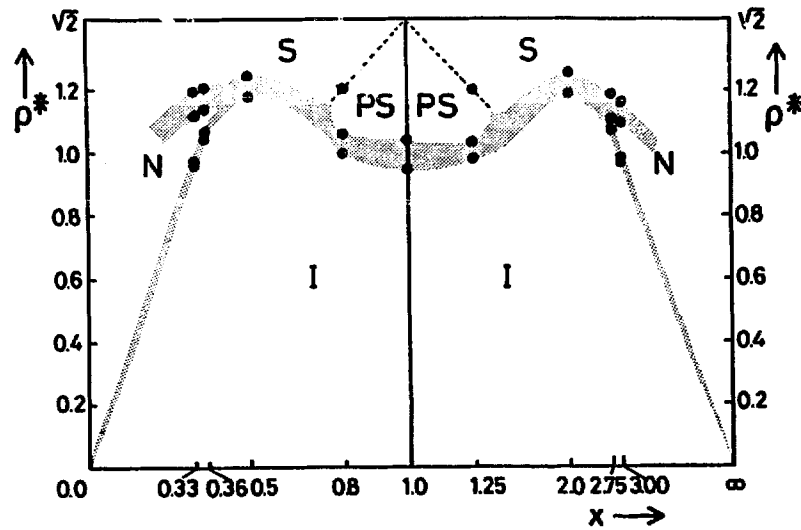


Fig. 1. Phase diagram of a system of hard ellipsoids-of-revolution.  $x$  is a measure of the anisotropy of the ellipsoids. It is defined as the ratio of the length of the semi-major axis ( $a$ ) to that of the semi-minor axis ( $b$ ).  $x = 1$  corresponds to hard spheres,  $x > 1$  corresponds to prolate ellipsoids,  $x < 1$  to oblate ellipsoids. The density  $\rho^*$  is defined as  $\rho^* \equiv 8(N/V)ab^2$ . This definition ensures that the density of regular close packing is always equal to  $\sqrt{2}$ . The dots denote the densities of the coexisting phases, as found in the simulations. The gray area is the two-phase region separating the solid from the liquid (or liquid crystalline) phase. In the figure, I denotes the isotropic fluid phase, N the nematic liquid crystalline phase, S the (orientationally ordered) crystalline phase and PS the (orientationally disordered) plastic crystalline phase. Note that no stable liquid crystalline phases are found for  $0.4 < x < 2.5$ .

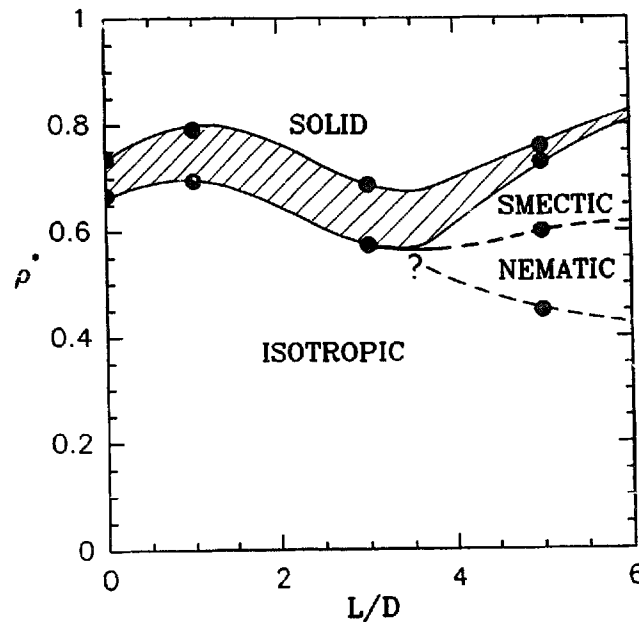


Fig. 2. Phase diagram of a system of hard spherocylinders. The diameter of the hemispherical caps is denoted by  $D$ , the length of the cylindrical segment by  $L$ . The ratio  $L/D$  is a measure for the anisotropy of the spherocylinders.  $L/D = 0$  corresponds to hard spheres,  $L/D = \infty$  corresponds to hard needles.  $\rho^*$  denotes the density divided by the density at regular close packing. The dots denote the densities of the coexisting phases, as found in the simulations. The gray area is the two-phase region separating the solid from the liquid (or liquid crystalline) phase. Note that no stable liquid crystalline phases are found for  $L/D < 3$ .

