THE EQUILIBRIUM PROPERTIES OF A
ONE-DIMENSIONAL KINETIC SYSTEM*

by

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ABSTRACT

One-dimensional systems of $N = 500$ and 250 particles in equilibrium are numerically simulated utilizing the method of molecular dynamics. Periodic boundary conditions are imposed. The classical two-body interaction potential is short-range, repulsive and has a corresponding finite force.

The equations of state are determined for densities both less and greater than one. Corresponding theoretical isochores are determined from models based on nearest-neighbor interactions and on a truncated virial expansion, and a comparison is made with the experimental isochores.

Time independent radial distributions are constructed numerically and discussed. A change of state from a solid-like state to a fluid-gas state based on the penetrability of the particles is predicted. The transition temperatures are estimated from the radial distribution functions and the nearest-neighbor model. Self-diffusion is observed and the corresponding constants are determined from the velocity autocorrelation functions.

I. INTRODUCTION

The primary objective of statistical physics, the derivation of physical properties of real statistical systems, is for the most part unattainable. For certain kinetic systems, the problem is greatly simplified by representing these systems in terms of models that are based on particularly ideal interaction potentials. This paper is concerned with the study of a simple one-dimensional kinetic system by application of the techniques of computer simulation known as the method of molecular dynamics, and, when applicable, by direct comparison with the predictions of one-dimensional statistical mechanics. The properties studied are those of a model system at a fixed total energy and density, and containing, typically, hundreds of particles in thermodynamic equilibrium. In the method of molecular dynamics developed by Alder and Wainwright^{1,2,3}, the equations of motion of the particles of the model are solved by step-wise numerical integration. The equilibrium properties of the system are calculated from averages taken over a sufficiently long time interval.

Section II discusses the model. Section III treats the experimental and theoretical development of the equation of state. In Section IV the general behavior of the measured stationary radial distribution functions is presented. Section V exhibits typical

velocity autocorrelations and their corresponding Fourier time transforms in an attempt to estimate the self-diffusion constants.

II. THE MODEL

One-dimensional kinetic systems, heretofore, have been modeled on the requirement that the constituents cannot entirely penetrate one another, i.e., the assumed two-body interaction potential has an infinitely positive value at zero particle separation. The fact that particles can get around each other is of fundamental importance in the three-dimensional world. To allow particles to become unordered in the problem to be considered, a two-body interaction potential of the form

$$\begin{aligned} V(|r_{ij}|) &= -(|r_{ij}| - r_0)V_0 & 0 \leq |r_{ij}| \leq r_0 \\ V(|r_{ij}|) &= 0 & |r_{ij}| > r_0 \end{aligned} \quad (2.1)$$

is assumed, where V_0 is a constant. Consequently, a liquid state cannot exist but both solid-like and fluid-gas states can exist.

The system behaves as a solid when the particles remain in an ordered configuration, whereas the fluid-gas state exhibits little ordering. A change of state is expected for these isochoric systems. This follows from the consideration of two interacting particles. At a mutual kinetic energy greater than the interaction potential

energy, the two particles penetrate one another, and consequently, the initial ordering of the two-particle lattice is lost. Another consequence of a finite force model is that it insures the existence of many-body collisions taking place simultaneously. The average duration time of a two-body interaction is the same order of magnitude as the time it takes for a thermal particle to traverse an interaction range.

It has been determined analytically elsewhere^{4,5} that there exists no phase transition in a one-dimensional system, where the two-body interaction is made up of an infinitely repulsive core and a finite range force of finite magnitude. If the force has an attractive tail, and its range is infinite, condensation is predicted for a one-dimensional system.^{6,7} An objective of this paper is to determine not only whether a transition from a solid to a fluid-gas exists, but also whether such a transition is continuous or discontinuous. Two particles which have obtained sufficient thermal energy may penetrate one another and consequently, remove the ordering of the two particles. If a system consisting of many particles which possesses a designated ordering is raised in temperature, a value must be reached where the constituents obtain enough thermal energy to become disordered. Since many particle interactions are occurring, the transition temperature need not be equivalent to the strength of the two-body potential. This disordering process in a kinetic system constitutes a change of state. The results indicate that for every density considered, there exists a change of state.

