Correlation between Kolmogorov-Sinai entropy and self-diffusion coefficient in simple fluids

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The relationship between the Kolmogorov-Sinai entropy, $h_{KS}$ and the self-diffusion coefficient $D$ is studied for two classical simple fluid systems with purely repulsive potentials (one system with a Wayne-Chandler-Anderson potential and the other with a hard-sphere potential). Numerical simulation data for $h_{KS}$ and $D$, normalized by the average collision frequency $v$ and the diameter of the particle $\sigma$ as natural units of time and distance, reveal that, in the region spanning from normal liquid up to near solidification ($0.50 < \rho < 0.93$), the Kolmogorov-Sinai entropy has a power law dependency on the self-diffusion coefficient of the form $h_{KS} / v \propto (D / \sigma^2 v)^{\eta}$, in which $\eta$ is independent of density and temperature.

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\begin{equation}
\frac{h_{KS}}{N v} \approx \ln \left( \frac{D}{\nu \sigma^2} \right) .
\end{equation}

Here, $h_{KS}$, defined as the sum of positive Lyapunov exponents according to Pesin’s theorem, is normalized by the number of particles $N$ and the average collision frequency $\nu$ given by Enskog’s theory [11,12]

\begin{equation}
\nu = \rho \sigma^2 \left( \frac{\pi k_B T}{m} \right)^{1/2} g(\sigma_1),
\end{equation}

where $\sigma_1$ is the effective atomic radius, defined as the first maximum of the radial distribution function $g(r)$, and $\rho$ is the number density. Our previous work, which studied the relationship between the self-diffusion coefficient normalized by the Enskog transport coefficient $D_E$, and the KS entropy normalized by the largest Lyapunov exponent $\lambda_1$, suggests that the relation in Eq. (1) can hold in the low-density region [13]. However, the self-diffusion coefficient decreases much faster than expected in the normal and high-density regions. It should be mentioned that, for Eq. (1) to hold, $h_{KS}$ must go to a negative value as $D$ approaches zero, which is not physically allowed.

$h_{KS}$ measures the rate of information loss of a given system in tangent space, whereas the diffusion coefficient is the response function of the system that measures the information loss in physical space. Hence, we propose the following algebraic relation:

\begin{equation}
\frac{h_{KS}}{N v} \propto \left( \frac{D}{\nu \sigma^2} \right)^{\eta},
\end{equation}

where $\eta$ varies depending on the type of interaction potential function, but is independent of temperature and density. This form is similar to the one proposed by Barnett et al., except that in the relation presented here $\eta$ is system dependent rather than being fixed at a value of 1/3.

In the present work, we carry out a numerical simulation study of the Wayne-Chandler-Anderson (WCA) fluid and hard-sphere (HS) fluid. The WCA potential is defined as...
where $\sigma$ is the interaction range of the potential. Each system has $N$ identical particles of mass $m$ in the three-dimensional volume $V$, and the dynamical state is represented by a $3N$-dimensional momentum vector $p$ and a $3N$-dimensional position vector $q$. Conventionally, we write these vectors in $6N$-dimensional phase space. The governing equations of the motion are given by $3N$ coupled ordinary differential equations:

$$\dot{\Gamma} = \left( \begin{array}{c} \dot{p} \\ \dot{q} \end{array} \right) = \left( \begin{array}{c} -\frac{\partial U}{\partial q} \\ \frac{p}{m} \end{array} \right) = G(\Gamma),$$

where $U$ is the interaction potential energy of the system.

In contrast to the continuous dynamics of the WCA fluid, the dynamics of the HS fluid is not continuous because the momentum changes in a HS system occur only at the instants at which particles collide. Thus, the equation of motion at each moment of collision has the form of a discrete map $F$,

$$\Gamma' = F(\Gamma'),$$

where the superscripts $i$ and $f$ refer before collision and “after collision,” respectively [14].

For the numerical calculation of Lyapunov exponents, we use the method proposed originally by Benettin et al. [1], and developed later by Hoover and Posch [15–18]. Consider a reference trajectory $\Gamma(t)$ and a bundle of comoving neighbor trajectories $\Gamma(t) + \delta_i(t)$ for initial perturbation $\delta_i(0) (i = 1, \ldots, 6N)$. According to the multiplicative theorem of Oseledec, there are $6N$ orthogonal initial vectors yielding a set of exponents referred to as the Lyapunov spectrum of the system [19]. These exponents are independent of the metric and initial conditions of $\delta$. In systems whose motion is governed by Hamilton’s equations, the time evolution of $\delta_i$ is obtained by integrating the following equation, which is obtained by linearizing the original equations of motion given in Eq. (5):

$$\dot{\delta}_i(t) = \frac{\partial G(\Gamma(t))}{\partial \Gamma} \cdot \delta_i(t).$$

