

arise naturally in a variety of physical contexts, including the numerical path integral study of quantum dynamics. The development of the present approach and the related method, the coordinate rotation technique,^{5,6} suggests that progress is being made toward the development of a general Monte Carlo theory of quantum dynamics. It is likely that the methods described here will find use in other problem areas where there are difficulties associated with phase oscillations.

It is important to recognize that there are a number of potential pitfalls associated with applications of any of the approximate forms of the damping function. Perhaps the most serious is the fact that the results of integrations using an approximate damping function are not exact. There is an additional difficulty in applications of any of the second-order damping functions [eq 13 or 15]. For multidimensional integrations the second derivatives required in the evaluation of the second-order damping functions take the form of determinants. The generation of such deter-

minants for many-dimensional systems may prove to be difficult. A more useful procedure may be one requiring only first derivatives which can be corrected to the exact result. Such a procedure is given in ref 12.

Acknowledgment. We thank J. O. Hirschfelder, R. Wyatt, and R. D. Coalson for organizing the Lasers, Molecules and Methods Conference last summer at Los Alamos. That conference served as an initial sounding board for many of the ideas presented here. The timely quantum dynamics meetings organized this spring at Courant by M. Kalos and J. Lebowitz and this summer at CE-CAM by M. Gillan and P. Madden were likewise of substantial assistance. Work at the University of Rhode Island was supported in part by grants from Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University of Rhode Island Academic Computer Center.

Structure of Hard-Core Models for Liquid Crystals

Daan Frenkel

FOM Institute for Atomic and Molecular Physics, P.O. Box 41883, 1009 DB Amsterdam, The Netherlands
(Received: July 16, 1987; In Final Form: October 28, 1987)

The results of recent computer simulations on fluids of nonspherical hard-core particles are discussed. New data are presented on the structure and dynamics of a system of hard spherocylinders with length-to-width ratio $L/D = 5$. These data show that such spherocylinders can occur in at least four stable phases, viz., isotropic fluid, nematic liquid crystal, crystalline solid, and, surprisingly, a smectic A phase.

Introduction

Computer simulations of classical many-body systems can be used to gain insight in the microscopic behavior of real liquids and solids. Two distinct, and often complementary, approaches may be distinguished. On the one hand, one may carry out simulations on a realistic models in order to assist the interpretation of real experiments. On the other hand, computer simulations on idealized models of dense phases may be used to test theoretical concepts. Occasionally, computer simulations on simple model systems have yielded results that were qualitatively different from what was expected on the basis of the theories current at the time. A prime example of such a "computer discovery" is the observation by Alder and Wainwright of the long-time tails in the velocity-autocorrelation function of hard spheres.¹ Our current theoretical understanding of simple liquids is, to a large extent, based on the results of such simulations.

The situation is different for more complex fluids, such as liquid crystals. For the latter class of materials, direct comparison between experiment and simulation is difficult, because such simulations are very time-consuming (although not impossible; see ref 2). Simulation of idealized models for liquid crystals is also less than straightforward because there is no consensus as to what constitutes an "ideal" liquid crystal.

For atomic liquids it is well-known that the structure of the fluid is almost completely determined by the short-range repulsive forces acting between the atoms. In fact, the success of the hard-sphere fluid as a reference system in thermodynamic perturbation theories for simple liquids^{3,4} is largely a consequence of this fact. In contrast, it is at present not known whether the structure of more complex liquids, such as liquid crystals, is also

primarily determined by excluded volume effects. From the theoretical work of Onsager⁵ we know that a fluid of (infinitely) thin spherocylinders with length L and diameter D must undergo a transition from the isotropic to the nematic phase at a number density of order $1/(L^2D)$. At this density the fraction of the volume occupied by the spherocylinders is still vanishingly small (of order D/L). Recent computer simulations on hard ellipsoids-of-revolution with more realistic shapes^{6,7} have shown that a stable nematic phase is possible for this class of hard-core molecules if the length-to-breadth ratio is either larger than 2.5 or less than 0.4.⁸ These results do not yet imply that nonspherical hard-core interactions are the cause of orientational order in real nematic liquid crystals. In fact, two additional factors are often invoked to explain the stability of nematic liquid crystals, namely, (1) long-range anisotropic forces⁹ which tend to induce orientational order and (2) the presence of flexible tails attached to the rigid molecular core.¹⁰ The effect of the flexible tails is to stabilize the liquid phase with respect to the crystalline solid. However, now that we know that hard spheroids, that have neither long-range interactions nor flexible tails, form a nematic phase over a rather wide range of length-to-breadth ratios, we can begin to test thermodynamic perturbation theories. Such tests should enable us to ascertain whether nonspherical hard-core fluids can serve as "reference" systems for nematic liquid crystals in the same way that the hard-sphere fluid is a reference system for, say, liquid argon.

(5) Onsager, L. *Ann. N. Y. Acad. Sci.* **1949**, *51*, 627.

(6) Eppenga, R.; Frenkel, D. *Mol. Phys.* **1984**, *52*, 1303.

(7) Frenkel, D.; Mulder, B. M. *Mol. Phys.* **1985**, *55*, 1171.

(8) Pioneering simulations of hard spherocylinders with $L/D = 2$ were carried out by Vieillard-Baron *Mol. Phys.* **1974**, *28*, 809. However, in that system Vieillard-Baron did not observe nematic ordering.

(9) Maier, W.; Saupe, A. *Z. Naturforsch., A: Astrophys., Phys., Phys. Chem.* **1958**, *13A*, 564.

(10) Dowell, F.; Martire, D. E. *J. Chem. Phys.* **1978**, *68*, 1088. *Ibid.* **1978**, *68*, 1094. *Ibid.* **1978**, *68*, 2322. Dowell, F. *Phys. Rev. A* **1983**, *28*, 3526.

(1) Alder, B. J.; Wainwright, T. E. *Phys. Rev. A* **1970**, *1*, 18-21.

(2) Picken, S. J. Internal Report; University of Groningen, 1984.

(3) Barker, J. A.; Henderson, D. *J. Chem. Phys.* **1967**, *48*, 4714.

(4) Weeks, J. D.; Chandler, D.; Andersen, H. C. *J. Chem. Phys.* **1971**, *54*, 5237.