The systems studied at various densities and temperatures utilizing periodic boundary conditions consisted primarily of 500 particles. In addition systems containing $N = 250$ and $N = 1000$ were also considered, in order to insure similar behavior of finite-number-particle systems to that of many-particle systems ($N \sim 10^{23}$). All measurements presented were made on $N = 500$ particle systems, unless otherwise specified. To preserve consistency, all resulting quantities are presented per particle. In addition, all quantities are made dimensionless by

$$\begin{aligned} r &\longrightarrow (r_0)r \\ v &\longrightarrow (\sqrt{T^*/m})v \\ t &\longrightarrow (r_0\sqrt{m/T^*})t \\ V(r_{ij}) &\longrightarrow (V_0)V(r_{ij}) \end{aligned} \quad (2.2)$$

where the natural unit of length is the range of the interaction r_0 , the natural unit of velocity is a thermal velocity defined by $\sqrt{T^*/m}$. The unit of time is the time required for a thermal particle to traverse the range of the two-body interaction. The quantity V_0 represents the strength of the interaction and is taken as some multiple of T^* . For all systems studied the multiple is 10, i.e., $V_0 = 10 T^*$. The mass of a constituent of the one-species system is taken as unity.

To insure the achievement of an equilibrium state instead of some metastable state, various phase space configurations were specified as initial conditions in a system of designated density and energy. It was determined from these measurements that the equilibrium state was established when the kinetic and potential energy had equal mean square deviations.

According to the fundamental assumption of statistical mechanics, averages of a system taken over the proper time interval are equivalent to the ensemble averages of the microcanonical systems involved. Consequently, the macroscopic thermodynamic quantities of the systems which are constant in energy, length, and particle number are determined through time averages. The time average of the temperature is obtained by computing the time average of the kinetic energy.

$$\langle K_B T \rangle = \overline{K_B T} = \frac{1}{N} \overline{\sum_{i=1}^N m_i v_i^2} \quad (2.3)$$

where $\langle A \rangle$ and $\overline{A}$ denote the ensemble and time averages respectively.

The quantity $\overline{K_B T}$ is obtained as a multiple of T^* in these dimensionless units. The determination of the pressure is made through the time averages of the kinetic energy and the virial.

$$\langle P \rangle = \bar{P} = \frac{1}{L} \left[\sum_{i=1}^{N-1} \sum_{j=1+1}^N r_{ji} F_{ji} + \sum_{i=1}^N m_i V_i^2 \right], \quad (2.4)$$

It should be mentioned that the virial expression also takes into account the ability of the particles to interact through the periodic boundaries. Numerically, the kinetic energy and the virial per particle were computed after each ΔT interval, and then the average of each was determined over a large number of such intervals. The time interval ΔT was judiciously chosen as much larger than the integration step and much less than the total time the system was monitored in the equilibrium state.

The results presented are in all cases the time averages computed from the end portions of long simulation runs. It was found that the deviations of the total energy from the average remained minimal in this time interval. Even though the choice of the two-body interaction proves attractive analytically, the existence of discontinuities at $|r_{ij}| = 0$ and $|r_{ij}| = r_0$ separations causes numerical deviations from the exact orbits which made it impossible to conserve energy exactly. However, all system averages were determined in time intervals during which the percent total energy deviation was less than five percent, and in fact, in at least one-half of the cases much less than two percent. This is sufficient accuracy to justify the measurements representative of the microcanonical requirements.

III. THE EQUATION OF STATE

The methods utilized in the pressure and temperature measurements were outlined in the introduction. The relation expressing the determination of experimental pressure can be written as

$$P = \frac{1}{\langle \ell \rangle} (T + v) \quad , \quad (3.1)$$

where P , T , and v are, respectively, the pressure, temperature and virial time averages per particle and $\langle \ell \rangle$ is the specific length per particle. The virial per particle is

$$v = \frac{V_0}{2N} \sum_{\substack{i,j \\ i \neq j}}^N \theta(1 - |x_{ij}|) |x_{ij}| \quad , \quad (3.2)$$

where $\theta(x)$ is the usual theta function, and again, it should be noted that the particles are allowed to interact through the periodic boundaries.

The experimental equations of state are presented in Fig. 1 and 2. The experimental points have the corresponding measured average deviations indicated, if the deviations have significant magnitude.

The zero temperature values of pressure are in agreement with the analytic models presented in the following paragraphs.

An analytic expression for the equation of state for all parameter ranges has not been possible, however, expressions for the regions of low and high temperature have been obtained.