columnar phase by Stroobants et al. [5] was almost certainly based on an artefact due to the small size of the model system studied, subsequent simulations by Frenkel [6] and Veerman and Frenkel [7] did produce strong evidence for the existence of a stable columnar phase in a system of hard disk-like molecules. Moreover, the latter simulations suggest that there may be other hard-core liquid crystalline phases in addition to the ones listed above.

It would, however, be a serious mistake to extrapolate this finding and assume that excluded volume effects are *always* the most important factor determining the structure of a “non-simple” liquid or liquid crystal, no matter how complex its constituent molecules. A measure for the “complexity” of a molecule is the number of its internal degrees of freedom. The entropy associated with these degrees of freedom becomes increasingly important as the constituent molecules grow more complex. In the limit of a long polymer chain one may even, to a first approximation, ignore the excluded volume effects altogether, but never the conformational entropy.

This feature of complex molecules is, of course, well known and it poses a formidable challenge to computer simulators: it is essential that a numerical study of long chain molecules probes a representative sample of all accessible molecular conformations and positions. Much attention has therefore been paid to the development of efficient numerical schemes to sample polymer conformations. The recent review by Kremer and Binder [8] gives excellent account of Monte Carlo schemes to study lattice models of macromolecules. Most of the Monte Carlo techniques to sample chain conformations described in that review are based on some kind of *local* rule to rotate, change or break-and-remake bonds between polymer units. Although the existing techniques are quite sophisticated, the local nature of the algorithm results in slow *global* equilibration. Global equilibration may require large scale conformational changes of the molecules and, in the case of mixtures, appreciable changes in the local composition of the mixture. Such numerical problems are not limited to Monte Carlo simulations. In fact, although molecular dynamics simulations [9] have the advantage that they allow the molecules to perform collective motions in a natural fashion, the time scale for such diffusive motion is still very long.

Even more problematic than the simulation of equilibrium properties of polymer systems, is the computation of the chemical potential of chain molecules. The chemical potential is a quantity that is of central interest in the study of phase equilibria. In computer simulations of simple atomic or molecular systems, the chemical potential is often evaluated using the particle-insertion method first described by Widom [10]. This method exploits the relation between the excess chemical potential  $\mu^{\text{ex}}$  (i.e. the chemical potential of a species minus the chemical potential of an ideal gas at the same density)

and the change in the potential energy of the system  $\Delta V_{\text{test}}$ , due to the insertion of a test particle at a random position in the fluid:

$$\mu^{\text{ex}} = -k_{\text{B}} T \ln \langle \exp(-\Delta V_{\text{test}}/k_{\text{B}} T) \rangle . \quad (1)$$

The angular brackets in eq. (1) denote an ensemble average over all possible configurations of the molecules already present in the system. In Monte Carlo simulations this average has a very simple interpretation: it can be thought of as the probability of acceptance of a (virtual) Monte Carlo move which consists of the random addition of a test particle to the system of interest.

Whether or not eq. (1) can be used in practice depends on the value of this insertion probability. If the latter is very low, the statistical accuracy is low, and long runs are needed to obtain a reliable estimate of  $\mu^{\text{ex}}$ . This limitation of the method is particularly relevant for polymer simulations where a naive application of the particle-insertion method would result in extremely low insertion probabilities.

Clearly, the numerical study of the chemical potential of polymers is difficult. But even more difficult is the direct simulation of phase equilibria involving polymers. In this case, the number of chain molecules fluctuates, while the chemical potential (i.e. the osmotic pressure) is held constant. An example of considerable practical interest is a mixture of colloidal particles and (ideal) polymers. In this system, the polymers cause an “entropic” attraction between the colloidal particles. Direct numerical simulation of this “polymer-induced” clustering would be so time-consuming as to be almost prohibitive.

