

MONTE CARLO SIMULATION OF HARD SPHEROIDS

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We present Monte Carlo simulations of the equation of state and radial distribution function for a model fluid composed of hard spheroids.

Hard ellipsoids are the simplest yet most flexible model of molecular cores. Ellipsoidal and fused ellipsoidal fluids may well be the most natural reference systems for a perturbation theoretical treatment of real molecular fluids and fluid mixtures.

A systematic investigation of ellipsoidal fluids has not yet been carried out because of the problem of finding a suitable contact function for deciding whether or not two ellipsoids overlap. We define a contact function $F(1, 2)$, where $i = 1$ and 2 represents both the position r_i of the molecular center and the orientational angles Ω_i of molecule i , as a continuous function of position which satisfies

$$\begin{aligned} F(1,2) < 1 & \text{ if 1 and 2 overlap,} \\ & = 1 \text{ if 1 and 2 are externally tangent,} \\ & > 1 \text{ if 1 and 2 do not overlap.} \end{aligned} \quad (1)$$

Such a function is necessary for obtaining the pressure from simulations via the contact theorem, one form of which is given in eq. (6) below. The algorithm of

Vieillard-Baron [1] is not optimal for simulation work because it is not of this form. The problem of constructing a suitable $F(1,2)$ has recently been solved [2]. We present here the first reported simulation of hard spheroids using this contact function.

The spheroids are specified by the lengths of the semi-axes, denoted by b for the symmetry axis and a for the doubly degenerate axes. The elongation e is defined by $e = b/a$. The packing fraction or reduced density is $\eta = \frac{4}{3}\pi\rho a^2b$, where ρ is the particle number density. In this preliminary study, we restrict ourselves to the isotropic phase and report results for $e = 2, 3$ and 3.5 , in the range $0 < \eta < 0.6$. Subsequent papers will deal with orientational order transitions and with ellipsoids without a symmetry axis. We first discuss some technical details of the simulations.

The Monte Carlo method is particularly simple for hard core interactions. Starting from a configuration C in a periodic box in which none of the particles overlap, a new configuration C' is generated by giving a randomly chosen particle a small random displacement and rotation. If none of the particles overlap in the new configuration, the move is accepted. If an

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overlap is detected, then the process is repeated on C. In this way, a Markov chain of non-overlapping configurations is generated. The maximum size of the random displacements and rotations is adjusted so that roughly half the attempted moves are accepted.

The simulation is started by placing $N = 243$ spheroids in a cubic box of side 2 on a tetragonal lattice with spacing proportional to the semi-axes a and b . The volume of the spheroids is then adjusted to make $\eta = 0.1$, the lowest packing fraction considered. 10^5 particle moves are performed to remove spatial and orientational order, after which data is taken over an additional 10^5 particle moves. The final configuration from this run is then used to generate an initial configuration at a slightly higher packing fraction $\eta = 0.125$ in the following manner: The density is increased by a small amount by rescaling particle sizes. The resulting configuration is then examined for overlapping particles. The first offending particle is moved repeatedly until it no longer overlaps any of the others. This is repeated until all overlaps have been eliminated. This procedure is iterated until the desired new packing fraction has been reached, at which time 10^5 particle moves are performed to allow the system to equilibrate. In this way, the density is incremented without the cost of removing unwanted order at higher densities, which is a very time-consuming operation.

To compute the pressure from the simulations, we require the contact function for two identical spheroids, with centers separated by $R = r_2 - r_1$ and unit vectors u_1 and u_2 along their respective symmetry axes. We have [2]

$$F(1,2) = \max_{0 < \lambda < 1} \{ [\lambda(1-\lambda)/a^2] [R^2 + \alpha(R \cdot u_1)^2 + \beta(R \cdot u_2)^2 + 2\gamma(R \cdot u_1)(R \cdot u_2)] \}$$

$$= \max_{0 < \lambda < 1} F_\lambda(1,2), \quad (2)$$

where

$$\alpha = x(1-y)/D, \quad \beta = y(1-x)/D, \quad (3)$$

$$\gamma = xy(u_1 \cdot u_2)/D,$$

$$D = (1-x)(1-y) - xy(u_1 \cdot u_2)^2, \quad (4)$$

$$x = (1-\lambda)(1-e^2), \quad y = \lambda(1-e^2). \quad (5)$$

The properties of $F(1,2)$ described by eq. (1) lead to simple expressions for the pressure p in terms of $F(1,2)$. One such expression is given in ref. [2]. Another was proposed by Vieillard-Baron [1]:

$$Z = p/\rho kT = 1 + \lim_{\epsilon \rightarrow 0} (2/3N\epsilon) \sum_{i < j} F(i,j), \quad (6)$$

where the sum is carried out over all pairs for which

$$1 \leq F(i,j) \leq 1 + \epsilon. \quad (7)$$

In practice a value for ϵ is chosen to both maximize the statistics and minimize their variance. It was found that a value of $\epsilon = 0.01$ was satisfactory at all densities, in agreement with Vieillard-Baron's simulation of hard spherocylinders [3].

The contact function (2) is particularly well suited for simulation, because the overwhelming proportion of tests reveal non-overlap. When computing $F(1,2)$ by iteration towards the maximum of $F_\lambda(1,2)$ as a function of λ , no further computation is required once a value for $F_\lambda(1,2)$ greater than $1 + \epsilon$ is obtained. Most non-overlaps are in fact revealed by testing at $\lambda = 1/2$.