If the penetrability property of the particles is removed and only nearest-neighbor interactions are considered, equations of state can be derived from a partition function. These restrictions imposed upon the model considered here could then be expected to be applicable only for systems that are considered to be in a solid-like configuration. The isobaric grand partition function has been used to derive an equation of state for an assembly of particles undergoing only nearest neighbor two-body interactions defined by

$$\begin{array}{ll} V(r) = \infty & 0 \leq r \leq \epsilon \\ V(r) = -(r - r_0)V_0 & \epsilon < r \leq r_0 \\ V(r) = 0 & r > r_0 \end{array}$$

where r_0 is the interaction range, and ϵ represents the distance of closest approach.⁸ The infinite repulsive barrier and its range ϵ are introduced in order to prevent the particles from interpenetrating. We expect this assumption to be valid for low temperatures. The reader is referred to the article by Northcote and Potts for details. The

result is that the average specific length per particle, $\langle \ell \rangle = \frac{\langle L \rangle}{(N+1)}$, is given by

$$\begin{aligned} \langle \ell \rangle = \epsilon + \frac{P(r_o - \epsilon) + T}{P} + \frac{\frac{(P - V_o)(r_o - \epsilon)}{T} P(r_o - \epsilon)e}{P \left(1 - e^{\frac{(P - V_o)(r_o - \epsilon)}{T}} \right) - (P - V_o)} \\ + \frac{TV_o \left(1 - e^{\frac{(P - V_o)(r_o - \epsilon)}{T}} \right)}{P(P - V_o) \left(1 - e^{\frac{(P - V_o)(r_o - \epsilon)}{T}} \right) + (P - V_o)^2} \quad (3.4) \end{aligned}$$

If the system is an assembly of hard rods each with diameter r_o , then the "closeness" parameter ϵ becomes equal to the diameter which is also the interaction range, i.e., $\epsilon = r_o$. In this limit the equation of state defined by Eq. (3.4) reduces to the Tonk's equation of state⁹

$$P = \frac{T}{\langle \ell \rangle - r_o} \quad (3.5)$$

However, for the system considered here ϵ must be taken as zero.

In order to gain information on the possible solutions to Eq. (3.4), the zero temperature limit is considered. Then Eq. (3.4) reduces to

$$P(P - V_0)[P\langle\ell\rangle z(0) - (\langle\ell\rangle - r_0)V_0] = 0 \quad (3.6)$$

where $z(0) = \lim_{T \rightarrow 0} e^{\frac{(P - V_0)r_0}{T}}$. The solutions $P = 0$ and $P = V_0$

at $T = 0$ are easily seen.

Equation (3.4) has been numerically evaluated and the results are shown as solid lines in Fig. 1 and 2. The temperatures at which the experimental points begin to deviate from these lines represent the beginning of significant interpenetration of the particles and the onset of interactions other than nearest-neighbor interactions. Equation (3.4) was derived utilizing the isobaric ensemble. The computer simulation results are based on measurements of micro-canonical ensembles. In order to make an exact comparison between the observed average values and the isobaric ensemble predictions, the approximation procedure developed by Lebowitz and Percus¹⁰ to relate the two averages can be used. However, the two averages differ only by terms $\sim 1/N$, where N is the number of particles in the system.¹¹ It would then not enhance the comparison of the experimental results with the predictions of the isobaric ensemble averages, since the average deviations of the experimental results are larger than $1/N$. The results, however, do predict the general behavior of the equations of state for all system densities less than two, or $\langle\ell\rangle > \frac{1}{2}$.

The virial equation of state is a power series in the density. The exact equation of state using the dimensionless units of Eq. (2.2) is

$$\frac{P}{T} = \sum_{m=1}^{\infty} \frac{B_m}{\ell^m} \quad (3.7)$$

where $\ell = L/N$.

If a finite number of terms are used, the relative degree of accuracy in representing the equation of state depends both on the magnitudes of the density and the coefficients. Consequently, accurate predictions are expected for low densities. The coefficients B_m in the expression are functions of the temperature and the interaction potential. They are not functions of the length, L , of the system. We have evaluated the first four coefficients in the thermodynamic limit. (See Appendix.)

The virial equation of state is shown as the dashed lines in Fig. 1 and 2. For low densities the agreement with the numerical results is extremely good. Because the virial equation of state is a power series in density, it is not expected to predict nonzero values for the pressure at zero temperature for densities greater and equal to one. For high temperatures, the system tends toward an ideal gas and the virial equation of state is a reasonable representation for all densities considered.

