Universal Relation between the Kolmogorov-Sinai Entropy and the Thermodynamical Entropy in Simple Liquids

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We report computation of the Kolmogorov-Sinai entropy in a variety of simple liquids studied by molecular dynamics. It is found that this quantity, when expressed in terms of the atomic collision frequency, is uniquely related to the thermodynamic excess entropy by a universal linear scaling law. We also present a simple probabilistic model for relaxation in condensed atomic systems in which the observed scaling relation arises naturally. [S0031-9007(98)07046-X]

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The intuition about the deep relation between the statistical mechanics of a system with many degrees of freedom and the instability of its dynamical evolution is already present in the work of Boltzmann. Nevertheless, only in the seminal contributions of Krylov [1] has the relevance of the exponential instability for the processes of relaxation been stated in a clear way. In particular, that work showed that the relaxation rate in a system of hard spheres is related to the rate at which a beam of trajectories diverges in the phase space. This rate can be quantified by the sum of all of the positive Lyapunov exponents which, according to the Pesin formula, expected to be true for generic chaotic systems, is equal to the Kolmogorov-Sinai (KS) entropy [2]. The latter can thus be regarded as a measure for the loss of information about the state of the system, per unit of time. This quantity is extensive; it has been shown that there is a thermodynamic limit for the KS entropy per particle in the hard-sphere gas [3]. In addition, there is clear numerical evidence [4] that in a large class of high-dimensional systems, e.g., products of random matrices, symplectic maps, chain of nonlinear oscillators, and models of simple liquids, there exist well-defined thermodynamic limits for the Lyapunov exponents; i.e.,

$$\lambda_i \simeq \lambda^* f(i/N), \tag{1}$$

where $N \gg 1$ is the number of degrees of freedom and λ^* is the first Lyapunov exponent in the limit $N \to \infty$. For the hard-sphere gas, Eq. (1) has also been established rigorously [5]. From Eq. (1) and the Pesin formula, one knows that the KS entropy is $\simeq h_{\mathrm{KS}} N$, where

$$h_{\mathrm{KS}} = \lambda^* \int_0^1 f(x)\theta[f(x)]\,dx, \tag{2}$$

where θ is the step function.

Pioneering numerical investigations of the spectra of Lyapunov exponents in liquids were performed by Posch and Hoover [6]. For a discussion on the thermodynamic limit of the KS entropy per particle in the hard-sphere gas, see [3].

An important issue is the relation between statistical properties, e.g., transport coefficients, and dynamical indicators as Lyapunov exponents and the KS entropy. In simplified models, as Lorentz gas, which are highly nontrivial from the mathematical point of view, some relevant results have been obtained (see, e.g., [7,8]).

On the other hand, it has recently been found [9] that the diffusion coefficient in simple atomic condensed systems, expressed in terms of the frequency of atomic collisions, is related to the thermodynamic entropy by a universal scaling law. This law is valid for the cage diffusion, a characteristic mechanism of atomic dynamics at high densities [10,11], whereby the atomic transport is controlled by the structural relaxation. Therefore, it is conceivable to expect that, for this kind of dynamics, a similar universal relation between the KS entropy and the thermodynamic entropy may be observed. In this Letter, we present strong evidence, based on the molecular dynamics simulations, that, at least in the case of simple liquids, such a relation, indeed, exists.

Let us note that the KS entropy, at variance with the thermodynamic entropy, is a quantity related to the time evolution. The KS entropy measures the time rate of loss of information as a chaotic phase-space trajectory evolves [12].

Since the KS entropy has the dimensionality of inverse time, its unifying description requires a universal time scale. Following the arguments presented earlier [9], we adopt the Chapman-Enskog approach [13], whereby the atomic dynamics is scaled in terms of the average collision frequency. This quantity can be calculated as [14,15]

$$\Gamma_{\mathrm{coll}} = 4\sigma^2 \rho g(\sigma) \sqrt{\frac{\pi k_B T}{m}}. \tag{3}$$

Here σ is the effective atomic diameter, defined as the position of the first maximum of the pair correlation function $g(r)$; ρ is average number density; $\rho g(\sigma)$ is the density of neighbors at the collision distance.

The excess entropy, S_{ex}, is the difference between the thermodynamic entropy and that of the ideal gas at the same thermodynamic state. The difference between the entropy of two states of a system can be calculated using thermodynamic integration along a reversible thermodynamic path connecting the two states [16]. If this path represents expansion at the constant temperature T, the change in the entropy is

$$S_2 - S_1 = \frac{1}{T}\int_{V_1}^{V_2} P\,dV + \frac{1}{T}(E_2 - E_1), \qquad (4)$$

where P is pressure and E is the energy. At constant density, the entropy change can be calculated as

$$S_2 - S_1 = \frac{E_2}{T_2} - \frac{E_1}{T_1} + \int_{T_1}^{T_2} dT\,\frac{E}{T^2}. \qquad (5)$$

To obtain S_{ex} by integration, equilibrium values of the quantities involved must be calculated at state points along a reversible path connecting the current state of a liquid with the perfect gas state. By using both the isothermal integration and the constant volume integration, it is possible to produce for each liquid such a path avoiding the irreversibility that may arise when crossing two-phase regions in the phase diagram.

