Journal of Statistical Physics, Vol. 3, No. 1, 1971

Molecular Dynamics of Two-Dimensional Gases with Realistic Potentials

Herman W. Harrison[1] and William C. Schieve[1]

Received September 28, 1970

Molecular dynamics calculations have mainly used hard-core interactions because of computational simplicity and increased speed. Algorithms for realistic intermolecular potentials have been used in studies of solids and liquids. By combining both techniques, an algorithm which can reasonably study dilute gases with realistic potentials has been achieved. The Boltzmann H-function is calculated for a hard-core and Lennard-Jones gas, and the latter is found to decrease more rapidly to equilibrium.

KEY WORDS: Molecular dynamics; Lennard-Jones disks; Boltzmann's H-function.

The Boltzmann entropy or H-theorem is given by the relationship $H = -S/k = \int f_1 \ln f_1 \, d\bar{r} \, d\bar{v}$, where f_1 is the one-particle velocity distribution function. It can be shown, theoretically, for a dilute gas, that $dH/dt \leqslant 0$, or simply that entropy is a monotonically increasing function of time.[1] Alder and Wainwright[2] in their pioneering molecular dynamics calculation used the H-function to show that a system of 100 hard disks approaches equilibrium. Recently, Orban and Bellemans[3] investigated the effects of the particle correlations on the Gibb's entropy in a hard-disk gas. All these earlier investigations using molecular dynamics techniques have been confined to hard-core interactions. Kohler and Bellemans[4] have calculated the approach to equilibrium of weakly coupled dipoles on a rigid lattice. To our knowledge, no calculation has been made with a Lennard-Jones (6–12) or similar potential

Work supported in part by the National Science Foundation under Grant No. NSF-USDP GU-1598 and the U. S. Air Force Office of Scientific Research under Grant No. AF-AFOSR 1257-67.

[1] Center for Statistical Mechanics and Thermodynamics, University of Texas at Austin, Austin, Texas.

for a dilute gas. Use of potentials such as the Lennard-Jones would represent a system with more natural physical conditions. In molecular dynamics calculations, the algorithms of these systems require much more computation time than does the hard-core algorithm. Rahman[5] has studied Lennard-Jones liquids and de Wette *et al.*[6] have studied crystallization and the surface dynamics of solids with a Lennard-Jones potential.

Because the particles in a liquid or solid are close together, they are either interacting with the strong repulsive part of the potential or confined to the region of the minimum in the potential, where the attraction is the greatest and has a more immediate effect. In dilute and moderately dense gases, the individual particles travel in regions where the attractive tail of neighboring particles is very weak, and only small perturbations, which are negligible, are made on the trajectory before the next collision. The deflection of the trajectory in the next interaction dominates and allows us to introduce a cutoff in the range of the potential. Obviously, this could not be done in gravitational problems (such as the motion of star clusters and galaxies), where the long-range effect is the most important.[7] By using this cutoff on the range in a program which combines the hard-core and realistic potential algorithm, sufficient speed and efficiency are achieved to study the H-function for dilute and moderately dense gases. The details of the H-function calculation are given by Alder and Wainwright.[2]

In Fig. 1, curve A, by first restricting the calculation to only the repulsive portion of the Lennard-Jones potential (cutoff in range is 1σ, where σ is the Lennard-Jones