IV. THE RADIAL DISTRIBUTION FUNCTION

In a spatially-uniform system, the radial or two-body configurational distribution function, $g(|\vec{x} - \vec{x}'|)$, is a measure of the correlation between any two particles. In the limit of large particle pair separation, the particles lose the ability to have any effect on one another and consequently, any correlation would vanish:

$$\lim_{|\vec{x} - \vec{x}'| \rightarrow \infty} g(|\vec{x} - \vec{x}'|) = 1 \quad (4.1)$$

If a one-dimensional system is in a solid or crystalline state, then the particles are restricted to be on or near lattice sites, and the corresponding radial distribution function would exhibit sharply peaked maxima located at integer multiples of the specific length. In the opposite extreme little local structure is present in a fluid-gas state, particularly at high temperatures, and the large separation limit expressed by Eq. (4.1) is achieved at relatively small particle pair separation.

In real physical systems and models that are based on particles being mutually impenetrable, the requirement on $g(r)$ is

$$\lim_{r \rightarrow 0} g(r) = 0 \quad (4.2)$$

where $r = |x - x'|$. However, for the model considered here which allows particles to interpenetrate completely, relation (4.2) is not applicable.

To construct the radial distribution function for a system of N particles with a system length L , we consider the number of pairs of particles $N(r)dr$ with a separation between r and $r + dr$. The radial distribution function is then given by

$$N(r)dr = \frac{N^2}{L} g(r)dr \quad (4.3)$$

for large N . The required condition on the behavior of $g(r)$ for large separations, Eq. (4.1), is obtained through the use of the periodicity of the system.

For low densities at temperatures approaching zero, the particles tend to gather approximately at separations $r = 1, 2, \dots$ rather than multiples of the specific length, ℓ . The mean free path of each particle in the system allows it to move unhindered to within an interaction length from one of its nearest-neighbors. (Remember, the separation r is measured in terms of the interaction length r_0 .) This behavior is illustrated by the form of the radial distributions for $\ell = 2$ at temperatures $T = 1.74$ and $T = 2.28$ presented in Fig. 3. For low temperatures, relatively little interpenetration of the particles is expected, and it is observed as minimal. However, as the temperature is increased, the interpenetration of the particles becomes

more pronounced, until finally $g(r) > 0$ at $r = 0$. That is, some of the interacting particle pairs are able to pass through one another completely. Any system which achieves a measurable nonzero $g(r = 0)$ is not in an ordered state, and hence, the solid or crystalline definition no longer applies. $g(r = 0) \geq 0.01$ has arbitrarily been chosen as the criterion of the change of state. This occurs at a dimensionless temperature much less than the height of the potential barrier, V_0 . Specifically for the case $\ell = 2$, this breakdown in the ordering is estimated to occur near the temperature $T = 2.28 \ll V_0 = 10$. (See Fig. 3.) Hence, this ordered structure breakdown is a direct consequence of the existence of particle clusters containing more than two interacting particles.

For densities greater than or equal to one, the implicit temperature dependences of the radial distribution functions are generally equivalent to one another. However, there exist a few notable exceptions. The zero temperature limit presents a sequence of evenly-spaced sharp peaks. These peaks appear at integer multiples of the specific length of the system under consideration. That is, for a system of specific length, ℓ , the peaks appear at $r_m = m\ell$, where $m = 1, 2, 3, \dots$. The peaks in each case decrease in amplitude with increasing index m until the limit expressed by Eq. (4.1) is reached. This phenomena is expected for these densities, since there exists no mean free path as in the low density cases ($\ell > 1$). See Fig. 4, in particular, the case when $T = 0.285$. With increasing

temperature the occurrence of the disordering phenomena for these systems takes place just as it did for $\ell > 1$ cases, i.e., the ordering breakdown or transition temperature decreases with increasing density. For instance, this is estimated to occur approximately at a temperature $T \geq 0.517$ for the $\ell = 0.9$ case illustrated in Fig. 4.

The structural ordering breakdown occurred for all system densities considered, as measured from the radial distribution functions. Because of the lack of data throughout the transition regions, only estimates can be made on the temperatures marking the onset of the transitions from solid to fluid-like behavior. The results are presented in Table 1. The maximum possible temperature for which a transition can take place is $T = V_0 = 10$, which occurs in the limit of zero density ($\ell \rightarrow \infty$). The corresponding minimum transition temperature is zero, and occurs in the infinite density limit ($\ell \rightarrow 0$). As the temperature is increased beyond the transition temperature, the magnitude of the peaks exhibited by the radial distribution functions decreases. This reflects the decreasing spatial correlation or coherence between pairs of particles. Also, the $g(r=0)$ values increase in magnitude. This process continues with increasing temperature until the ideal gas, or equivalently, the high temperature limit is reached. That is,

$$\lim_{T \rightarrow \infty} g(r) = 1 \quad (4.4)$$

for all r . (See Fig. 3 and 4.)

