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

Dongchul Ihm, Young-Han Shin, Jae-Weon Lee, and Eok Kyun Lee
Department of Chemistry and School of Molecular Science (BK21), Korea Advanced Instititute of Science and Technology, 373-1, Gusongdong Yusonggu, Taejeon, Korea

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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 ν and the diameter of the particle σ as natural units of time and distance, reveal that, in the region spanning from normal liquid up to near solidification $(0.50 \leqslant \rho \leqslant 0.93)$, the Kolmogorov-Sinai entropy has a power law dependeney on the self-diffusion coefficient of the form $h_{\mathrm{KS}}/\nu \propto (D/\sigma^2\nu)^{\eta}$, in which η is independent of density and temperature.

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A useful way to characterize chaotic phenomena in dynamical systems is by means of the Lyapunov exponents that describe the separation rate of systems whose initial conditions differ by a small perturbation. Considerable effort has been devoted to the computation and characterization of the Lyapunov exponents of various dynamical systems, and the efficiency and accuracy of the associated numerical methods have also been explored [1,2]. Recently, it has been recognized that the chaotic property of dynamical systems of many degrees of freedom is related to the thermodynamics of the systems. The Lorentz gas has been widely studied as a model chaotic system on account of its theoretical simplicity and numerical efficiency. For example, Gaspard *et al.* showed that the process by which trajectories escape from the vicinity of a repeller can be quantitatively understood as diffusive motion [3,4]. As a more realistic model, Evans *et al.* carried out molecular dynamics simulations of a simple fluid system in a nonequilibrium stationary state [5]. They determined the relation between the Lyapunov spectrum and viscosity coefficients, assuming that Smale's pairing rule of Lyapunov exponents for Hamiltonian systems can be extended to non-Hamiltonian systems in contact with a heat bath. The works of Evans *et al.* and Gaspard *et al.* have formed the basis for the majority of later theoretical studies of nonequilibrium molecular dynamics.

Recently, Barnett and Tajima proposed that the largest Lyapunov exponent is proportional to the 1/3 power of the self-diffusion coefficient for the one-component plasma system in the low-density regime, based on the assumption that the force autocorrelation function is proportional to the velocity autocorrelation function [6–8]. However, the diffusion properties of dense fluids with short-range potentials, and the molecular-level relationship between those properties and the Lyapunov instability, are still heavily dependent on the numerical approach employed. Dzutugov recently proposed universal relationships between the excess entropy and the self-diffusion coefficient, and between the excess thermodynamic entropy and the Kolmogorov-Sinai entropy, for dense fluids with various types of interaction potential [9,10]. Dzugutov's results imply that an exponential relationship should hold between the Kolmogorov-Sinai entropy (KS entropy) h_{KS} and the self-diffusion coefficient D,

$$\frac{h_{\mathrm{KS}}}{N\nu} \propto \ln\left(\frac{D}{\nu\sigma_1^2}\right). \tag{1}$$

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 ν given by Enskong's theory [11,12]

$$\nu = \rho\sigma_1^2\left(\frac{\pi k_B T}{m}\right)^{1/2} g(\sigma_1), \tag{2}$$

where σ_1 is the effective atomic radius, defined as the first maximum of the radial distribution function $g(r)$, and ρ 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 λ_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:

$$\frac{h_{\mathrm{KS}}}{N\nu} \propto \left(\frac{D}{\nu\sigma^2}\right)^{\eta}, \tag{3}$$

where η 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 η 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

$$\phi(r)=\begin{cases} 4\epsilon\left[\left(\dfrac{\sigma}{r}\right)^{12}-\left(\dfrac{\sigma}{r}\right)^{6}\right]+\epsilon, & r<2^{1/6}\sigma \\ 0, & r\geqslant 2^{1/6}\sigma, \end{cases} \tag{4}$$

where σ 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 $\boldsymbol{p}$ and a $3N$-dimensional position vector $\boldsymbol{q}$. Conventionally, we write these vectors in $6N$-dimensional phase space. The governing equations of the motion are given by $3N$ coupled ordinary differential equations:

$$\dot{\boldsymbol{\Gamma}}=\begin{pmatrix}\dot{\boldsymbol{p}}\\ \dot{\boldsymbol{q}}\end{pmatrix}=\begin{pmatrix}-\dfrac{\partial U}{\partial \boldsymbol{q}}\\ \boldsymbol{p}/m\end{pmatrix}=\boldsymbol{G}(\boldsymbol{\Gamma}), \tag{5}$$

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,

$$\boldsymbol{\Gamma}^{f}=\boldsymbol{F}(\boldsymbol{\Gamma}^{i}), \tag{6}$$

where the superscripts i and f represent 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 $\boldsymbol{\Gamma}(t)$ and a bundle of comoving neighbor trajectories $\boldsymbol{\Gamma}(t)+\boldsymbol{\delta}_l(t)$ for initial perturbation $\boldsymbol{\delta}_l(0)(l=1,\ldots,6N)$. 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 $\boldsymbol{\delta}_l$. In systems whose motion is governed by Hamilton's equations, the time evolution of $\boldsymbol{\delta}_l$ is obtained by integrating the following equation, which is obtained by linearizing the original equations of motion given in Eq. (5):

$$\dot{\boldsymbol{\delta}}_l(t)=\frac{\partial \boldsymbol{G}(\boldsymbol{\Gamma}(t))}{\partial \boldsymbol{\Gamma}}\cdot\boldsymbol{\delta}_l(t). \tag{7}$$

In the case of a HS fluid, the time delay between neighboring trajectories must be considered.