In the case of a HS fluid, the time delay between neighboring trajectories must be considered. The $i$th Lyapunov exponent $\lambda_i$ is obtained by taking an average of the local instability of $\delta_i$,

$$\lambda_i = \lim_{t \to \infty} -\frac{1}{t} \ln \left( \frac{\| \delta_i(t_0 + r) \|}{\| \delta_i(t_0) \|} \right)_{t_0}.$$

Here $\| \cdot \|$ and $\langle \cdot \rangle_{t_0}$ denote the norm and the average with respect to an initial time $t_0$, respectively. To avoid numerical divergence, Gram-Schmidt reorthonormalization is regularly applied. For more detail, we refer the reader to Refs. [13,14,16]. From the set of Lyapunov exponents, the Kolmogorov-Sinai entropy $h_{KS}$ is obtained from the sum of all positive Lyapunov exponents,

$$h_{KS} = \sum_{\lambda_i > 0} \lambda_i.$$

The Kolmogorov-Sinai entropy is an invariant quantity for the dynamical system that indicates the mean rate of information loss.

A similar approach can be applied to the diffusion because the self-diffusion coefficient $D$ is also a measure of information loss. The self-diffusion coefficient can be obtained from the mean-square displacement or velocity autocorrelation. Due to the long algebraic tail in the velocity autocorrelation function of the HS fluid, the Green-Kubo formalism provides numerically less accurate values of the diffusion coefficient. Hence, for both fluids, the self-diffusion coefficient is evaluated from the mean-square displacement:

$$D = \lim_{t \to \infty} \frac{1}{6Nt} \sum_{i=1}^{N} \langle \| r_i(t) - r_i(0) \|^2 \rangle_0.$$

For the WCA fluid, Eq. (5) is integrated with the fourth-order symplectic algorithm with $\Delta t = 5 \times 10^{-4}$ [20,21], whereas for the HS fluid the time evolution of the trajectory is obtained by iteration of the discrete map. To evaluate the self-diffusion coefficient, we monitored the particle displacements over $1 \times 10^5$ time steps after equilibration, and to obtain the Lyapunov exponents we averaged over $1 \times 10^6$ time steps. Here and throughout the paper, we use conventional reduced units: distance is made dimensionless by dividing by the molecular diameter $s$, mass by $m$, energy and temperature by the Lennard-Jones parameter $\epsilon$, and time by $\sqrt{m\sigma^2/\epsilon}$. In Fig. 1, we plot the self-diffusion coefficient $D^*$ vs. number density $\rho$ at temperatures $T = 0.7$ and $T = 1.0$.
the self-diffusion coefficients are nonzero. The normalized self-diffusion coefficient of the HS fluid shows negligible temperature dependence. This lack of temperature dependence comes about because the total energy of the system is linearly dependent on the temperature. Specifically, the Hamiltonian of the HS fluid is proportional to $T$, and the average time between collisions is proportional to $T^{-1/2}$. Hence, the diffusion coefficient and the average collision frequency are expected to be proportional to $T^{1/2}$ and, as a consequence, the self-diffusion coefficient normalized by the average collision frequency, $D^*$, is independent of temperature. On the other hand, the normalized self-diffusion coefficient of the WCA fluid shows temperature-dependent behavior, and the strength of this temperature dependence becomes stronger with increasing density.

The molecular level mechanism of diffusion in WCA fluids differs from that in HS fluids, especially in the high-density region. Diffusion in HS fluids proceeds via successive binary collisions between particle pairs, whereas in a WCA fluid diffusion behavior is determined not only by successive collisions but also by structural relaxations on the continuous landscape of the potential energy surface, which is sensitive to temperature and causes the reduction of the internal pressure. The additional factors influencing diffusion in WCA fluids cause these fluids to have larger diffusion coefficients than HS fluids at the same density and temperature. For example, the pressure of a WCA fluid of density $\rho = 0.93$ at $T = 0.7$ is approximately 4.5 times larger than the pressure of the corresponding HS fluid.