Similar observations concerning the change of state may be made from considering the equation of state of Section II. Neither the nearest-neighbor nor the virial model predicts changes of state of the systems, but the breakdown of the nearest-neighbor model in describing the experimental results does lend insight into this phenomena. In consideration of Fig. 1 and 2, these points of deviation from the experimental isochores cannot be determined exactly, since the theoretical and experimental isochores are the results from two different ensembles, and the experimental points are not measured continuously through the regions of deviation. However, estimates can be made and are presented in Table 1. The observed temperature values or regions of temperature, where the experimental data begin to deviate significantly from that predicted by the nearest-neighbor model, compares favorably to the temperature estimates for a change of state as determined from the radial distribution functions. It was concluded previously that the deviations of the experimental isochores (Fig. 1 and 2) from the predictions of the nearest-neighbor model are caused by the onset of interactions besides those of nearest-neighbors. Hence, the changes of state observed by consideration of the radial distribution functions are caused by the onset of interactions other than nearest-neighbor interactions. In terms of particle motion this would mean that a particle does not pass through one of its nearest-neighbors unless it is also interacting with at least a next-nearest-neighbor.

V. AUTOCORRELATIONS AND SELF-DIFFUSION

A. Velocity Autocorrelations

Collective particle motions can be described by various means for systems in thermal equilibrium. One such way is through the normalized velocity autocorrelation function:

$$F(t) = \frac{1}{2T} \langle V(0)V(t) \rangle, \quad (5.1)$$

where the bracket $\langle \rangle$ indicates an ensemble average is performed over the test particle velocity configuration in a one-dimensional system. T is the dimensionless temperature. The structure of the velocity autocorrelation function is dependent upon the effect the particle interactions in the system have on the rate of change of particle velocities. Because the system is in thermal equilibrium, and hence, a stationary state, the time dependence relates only to relative times as implied by Eq. (5.1). Then the initial configuration of the system ($t = 0$) can be chosen arbitrarily.

In practice, the velocity autocorrelations are found using averages over the possible time origins.¹² The particle velocities of successive equilibrium system configurations of a particular microcanonical ensemble were recorded at judiciously chosen equal time intervals. Then for each ensemble considered (at a specified

temperature and density), the velocities were used numerically to construct the corresponding velocity autocorrelation functions. In this manner the normalized $F(t)$ can be rewritten as

$$F(t) = \frac{1}{2NT} \left\langle \sum_{i=1}^N v_i(0)v_i(t) \right\rangle_I, \quad (5.2)$$

where the brackets indicate that the average is taken over the $I = [(T.T. - t)/d.p.] + 1$ possible choices for the origin time. T.T. designates the total time the velocities of each particle were recorded, t represents the time at which $F(t)$ is to be determined, and d.p. is the total number of velocities recorded per particle.

For the system density of 1.25 ($\langle l \rangle = 0.8$), a sequence of velocity autocorrelations is presented in Fig. 5 and 6. For all correlations exhibited, the temperatures are above that predicted by the nearest-neighbor model to be the transition temperature. (See Table 1.) The "cutoff" times ($t_{c.o.}$) represent the estimates beyond which the curve is primarily stochastic noise. At times less than the indicated "cutoff" times, the velocity autocorrelation functions presented are reasonable facsimilies of the real functions.

The estimated statistical error¹³ is

$$\delta F(t) = \pm \left[\frac{2t_{c.o.}}{M(T.T.)} \right]^{\frac{1}{2}} |1 - F(t)|, \quad (5.3)$$

where M represents the equivalent number of test particles used to construct $F(t)$. The statistical error increases as time increases. The maximum statistical error is encountered at each $t_{c.o.}$ and is highest for $T = 8.45$ and lowest for $T = 0.162$ with the approximate range $3 \leq \delta F(t) \leq 4.5\%$. The associated numerical deviation in the kinetic energy, less than 2% in all cases, must be considered in any quantitative calculation made from the autocorrelations in Fig. 5 and 6. The oscillatory behavior of the velocity autocorrelation function has also been observed in other systems.^{14, 15, 16} The longevity of the first minimum in $F(t)$ at $T = 8.45$ (Fig. 6) is similar to that appearing in simulation studies of high density, low temperature liquid argon.¹²