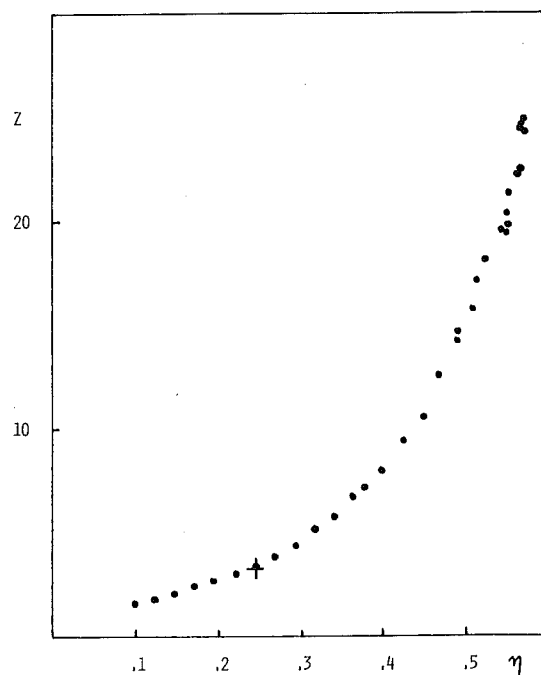


Fig. 1. The compressibility factor $Z = p/\rho kT$ as a function of packing fraction η for hard spheroids with elongation $e = 2$. For comparison, a result for a system of spherocylinders is shown by +.

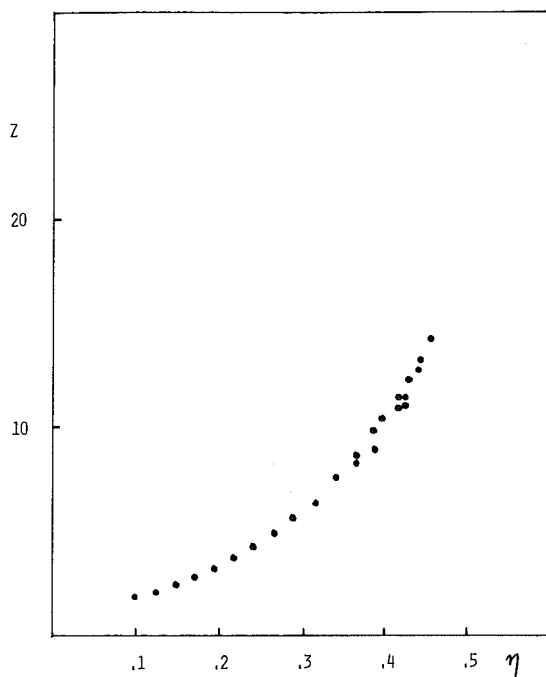


Fig. 2. The compressibility factor $Z = p/\rho kT$ as a function of packing fraction η for hard spheroids with elongation $e = 3.5$.

Using the methods described above, we have determined the equations of state for hard spheroids with $e = 2$ and $e = 3.5$, which are shown in figs. 1 and 2. In fig. 1, we also present for comparison published data for hard spherocylinders of elongation $e = 2$ [4]. The pressure at a given packing fraction appears to increase with e , at least for $e > 1$.

We have also determined the radial distribution function $g(r)$, given by

$$g(r) = \rho^{-2} \langle \rho^{(2)}(1, 2) \rangle, \quad (8)$$

where $\rho^{(2)}(1, 2)$ is the usual pair correlation function, and $\langle \rangle$ denotes an average over orientations. We present results for a single run with $e = 3$ and $\eta = 0.4$ in fig. 3. The curve is characterized by a very broad first peak, but is otherwise unremarkable*.

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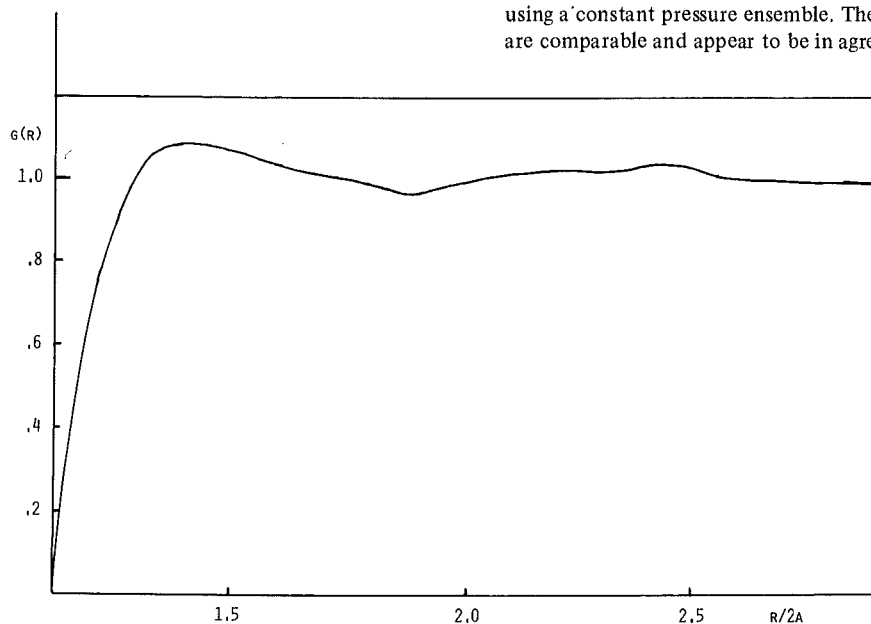


Fig. 3. The radial distribution function $g(r)$ as a function of $r/2a$ for hard spheroids of elongation $e = 3$ at a packing fraction $\eta = 0.4$.

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