

Liquid-crystal behavior of hard ellipsoid dimers

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Liquid crystals exhibit orientation-dependent phases ranging from a disordered (isotropic) phase to a highly ordered crystalline phase. In between these extremes, increasing order can result in nematic and smectic phases. Typically, molecular simulation studies of liquid-crystal behavior use a nonspherical hard-body monomer. In this work, molecular simulation is used to study dimers of hard prolate ellipsoids. The results indicate that dimers of hard prolate ellipsoids exhibit a rich diversity of liquid-crystal behavior including smectic phases. In some cases, the dimer model may be a more realistic alternative to the conventional monomer model for liquid-crystal behavior.

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INTRODUCTION

Liquid crystals exhibit orientation-dependent phases¹ ranging from a disordered (isotropic) phase to a highly ordered crystalline phase. In between these extremes, increasing order can result in nematic and smectic phases.¹ The ability of liquid crystals to undergo these subtle transitions has been utilized in many practical applications,² such as lightweight computer screens, that have transformed the nature of many manufactured goods.

Molecular simulation³ can be used to predict the salient features of liquid-crystal transitions using a hard-body such as a rod to represent the liquid-crystal molecules. Simulations of hard spheres show^{4,5} only a first-order freezing transition whereas nonspherical geometries are required to observe other liquid-crystalline behavior. Nonspherical hard-body fluids exhibit a diversity of phases such as biaxial nematic,⁶ smectic, and plastic solid phases.^{7,8} A comprehensive review of the influence of shape on liquid-crystal behavior is available elsewhere.¹

Irrespective of the shape, molecular simulation studies have focused almost exclusively on monomers. A recent exception is the work of Camp *et al.*,⁹ which reports simulations of dimer rods bent at different angles. Simulations of multi-segment hard-body fluids are potentially of interest because they can provide a more realistic description of the molecular geometry of many real polyatomic fluids. In this work, we report molecular simulation data, which indicate that dimers of hard prolate ellipsoids exhibit a rich diversity of liquid-crystal behavior including smectic phases. The results provide an alternative to the conventional monomer model of liquid crystals that may more accurately reflect the characteristics of real molecules.

SIMULATION DETAILS

Monte Carlo simulations³ were performed in the canonical (NVT) ensemble in which the number of molecules (N), temperature (T), and volume (V) are held constant. Typi-

cally, 500 hard prolate ellipsoid dimers were used. The dimers were modeled as two end-to-end hard prolate ellipsoid monomers and, as such, they represent a fixed rigid linear chain. A prolate ellipsoid monomer is the shape generated by rotating an ellipse on its major axis through 360 deg. It is a “hard” body because penetration of the outer surface is not allowed in the simulation. The rationale for using an ellipsoid is that this shape is likely to be a reasonable coarse grain description of overall shape of many real polyatomic molecules.

The overall dimension of the ellipsoid monomers is governed by an “elongation” parameter (γ), which is the maximum length/breadth ratio. The initial configuration of the system was a face-centered cubic lattice with unified angles of $\pi/4$. The simulation was performed in cycles with each cycle consisting of both trial translational displacements and trial orientation changes for each molecule. A contact function was used¹⁰ based on the geometry of the ellipsoid dimer. Moves that resulted in an overlap (penetration of the hard-body surface) were rejected. The trial orientations are chosen to guarantee a universal orientation in space. The maximum translational displacement was adjusted to obtain an overall acceptance rate of approximately 50%. The maximum translational displacement was adjusted to obtain an overall acceptance rate of approximately 50%.

For each system at a specified value of γ , the simulations start from the lowest density by melting the initial face-centered cubic (fcc) lattice. Results for progressively higher densities were obtained by using the final configuration of the previous density as the new initial starting point. This enables us to reach equilibrium much more rapidly than by restarting the simulation from an fcc lattice. Typically, 10 000 to 20 000 cycles were performed for equilibration and a further 10 000 cycles were used to accumulate the equilibrium averages. Averages of the compressibility factor ($Z = pV/NkT$, p is the pressure and k is Boltzmann’s constant) were recorded by using a modified version of the formula for hard ellipsoids.¹¹ The degree of ordering was quantified by calculating the order parameter (S).¹²

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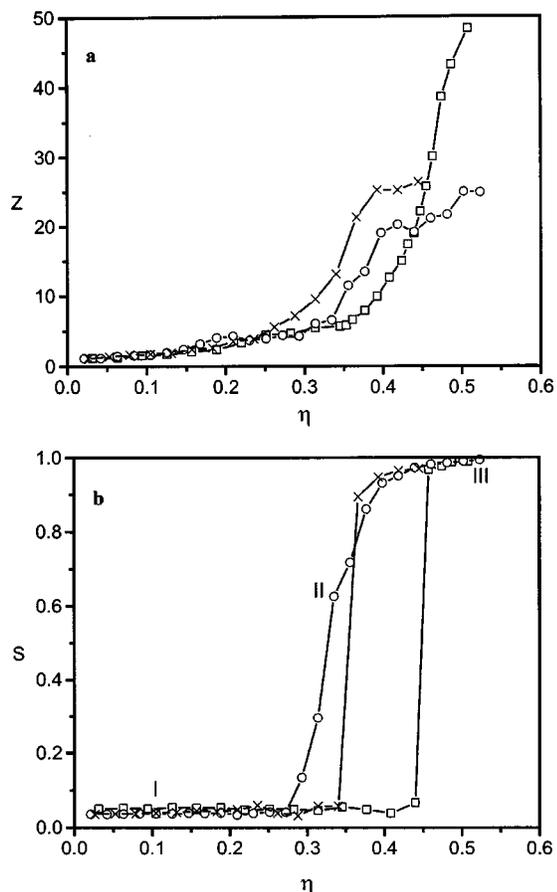


FIG. 1. Comparison of (a) the compressibility factor and (b) the order parameter as a function of packing fraction for hard prolate ellipsoid dimers with monomers of $\gamma=1.5$ (\square), 2 (\circ), and 2.5 (\times). The Roman numerals (I, II, and III) identify the location of the snapshots illustrated in Fig. 2.