B. Self-diffusion

Since the autocorrelations in Fig. 5 and 6 all exhibit a convergence to zero, a self-diffusion constant at each temperature is expected. In a one-dimensional system the mean square displacement after time t is given by

$$\overline{[r(t)]^2} = 2T \int_0^t d\tau (t - \tau) F(\tau) \quad . \quad (5.4)$$

If the velocity autocorrelation approaches zero for a finite value for τ , the long time limit on the time t gives

$$\lim_{t \rightarrow \infty} \left\{ \overline{[r(t)]^2} = 2Tt \int_0^t d\tau F(\tau) \right\} . \quad (5.5)$$

The macroscopic law for diffusion states that the probability for a system particle to have a displacement $r(t)$ in time t is normally distributed and that the width of the distribution (mean square displacement), $\overline{[r(t)]^2}$, in time t , is $2Dt$ for a one-dimensional system, where D is the self-diffusion constant.¹⁷ This is a phenomenological law.¹⁸ The diffusion constant can be written in terms of the normalized velocity autocorrelation function as

$$\frac{D}{2T} = \int_0^\infty d\tau F(\tau) . \quad (5.6)$$

The Fourier transform of $F(t)$ is

$$\tilde{F}(\omega) = \int_{-\infty}^{\infty} dt F(t) \cos(2\pi\omega t) , \quad (5.7)$$

where the required normalization is

$$\int_{-\infty}^{\infty} d\omega \tilde{F}(\omega) = 1 \quad (5.8)$$

and the zero-frequency value is

$$\tilde{F}(\omega = 0) = \frac{D}{T} \quad . \quad (5.9)$$

The numerically determined normalized velocity autocorrelation functions designated by $F(t)$ in Fig. 5 and 6 were Fourier transformed according to the prescription given by Eq. (5.7). The results for temperatures $T = 0.162$, 0.866 , and 8.45 are illustrated in Fig. 7 as are the self-diffusion constants determined from Eq. (5.9). For temperatures $T = 1.38$ and 2.35 , the corresponding diffusion constants were found to be $D = 0.163$ and 0.240 , respectively.

The second approach used in the determination of the self-diffusion constants was through Eq. (5.4). The resulting numerical integrations show in Fig. 8 that the long time limit for the mean square displacement predicted by the Einstein relation is achieved. The self-diffusion constants as determined from the asymptotic limit of $\overline{[r(t)]^2}$ are indicated in Fig. 8. For $T = 1.38$ and 2.35 it was found that $D = 0.148$ and 0.225 , respectively. As a result it is noticed that self-diffusion becomes more extensive with increasing temperature. However, no functional relationship between self-diffusion and the temperature can be expressed with the limited amount of data available, and the associated numerical and statistical uncertainty in that data. It can be ascertained that the rate of increase of self-diffusion as a function of temperature is much greater

than a linear relationship would predict. In the zero temperature limit, self-diffusion is nonexistent as prescribed by Eq. (5.9). Also, it is expected that self-diffusion will cease to exist in the high temperature, or ideal gas, limit.

C. Particle Motion

Particle motion classified as Brownian motion would have a normalized velocity autocorrelation function of the form

$$F(t) = e^{-\gamma t}, \quad t > 0 \quad (5.10)$$

where γ is a friction constant. The corresponding Fourier transform is

$$\tilde{F}(\omega) = \frac{2\gamma}{(2\pi\omega)^2 + \gamma^2} \quad (5.11)$$

If the particle motion were simply oscillatory, then

$$F(t) = \sum_{i=1}^M A_i \cos(2\pi\omega_i t), \quad (5.12)$$

where ω_i is the frequency of the i^{th} oscillator and A_i is the oscillator strength. The Fourier transform is

$$\tilde{F}(\omega) = \frac{1}{2} \sum_{i=1}^M A_i \delta(\omega - \omega_i) \quad . \quad (5.13)$$

Comparing Eq. (5.10) and (5.12) with Fig. 5 and 6, and Eq. (5.11) and (5.13) with Fig. 7, it is concluded that the actual particle motion cannot be classified as either Brownian or a series of harmonic oscillators. Both phenomena are present.

A model which predicts the general behavior of the systems studied allows a particle to vibrate about its equilibrium position which is undergoing Brownian motion.^{19,20} However, the model does not allow the existence of more than one oscillator mode and is little more than a curve fitting device. The diffusive mode exists at all temperatures considered (see Fig. 7). The vibrational modes, not present at low temperatures ($T = 0.162$), appear at high frequencies and continuously shift to lower frequencies with increasing temperature ($T = 0.866$ and $T = 8.45$).