The aim of the present paper is to show that a radically different approach to Monte Carlo sampling of polymers is possible, using techniques that have been developed in a very different context, namely for the study of tagged-particle velocity-autocorrelation functions in lattice gases [11–13]. The basic idea behind these algorithms is that a “brute-force” sampling of random walks on a lattice is not only very time consuming but, more importantly, often yields much more information than needed. To give a specific example: If we wish to compute the excess chemical potential of a polymer in a colloidal dispersion, we need to know the total number of polymer conformations that do not intersect a colloidal particle. However, “brute-force” sampling gives us much more than that: from it, we could, in principle, deduce the full  $n$ -body distribution function of a  $n$ -unit polymer. The “moment-propagation” methods of refs. [11–13] allow us to compute certain averages of the  $n$ -body distribution function directly, without attempting to compute the function itself. This approach results in a very appreciable gain in computing speed: for instance, in the case of velocity autocorrelation functions in lattice gases, the method has resulted in a speed-up that varied between  $10^6$  and  $10^{10}$  [11, 12].

A closely related moment-propagation method can be applied to certain classes of polymer simulations. To explain how the method works, let us consider a specific example of some practical interest, namely a system of *ideal*, non-interacting polymers in the external potential provided by a dispersion of “hard-sphere” colloidal particles.

We assume that the ideal polymer conformations correspond to random walks on a lattice. Suppose that every lattice site has  $b$  neighbors, that the polymer consists of  $p$  segments and that there are  $N$  lattice sites. Clearly, for an ideal polymer in the absence of any obstacles, the total number of allowed conformations is  $\Omega_{\text{id}} \equiv N \times b^p$ . If obstacles are present, some random walks are blocked, and the total number of allowed conformations,  $\Omega_{\text{T}}$ , is less than  $\Omega_{\text{id}}$ . The “brute-force” method to determine the ratio  $\Omega_{\text{T}}/\Omega_{\text{id}}$  would be to attempt a large number of insertions of chains with arbitrary conformation at random points on the lattice. The ratio of the number of “accepted” trial moves to the total number of attempted insertions can be used to compute the excess chemical potential of an ideal polymer chain in this system:

$$\mu^{\text{ex}} = -k_{\text{B}}T \log \langle P_{\text{acceptance}} \rangle . \quad (2)$$

This is the usual “Widom” expression for the excess chemical potential [10]. However, unless the density of obstacles is quite low, the relative statistical error in the insertion probability will be quite large (see ref. [14]). Next, consider the “moment-propagation” approach. To this end, let us first compute all  $N$  Boltzmann factors associated with the insertion of a point particle at any lattice site. Clearly, the sum of these Boltzmann factors is simply the partition function of a point-particle on a lattice, in an external potential. Let us denote the Boltzmann factor associated with site  $i$  by  $f_i^{(0)} \equiv \exp[-u(r_i)/k_{\text{B}}T]$ . The partition function for a 1-segment polymer (2 points) is computed as follows. Starting from site  $i$ , we have  $b$  ways to grow one segment. But all  $b$  directions will, in general, have different Boltzmann weights  $f_j^{(0)}$ , where  $j$  denotes one of the nearest neighbors of  $i$ . The total Boltzmann weight associated with the addition of a 1-segment polymer at site  $i$  is then

$$f_i^{(1)} \equiv f_i^{(0)} \left( \sum_j^b f_j^{(0)} \right) , \quad (3)$$

where the sum runs over the nearest neighbors of  $i$ . The partition function of a 1-segment polymer on a lattice is then simply

$$Z_1 = \sum_{i=1}^N f_i^{(1)} \quad (4)$$

(where, for convenience, I have assumed that the polymer “head” and “tail” are distinguishable). Repeating the same argument  $p$  times, it is clear that the Boltzmann factor associated with *all possible conformations* of a  $p$ -segment polymer starting at site  $i$  is given by