The lth Lyapunov exponent λ_l is obtained by taking an average of the local instability of $\boldsymbol{\delta}_l$,

$$\lambda_l=\left\langle \lim_{\tau\to\infty}\frac{1}{\tau}\ln\left\{\frac{\|\boldsymbol{\delta}_l(t_0+\tau)\|}{\|\boldsymbol{\delta}_l(t_0)\|}\right\}\right\rangle_{t_0}. \tag{8}$$

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,

$$h_{\mathrm{KS}}=\sum_{\lambda_l>0}\lambda_l. \tag{9}$$

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

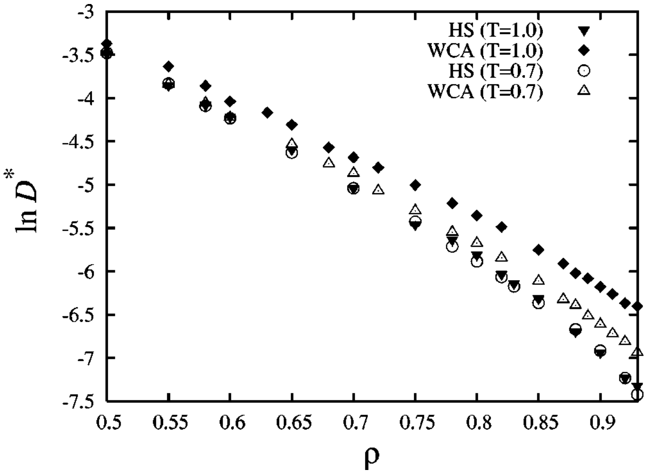

FIG. 1. Plot of the scaled self-diffusion coefficient D^* vs number density ρ at temperatures $T=0.7$ and $T=1.0$.

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:

$$D=\lim_{t\to\infty}\lim_{N\to\infty}\frac{1}{6Nt}\sum_{i}^{N}\langle\|\boldsymbol{r}_i(t)-\boldsymbol{r}_i(0)\|^2\rangle_0. \tag{10}$$

For the WCA fluid, Eq. (5) is integrated with the fourth-order symplectic algorithm with $\Delta t=5\times10^{-4}$ [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 1×10^{5} time steps after equilibration, and to obtain the Lyapunov exponents we averaged over 1×10^{6} time steps. Here and throughout the paper, we use conventional reduced units: distance is made dimensionless by dividing by the molecular diameter σ, mass by m, energy and temperature by the Lennard-Jones parameter ϵ, and time by $\sqrt{m\sigma^2/\epsilon}$.

In Fig. 1, we plot the self-diffusion coefficient $D^*=D/(\nu\sigma^2)$, normalized with respect to the average collision frequency, against the number density at temperatures of $T=0.7$ and $T=1.0$, respectively, for systems of 500 particles. Up to $\rho\approx0.93$ the fluids remain in the dense liquid phase and

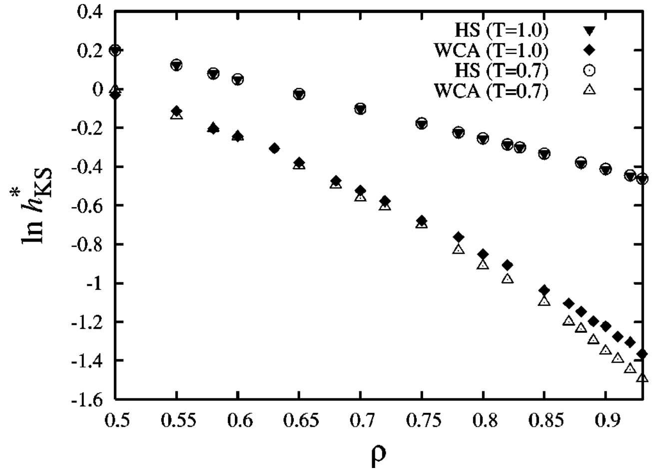

FIG. 2. Plot of the scaled Kolmogorov-Sinai entropy h^*_{KS} vs number density ρ at temperatures $T=0.7$ and $T=1.0$.