The amount of computer time necessary to numerically construct the velocity autocorrelation functions made the study at lower densities, i.e., less than one, prohibitive at the present time. It has been determined, however, that a self-diffusion constant does exist for this one-dimensional system for the density equal to 1.25, $\langle l \rangle = 0.8$. It is not unreasonable to conclude that a diffusion constant exists for all densities in this system.

VI. SUMMARY

Perhaps the most interesting aspect of the model studied is the possibility of a change of state from a solid to a fluid-gas as the temperature is increased along an isochore. The temperature at which the experimental equation of state for a specific isochore deviates from that predicted by the nearest-neighbor model (Fig. 1 and 2) is more easily determined than the temperatures associated with the onset of the complete interpenetration of the particles determined from the radial distribution functions (see, e.g., Fig. 3 and 4). However, it is found that the transition temperatures estimated from the radial distribution functions are generally higher than those determined from the nearest-neighbor model (Table 1). This indicates that the breakdown of the solid-like configuration as defined in Section II of the one-dimensional systems studied is caused by the onset of interactions besides those of nearest-neighbors.

The transition for each isochore is continuous. The only discontinuity which appears is in the zero temperature limit as the specific length approaches $\langle \ell \rangle = 1$ from either above or below. This limiting discontinuity is independent of the change of state which is observed to occur for each isochore, and is dependent on the specific length $\langle \ell \rangle$ and the form of the two-body interaction potential, Eq. (2.1).

The equations of state determined from the truncated virial expansion accurately predict the experimental isochores for all densities considered in certain temperature ranges. This is in spite of the fact that the virial equation of state is a power series in density, Eq. (3.7). The excellent correspondence at high densities ($\langle \ell \rangle \leq 1$) is the result of the temperature dependence of the virial coefficients. The virial coefficients B_2 , B_3 , and B_4 approach zero rapidly with increasing temperature.

Another interesting feature of the model was the structure of the velocity autocorrelation functions which is not fully understood. The normalized velocity autocorrelations (Fig. 6 and 7) for the isochore $\langle \ell \rangle = 0.8$ lose any structure attributed to self-correlations in a finite time despite the persistence of the observed oscillations as the temperature increases. The self-diffusion constant determined from the Fourier time transform of each normalized velocity autocorrelation function, Eq. (5.9), compared favorably ($\leq 10\%$) to that determined from the long time asymptotic limit of the mean square displacement, Eq. (5.4) and (5.5), and the Einstein relation, in each case. It is expected that a self-diffusion constant can be defined for every finite density and temperature in this one-dimensional system. Without detailed information on the actual trajectories of the particles, the type of self-diffusion that is occurring, and the specific cause of the observed well-defined oscillations in the normalized velocity autocorrelations (Fig. 6 and 7), and the corresponding Fourier time transforms (Fig. 8) cannot be determined at this time.

In conclusion, the utilization of the method of molecular dynamics to simulate a one-dimensional kinetic system in thermal equilibrium has provided accurate results when compared with theoretical predictions. The accuracy of the results is dependent on the choice of the numerical algorithm and the computer "round-off" error incurred. In principle all quantities representative of the system are obtainable. The primary restriction is the difficulty of the calculation. The macroscopic quantities calculated and presented here were chosen for the purpose of defining an equation of state. The microscopic quantities reflect the spatial configuration and the motion of the constituent particles. One-dimensional kinetic systems are an artificial means of attempting to describe the behavior of real systems. However, the control that exists over a computer simulated system, and the relative simplicity of one-dimensional calculations lend insight into the physical phenomena that are observed.

APPENDIX

For a one-dimensional system of length L , the first four virial coefficients are

$$B_1 = 1 \quad , \quad (A.1)$$

$$B_2 = \frac{1}{2L} \int_0^L \int_0^L f(1,2) dx_1 dx_2 \quad , \quad (A.2)$$

$$B_3 = -\frac{1}{3L} \int_0^L \int_0^L \int_0^L f(1,2)f(2,3)f(3,1) dx_1 dx_2 dx_3 \quad , \quad (A.3)$$

and

$$B_4 = \frac{-1}{8L} \int_0^L \int_0^L \int_0^L \int_0^L f(1,2)f(2,3)f(3,4)f(4,1) \\ \times [3 + 6 f(1,3) + f(1,3)f(2,4)] dx_1 dx_2 dx_3 dx_4 \quad , \quad (A.4)$$

where $f(i,j) = e^{-\frac{V(x_{ij})}{T}} - 1$, and $V(x_{ij})$ is defined by Eq. (1.1).