$$f_i^{(p)} = f_i^{(0)} \left( \sum_j^b f_j^{(p-1)} \right). \quad (5)$$

And the total partition function is given by

$$Z_p = \sum_{i=1}^N f_i^{(p)}. \quad (6)$$

The important fact to note is that the computation of  $Z_p$ , a quantity that depends on  $N \times b^p$  conformations, requires only  $p$  iterations of  $b \times N$  local “propagations” of real numbers. For a fixed external potential, the partition function thus computed is *exact*. In a practical situation, as with the addition of a polymer to a colloidal dispersion, the external potential is not fixed, but depends on the (continuous) coordinates of all  $M$  colloidal particles,  $\{\mathbf{r}^M\}$ . Hence, the total partition function of the polymer also depends on these coordinates:  $Z_p = Z_p(\mathbf{r}^M)$ .

The approach sketched above is not limited to completely random polymer conformations. In fact, it is simple to exclude  $180^\circ$  reversals or to account for the different weight of gauche- and trans-conformations [15]. In the latter case, instead of adding the random walks coming from all different directions to a given lattice site, we can separately store for every nearest-neighbor bond  $i \rightarrow j$ , the total number of walks that arrived at site  $i$  along bonds other than  $j \rightarrow i$ . With this bookkeeping device, it is easy to count all non-reversing random walks.

### 1.1. Self-avoiding polymers

In many applications, we do not only wish our polymer conformations to be non-reversing, but also self-avoiding. This latter condition cannot be implemented in a “local” iterative algorithm based on eq. (5). Rather, the test for self-overlap has to be made after a particular non-self-avoiding polymer conformation has been selected. In practice, a large number of non-reversing random walks are sampled and the fraction of self-avoiding walks (SAWs) is computed. Multiplying this fraction with the total number of non-reversing random walks, yields an estimate of the total number of SAWs.

In order to arrive at a correct sampling of the fraction of SAWs, we must generate a number of non-self-avoiding polymer conformations with the appro-

priate Boltzmann weight. This is easily achieved because we already know the total number of random walks of length  $p, p-1, p-2, \dots, 1$  starting from any lattice site  $i$ :  $Z_p(i), Z_{p-1}(i), \dots, Z_1(i)$ . We now use this information as follows. First we select the starting position  $i$  of a non-self-avoiding random walk (NSAW) of length  $p$  with a probability proportional to  $Z_p(i)$ . Next we consider all neighbors  $j$  of site  $i$ . The total number of NSAWs of length  $p-1$  starting from site  $j$  is equal to  $Z_{p-1}(j)$ . We now continue our random walk from  $i$  to  $j$  with a probability proportional to  $Z_{p-1}(j)$ . Next we consider all NSAWs of length  $p-2$  starting from any of the sites neighboring  $j$ , and so on.

It should be stressed that we can enumerate the total number of NSAWs exactly (and cheaply), but that sampling of SAWs is a “biased” Monte Carlo process, which can be more time consuming.

### 1.2. Grand-canonical simulations

An interesting application of the moment-propagation scheme is that it allows us to perform simulations of a polymer system *at constant osmotic pressure*,  $\Pi$ . This corresponds to a very common experimental condition. To see how this can be achieved, let us consider the partition function of  $n$  ideal polymers of length  $p$  in an external field. Clearly,

$$Z_p^{(n)}(\mathbf{r}^M) = [Z_p^{(1)}(\mathbf{r}^M)]^n / n! , \quad (7)$$

where  $Z^{(1)}$  ( $Z^{(n)}$ ) denotes the partition function for one ( $n$ ) polymer(s). Now let us transform to an ensemble where the polymer chemical potential,  $\mu$ , is held constant. To be specific, let us again consider the polymer colloid mixture. For convenience, we assume that the total number of colloid particles is held constant. The potential energy function that describes the direct interaction between the colloid particles is denoted by  $U(\mathbf{r}^M)$ . The partition function for this constant  $M, V, T, \Pi$ -ensemble is

$$\Xi = \text{constant} \times \int d\mathbf{r}^M \exp[-U(\mathbf{r}^M)/k_B T] \sum_{n=0}^{\infty} \exp(n\mu/k_B T) [Z_p^{(1)}(\mathbf{r}^M)]^n / n! \quad (8)$$