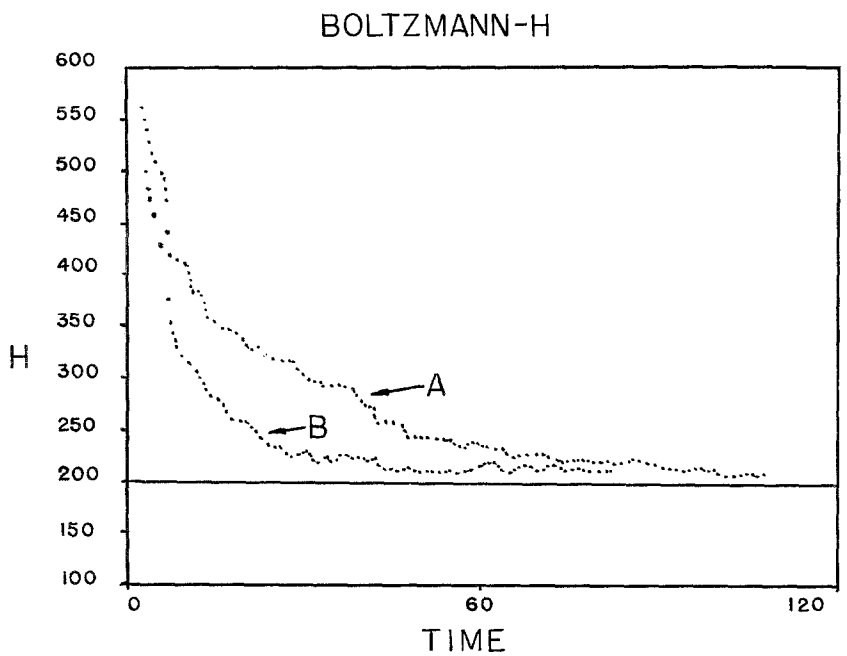

Fig. 1. Comparison of Boltzmann H for Lennard-Jones potential with (A) cutoff equal to 1σ, (B) cutoff equal to 3σ. Unit of time is 2.16×10^{-12} sec.

repulsive core range), a comparison can be made between this technique and the Alder–Wainwright results. In curve *B*, the attractive portion can be added by increasing the range to 3σ. Initially, in both cases, the system contains 100 particles in a randomized lattice configuration. This places the particles in a lattice configuration and disrupts the order by giving each particle a small displacement which is random in direction and size. The speed of each particle is 2.3×10^4 cm/sec and the velocities are in random directions. The unit of time is 2.16×10^{-12} sec and curve *A* runs for 375 collisions while curve *B* has a total of 450 collisions. The Lennard-Jones parameters (σ, ϵ) are those for argon gas, and the density is 9.0×10^{12} atoms/cm^2. The second virial correction to the equation of state is two orders of magnitude smaller than unity. It was found that equilibrium for the Lennard-Jones repulsive core was achieved in 2–3 collisions per particle, in agreement with the Alder–Wainwright results. When the attractive tail was added, the *H*-function decreased more rapidly, the particle making 4–5 collisions per particle in the same amount of time. The cutoff was changed from 3σ to 4.5σ and no significant change was seen in the results shown in Fig. 1.

The hard core is the dominant mechanism for bringing the system to equilibrium. The effect of the attractive tail in the collision process is to increase the cross section[8] for the particles in the system and induce more repulsive core encounters. The effective mean free path is decreased and equilibrium is achieved more rapidly. Figure 2 shows trajectories of a beam of 10 noninteracting Lennard-Jones particles, each with a different impact parameter (0.2σ to 2.0σ), which have scattered off a target particle. Both the hard-core effects and the way that trajectories can be altered by large-angle scattering (which is not present in the hard-core system alone) are evident. Classical orbiting has also been observed for the appropriate choice of energy and

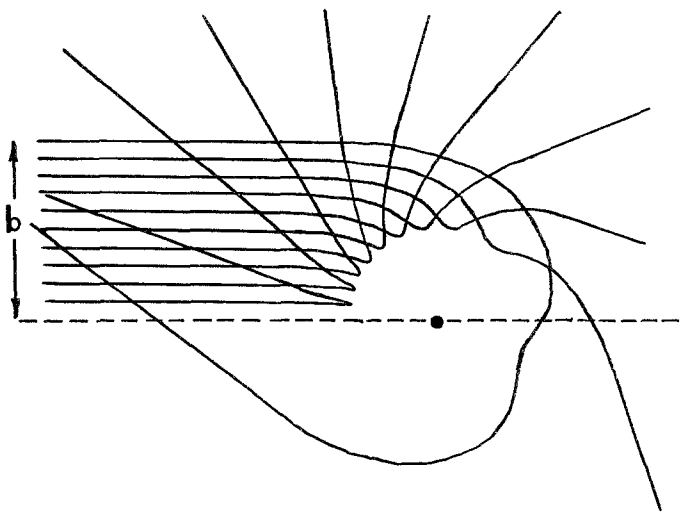

Fig. 2. Molecular dynamics scattering for a beam of 10 noninteracting particles with a Lennard-Jones potential. Impact parameters range from 0.2σ to 2.0σ in increments of 0.2σ.

impact parameter.[9] By means of these techniques, we intend to investigate quantitatively the effects of initial correlations on the approach to equilibrium.[10]

ACKNOWLEDGMENTS

We would like to thank F. W. de Wette and R. E. Allen, from whom we learned the Rahman technique, for their many helpful conversations and criticisms. We also wish to thank A. Bellemans for his comments on a preliminary version of this manuscript.

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