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 $h^*_{\mathrm{KS}}=h_{\mathrm{KS}}/N\nu$ 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 $T=0.7$, $h_{\mathrm{KS}}/N=5.08$ 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 $\boldsymbol{\delta}=\{\delta\boldsymbol{r},\delta\boldsymbol{p}\}$. If a system has a continuous pairwise potential and a nonzero Hessian matrix $\boldsymbol{H}$, then the evolution of $\boldsymbol{\delta}$ after a certain time δt is approximately $\{\delta\boldsymbol{q}+(\delta\boldsymbol{p}/m)\delta t,(\delta\boldsymbol{p}-\boldsymbol{H}\cdot\delta\boldsymbol{q})\delta t\}$. If the system is in a region of sufficiently high density, the ensemble average of $\boldsymbol{H}\cdot\delta\boldsymbol{q}$ 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].

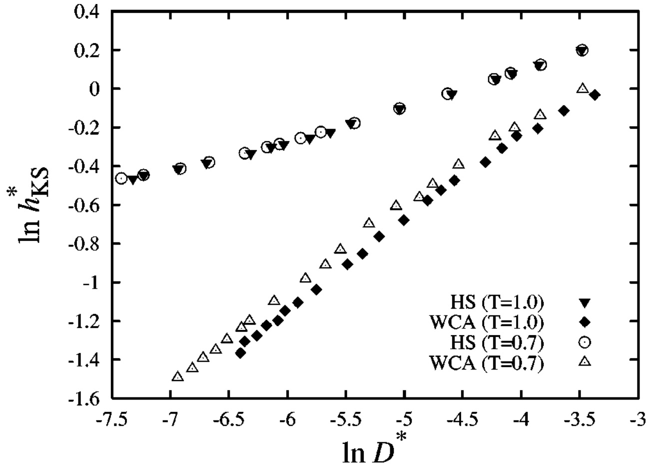

FIG. 3. Plot of the reduced Kolmogorov-Sinai entropy h^*_{KS} vs the reduced diffusion coefficients D^* at temperatures $T=0.7$ and $T=1.0$.

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 $\eta\simeq0.17$ within an error of 3%. For the WCA fluids, the value of η is also independent of temperature, with a value of $\eta\simeq0.44$, and the temperature dependence can be reflected in a prefactor $p(t)$ as follows:

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

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 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 4.26×10^{-3} and 4.14×10^{-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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[1] G. Benettin, L. Galgani, and J.M. Strelcyn, Phys. Rev. A **14**, 2338 (1976).
[2] I. Shimada and T. Nagashima, Prog. Theor. Phys. **61**, 1605 (1979).
[3] P. Gaspard and G. Nicolis, Phys. Rev. Lett. **65**, 1693 (1990).
[4] P. Gaspard and J.R. Dorfman, Phys. Rev. E **52**, 3525 (1995).
[5] D.J. Evans, E.G.D. Cohen, and G.P. Morriss, Phys. Rev. A **42**, 5990 (1990).
[6] D.M. Barnett, T. Tajima, K. Nishihara, Y. Ueshima, and H. Furukawa, Phys. Rev. Lett. **76**, 1812 (1996).
[7] D.M. Barnett and T. Tajima, Phys. Rev. E **54**, 6084 (1996).
[8] A. Torcini, C. Dellago, and H.A. Posch, Phys. Rev. Lett. **83**, 2676 (1999).
[9] M. Dzugutov, Nature (London) **381**, 137 (1996).
[10] M. Dzugutov, Phys. Rev. Lett. **81**, 1762 (1998).
[11] J.B. Pesin, Sov. Math. Dokl. **17**, 196 (1976).
[12] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-uniform Gas* (Cambridge University Press., Cambridge, 1939).
[13] H. Pang, Y.H. Shin, D. Ihm, E.K. Lee, and O. Kum, Phys. Rev. E **62**, 6516 (2000).
[14] C. Dellago and H.A. Posch, Physica A **240**, 68 (1997).
[15] W.G. Hoover, H.A. Posch, and S. Bestiale, J. Chem. Phys. **87**, 6665 (1987).
[16] H.A. Posch and W.G. Hoover, Phys. Rev. A **38**, 473 (1988).
[17] W.G. Hoover and H.A. Posch, Phys. Rev. Lett. **113**, 82 (1985).
[18] H.G. Hoover and H.A. Posch, Phys. Rev. Lett. **123**, 227 (1987).
[19] V.I. Oseledec, Trans. Mos. Math. Soc. **19**, 197 (1968).
[20] M.P. Calvo and J.M. Sanz-Serna, SIAM (Soc. Ind. Appl. Math.) J. Sci. Stat. Comput. **14**, 936 (1993).
[21] H. Ishida, Y. Nagai, and A. Kidera, Chem. Phys. Lett. **282**, 115 (1998).
[22] H. van Beijeren, J.R. Dorfman, H.A. Posch, and C. Dellago, Phys. Rev. E **56**, 5272 (1997).
[23] C. Dellago and H.A. Posch, Physica A **230**, 364 (1996).