RESULTS AND DISCUSSION

The compressibility factor for three different ellipsoid dimers is illustrated in Fig. 1(a) as a function of packing fraction ($\eta = N\pi\gamma\sigma^3/6V$, σ is the maximum breadth of the ellipsoid monomer). Results are presented for dimers with monomers of $\gamma=1.5$, 2, and 2.5. At low packing fractions ($\eta < 0.25$), all dimers exhibit an isotropic phase whereas transitions to ordered phases are apparent at higher packing fractions. The $\gamma=1.5$ or 2.5 dimers show a clear isotropic-nematic transition. In addition to this nematic transition, the additional plateaux for the $\gamma=2$ dimers indicate transitions to different smecticlike phases. This conclusion is supported by “snapshots” of the system, which show smecticlike orientations. Examples of these snapshots at different densities are illustrated in Fig. 2 for the case of $\gamma=2$. The existence of smectic phases in ellipsoid dimers is significant because smectic phases are not observed¹ in ellipsoid monomers. It appears that $\gamma=2$ provides the dimer with the maximum flexibility to adopt different ordered orientations. We believe that the smecticlike phases are stable but, in the absence of a detailed thermodynamic analysis of stability, the possibility of metastable phases cannot be ruled out entirely.

The point of transition between disordered-ordered phases is clearly apparent in Fig. 1(b), which illustrates the

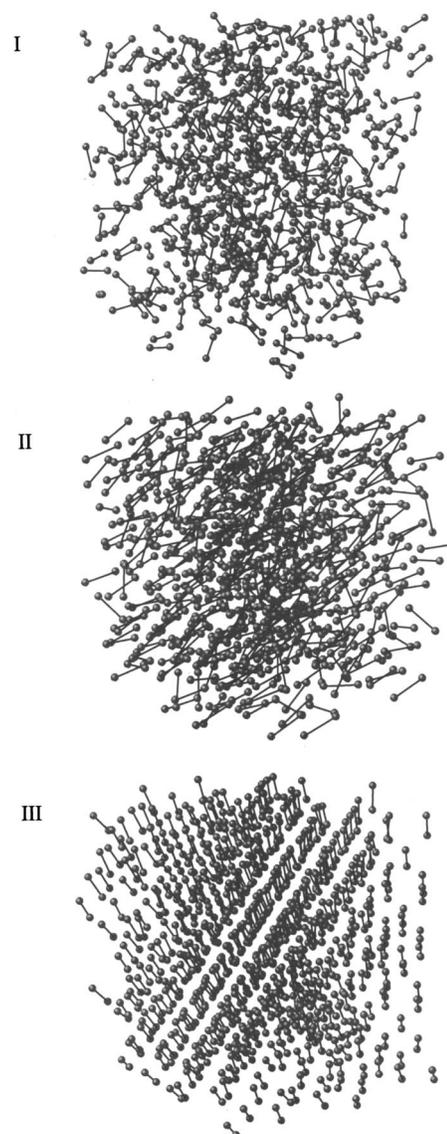


FIG. 2. Three-dimensional snapshots of prolate ellipsoid dimers ($\gamma=2$) illustrating different ordering at different packing fractions. The lines linking the circles represent the center-to-center distance of the ellipsoid dimer. The Roman numerals (I, II, and III) identify the position of the dimer in Fig. 1(b).

variation of the order parameter. Isotropic phases have values of S close to 0 whereas the limiting value of 1 indicates a fully crystalline phase. In general, as γ increases, the disorder-order transition for a hard-body monomer occurs¹ at progressively lower packing fractions. In contrast, the onset of the disorder-order transition for the ellipsoid dimer does not follow the behavior observed for monomers. Instead, the transition packing fraction for $\gamma=2.5$ ($\eta \approx 0.35$) is intermediate between the transition packing fraction observed for $\gamma=1.5$ ($\eta \approx 0.45$) and $\gamma=2$ ($\eta \approx 0.28$). The early onset of orientation ordering for $\gamma=2$ reflects the optimal orientation flexibility of this dimer.

The behavior of the $\gamma=2$ ellipsoid dimer is akin to the liquid-crystal behavior of “boomerang” molecules¹³ that can be modeled successfully⁹ as bent rods. However, unlike these systems, the ellipsoid dimers are fixed rigid linear mol-

ecules. This indicates that a rich diversity of liquid-crystal behavior can also be observed in linear chain systems with ellipsoid components.

CONCLUSIONS

Molecular simulation data indicate that dimers of hard prolate ellipsoids exhibit a rich diversity of liquid-crystal behavior including smectic phases. In contrast, smectic phases are not observed for ellipsoid monomers. In some cases, the dimer model may be a more realistic alternative to the conventional monomer model for liquid-crystal behavior

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