Clearly, the summation in eq. (8) yields an exponential,  $\exp[z Z_p^{(1)}(\mathbf{r}^M)]$ , where we have used the shorthand notation  $\exp(\mu/k_B T) \equiv z$ . Eq. 8 is the starting point for Monte Carlo simulations at constant  $\Pi$  [16]. In such simulations, the relative probability of different colloid configurations is proportional to

$$P(\mathbf{r}^M) = \exp[-U(\mathbf{r}^M)/k_B T + zZ_p^{(1)}(\mathbf{r}^M)] . \quad (9)$$

Note that  $Z_p^{(1)}$ , which describes the polymer-induced interaction between colloidal particles, can be calculated exactly for every colloid configuration. Of course, such constant- $\Pi$  simulations are not limited to polymer colloid mixtures. Another interesting application is the simulation of polymer-induced forces between two surfaces. It is worth pointing out that in constant- $\Pi$  simulations we have no direct knowledge of the actual polymer positions and conformations (although some averages can be computed easily). This demonstrates clearly that great gains in computational efficiency can be made by throwing away “irrelevant” information.

## 2. Results: simulations at constant osmotic pressure

As an example, let us consider a well known phenomenon in colloid chemistry, namely that the addition of polymer to a colloidal suspension causes an effective attraction between the colloidal particles. This attraction is purely entropic in origin. It stems from the fact that the total number of allowed polymer conformations is larger when two colloidal particles are close together than when they are far apart. Using the techniques described in section 1.2, it proved possible to observe this effect directly in a computer simulation. Fig. 3 shows the radial distribution function,  $g(r)$ , of a system of three-dimensional hard spheres (“colloidal particles”) in contact with a polymer reservoir, such that the polymer “osmotic pressure” is held constant. For the sake of comparison, the same figure also shows  $g(r)$  for the same system in the absence of polymers. Clearly, the addition of polymer to the hard-sphere suspension has resulted in a strong tendency of the spheres to cluster. A more quantitative discussion of this phenomenon can be found in ref. [16].

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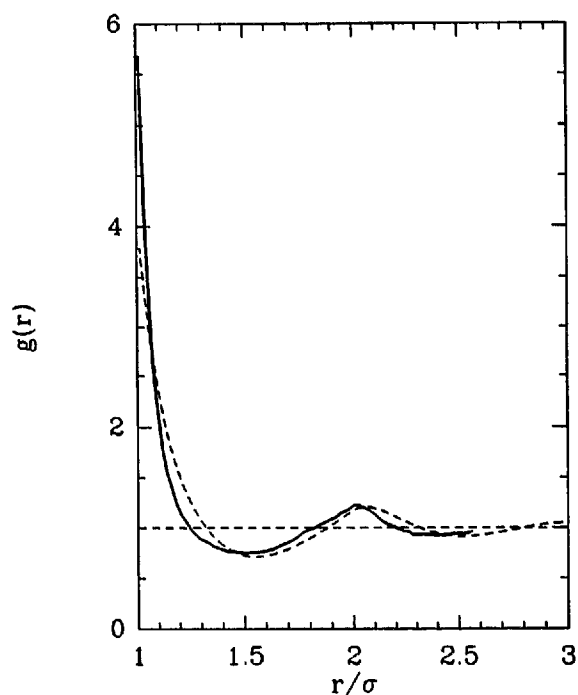


Fig. 3. Radial distribution function of a system of hard spheres ("colloidal particles") at a reduced density of  $\rho^* = 0.56$ . The dashed curve shows the result for the pure hard-sphere system. The drawn curve shows the effect of addition of polymer on  $g(r)$ . The present results were obtained for a system of 108 hard spheres in osmotic equilibrium with a bath of chain-molecules with 10 segments. The length of the fully stretched chain-molecule is 5% less than the diameter of the spheres. Hence, these "polymers" can only cause short-ranged attractions. The osmotic pressure has been chosen such that the average number of polymer molecules in the system is  $1.4 \times 10^3$ .

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