In Fig. 2 the density dependence of $h_{KS}^* = h_{KS}/N\nu$ is shown for the WCA and HS systems at temperatures of $T = 0.7$ and $T = 1.0$. Due to the long times required to calculate the Lyapunov exponents, the data presented here were obtained from systems of $N = 32$ particles for the WCA fluid and $N = 64$ particles for the HS fluid. The test calculations for WCA fluids of $N = 32$ and $N = 64$ showed that $h_{KS}/N$ has negligible dependence on the number of particles. For example, at $\rho = 0.92$ and $T = 0.7$, $h_{KS}/N = 5.08$ for both $N = 32$ and $N = 64$. We also confirmed for the HS fluids that the value of $h_{KS}/N$ shows no difference between results for $N = 64$ and $N = 108$, as observed by van Beijeren et al. [22]. Figure 2 clearly shows that $h_{KS}^*$ is independent of temperature for the HS fluid. This lack of temperature dependence is due to the linear dependence of the total energy of the system on temperature. In general, for systems at the same temperature and density, the numerical values of the Lyapunov exponents of the WCA fluid are smaller than those of the HS fluid. This arises because in WCA fluids the trajectory of the system more frequently passes through regions of concave potential energy surface, whereas the trajectory of the HS fluid system evolves freely between each collision. Consider a perturbed vector $\delta = \{\delta r, \delta p\}$. If a system has a continuous pairwise potential and a nonzero Hessian matrix $H$, then the evolution of $\delta$ after a certain time $\delta t$ is approximately $\{\delta q + (\delta p/m) \delta t, (\delta p - H \cdot \delta q) \delta t\}$. If the system is in a region of sufficiently high density, the ensemble average of $H \cdot \delta q$ can be regarded as an effective restoring force. This idea has been qualitatively verified by observing that the fraction of the unstable mode obtained from the Hessian matrix decreases as the density increases [23].

In Fig. 3, we plot the logarithm of $h_{KS}^*$ versus the logarithm of $D^*$. This graph clearly shows the algebraic relationship proposed in Eq. (3). For the HS fluids, the relationship between these two quantities is the same at the two temperatures considered, with a fixed value of $\eta = 0.17$ within an error of 3%. For the WCA fluids, the value of $\eta$ is also independent of temperature, with a value of $\eta = 0.44$, and the temperature dependence can be reflected in a prefactor $p(t)$ as follows:

$$h_{KS}^* = p(T) \left( \frac{D}{\nu \sigma^2} \right)^{\eta}. \quad (11)$$

The numerical values of the exponents for the HS and WCA systems are far from the value of 1/3 proposed by Barnett for a low-density plasma, and furthermore the exponent is system dependent. However, the mathematical form of the relation remains the same. Figure 3 shows that $h_{KS}^*$, which is a
measure of the global instability of the system, is related to $D^*$ by a simple algebraic relation, which supports the qualitative similarity between these two quantities. Next, to more closely examine quantitative differences, we focus on two cases. The first case considers the HS fluid at $\rho=0.83$ and $T=1.0$, and the WCA fluid at $\rho=0.60$ and $T=1.0$. As can be seen in Fig. 1, these two systems have almost the same value of $h_{KS}^*$ (0.740 for the HS fluid and 0.736 for the WCA fluid). However, the normalized self-diffusion coefficients $D^*$ of the two systems are markedly different. This difference is due to the different behavior of velocity autocorrelation function of each system. The velocity autocorrelation function of the HS fluid shows a fast initial decay, followed by a small peak that is due to backscattering. On the other hand, the velocity autocorrelation function of the WCA fluid shows only a slow monotonic decay without any sign of backscattering, resulting in a much larger value of $D^*$ for the WCA fluid. Further study shows that WCA fluids begin to show backscattering for $\rho > 0.78$. Thus, the second case we consider is the HS fluid at $\rho=0.75$ and the WCA fluid at $\rho=0.82$, with $T=1.0$ for both cases. The normalized self-diffusion coefficients $D^*$ of the HS fluid and WCA fluid are $4.26 \times 10^{-3}$ and $4.14 \times 10^{-3}$, respectively. Both systems show clear small peaks in the velocity autocorrelation function that are characteristic of backscattering, but $h_{KS}^*$ of the HS fluid is almost twice that of the WCA fluid. This large difference is a reflection of the fact that the effective restoring force mentioned above continually suppresses the separation rate of small perturbations in WCA systems.

In summary, we examined the KS entropy and the self-diffusion coefficient of HS fluids and WCA fluids. The KS entropy and the diffusion coefficient, normalized by the average collision frequency, show monotonic decay with respect to number density. From observations of the density dependence of these two quantities, we proposed an algebraic relationship between $h_{KS}^*$ and $D^*$ (depicted in Fig. 3). The numerical data for $h_{KS}^*$ and $D^*$ are fitted to Eq. (3) with high precision with values of $\eta=0.17$ and 0.44 for the HS fluid and WCA fluid, respectively.

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