Performing the indicated integrations yields

$$B_2 = 1 - \frac{T}{V_0} \left(1 - e^{-\frac{V_0}{T}} \right), \quad (A.5)$$

$$B_3 = 1 - \frac{T}{V_0} \left(2 - 5e^{-\frac{V_0}{T}} \right) - \frac{T^2}{2V_0^2} \left(7e^{-\frac{V_0}{T}} - 8e^{-\frac{2V_0}{T}} + e^{-\frac{3V_0}{T}} \right), \quad (A.6)$$

and

$$\begin{aligned} B_4 = & \frac{23}{24} + \frac{T}{V_0} \left(-\frac{19}{4} + \frac{103}{8} e^{-\frac{V_0}{T}} + \frac{5}{16} e^{-\frac{2V_0}{T}} \right) \\ & + \frac{T^2}{V_0^2} \left(\frac{27}{8} - \frac{213}{8} e^{-\frac{V_0}{T}} + \frac{3407}{144} e^{-\frac{2V_0}{T}} - \frac{41}{12} e^{-\frac{3V_0}{T}} \right) \\ & + \frac{T^3}{V_0^3} \left(-\frac{755}{192} + \frac{4779}{144} e^{-\frac{V_0}{T}} - \frac{22613}{432} e^{-\frac{2V_0}{T}} \right. \\ & + \frac{4205}{144} e^{-\frac{3V_0}{T}} - \frac{3423}{576} e^{-\frac{4V_0}{T}} + \frac{61}{216} e^{-\frac{5V_0}{T}} \\ & \left. + \frac{13}{144} e^{-\frac{6V_0}{T}} \right). \end{aligned}$$

To offer any realism in describing the systems the equation of state must approach the ideal gas law as the temperature is increased. Because the coefficients expressed by Eq. (A.5) through (A.7) are power series in temperature, the ideal gas limit is not immediately obvious. However, if the exponentials in the coefficients of the powers of temperature T are expanded, each virial coefficient vanishes identically in the limit of high temperature, and the ideal gas limit is achieved.

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Table 1

The transition temperatures, T , estimated from (1) the radial distribution functions and (2) the nearest-neighbor model for the specific system lengths, $\langle \ell \rangle$, studied.

$\langle \ell \rangle$ T	0.8	0.85	0.9	1	1.1	2.0	4.0
1	~ 0.272	~ 0.495	~ 0.511	~ 0.944	≥ 0.96	~ 2.28	> 3.25 $<< 4.73$
2	< 0.162	$<< 0.495$	≥ 0.390	> 0.850 < 0.944	≥ 0.96	~ 2.28	~ 3.25

FIGURE CAPTIONS

- Fig. 1 Equations of state as predicted by nearest-neighbor model (—), and truncated virial expansion (-----) as compared to the experimental isochores, $\langle l \rangle > 1$.
- Fig. 2 Equations of state as predicted by nearest-neighbor model (—), and truncated virial expansion (-----) as compared to the experimental isochores, $\langle l \rangle \leq 1$.
- Fig. 3 Sequence of radial distributions, $g(r)$, at various temperatures for the specific length $\langle l \rangle = 2$.
- Fig. 4 A sequence of radial distributions, $g(r)$, at various temperatures for the specific length $\langle l \rangle = 0.9$.
- Fig. 5 A sequence of normalized velocity autocorrelations, $F(t)$, at temperatures $T = 0.162$, 0.866 , and 1.38 for the specific length $\langle l \rangle = 0.8$.
- Fig. 6 A sequence of normalized velocity autocorrelations, $F(t)$, at temperatures $T = 2.35$ and 8.45 for the specific length $\langle l \rangle = 0.8$.
- Fig. 7 Three Fourier time transforms (spectral densities), $\tilde{F}(\omega)$, of the normalized velocity autocorrelation functions for the temperatures $T = 0.162$, 0.866 , and 8.45 for the system specific length $\langle l \rangle = 0.8$. The estimated self-diffusion constant, D , in each case is indicated on the plot.

Fig. 8 The mean-square displacement, $\overline{[r(t)]^2}$, at the temperatures $T = 0.162$, 0.866 , and 8.45 for the system specific length $\langle \ell \rangle = 0.8$ as determined by numerical integration of the normalized velocity autocorrelation functions $F(t)$. The estimated self-diffusion constant, D , is indicated on the plot in each case.

Fig. 1

Fig. 2

Fig. 3

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Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8