In order to investigate the relation between the KS entropy and the excess entropy, we examine a set of simple monatomic liquid systems simulated by molecular dynamics (MD). These liquids, characterized by the pair potentials shown in Fig. 1(a), represent distinctly different prototypes of liquid structure. The local order in the Lennard-Jones (LJ) liquid is topologically related to the fcc packing. Another liquid [17], referred to as IC, is dominated by icosahedral order. The structure of the so-called "hexon" liquid (HX) [18], related to the primitive hexagonal lattice, has an anomalously small number of neighbors at the contact distance as compared to densely packed structures. It is important to note that structural diversity of these liquids, which is apparent from comparison of their $g(r)$ shown in Fig. 1(b), has a profound impact on their kinetic properties [9].

The KS entropy has been computed using the standard algorithm introduced by Benettin *et al.* [19]. For a system of N particles, $3N$ phase-space trajectories are generated by MD, initially separated from the reference trajectory by an orthogonalized set of tangent phase-space vectors of assumed small length Z_0. At each iteration i, after elapsed run-time T, one obtains $3N$ vectors measuring the deviation of the perturbed trajectories from the reference one, and the volume V_i of the phase space spanned by these vectors is computed. The next iteration starts with orthogonalizing the tangent vectors and scaling them to the initial size Z_0. The average value of the KS entropy after M iterations is

$$h_{\mathrm{KS}} = \frac{1}{MT}\sum_{i=1}^{M} \ln\left(\frac{V_i}{V_0}\right), \qquad (6)$$

where $V_0 = Z_0^{3N}$.

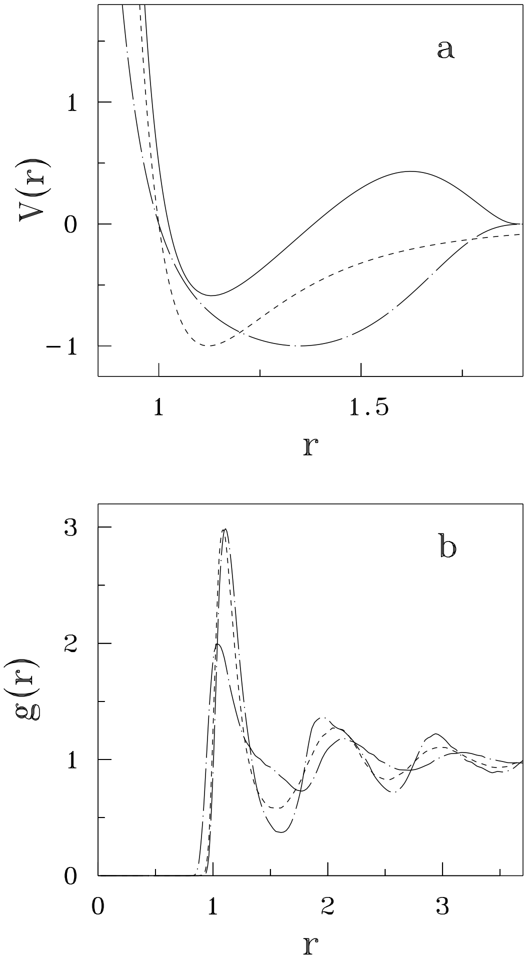

FIG. 1. (a) The pair potentials utilized in this simulation; (b) the pair correlation functions of the liquids generated by these pair potentials. Solid line, IC liquid [17]; dashed line, the Lennard-Jones (LJ) liquid; dash-dotted line, the hexon liquid [18].

The simulation has been carried out using a system of 500 particles. By choosing T within the range of 10–20 collision times and the $M = 100$, we achieved the statistical accuracy of 0.5% for h_{KS}.

The equations of motion were integrated using the Verlet algorithm [16] which, due to its symplectic nature, conserves the phase-space volume [20]. A cumulative error in the KS entropy caused by a limitation of numerical accuracy could be estimated from the spectrum of the Lyapunov exponents λ_i for $i \simeq 3N$. This error did not exceed 1%.

The results of this calculation are presented in Fig. 2. They show convincingly that there exists a unique and universal relation between the KS entropy, scaled by Γ_{coll}, and the excess thermodynamic entropy. Within a wide range of thermodynamic conditions which essentially cover the whole equilibrium liquid domain, the observed universal relation can be approximated by a linear law:

$$\frac{h_{\mathrm{KS}}}{\Gamma_{\mathrm{coll}}} = A + BS_{\mathrm{ex}}, \qquad A = 0.62, \qquad B = 0.106. \qquad (7)$$

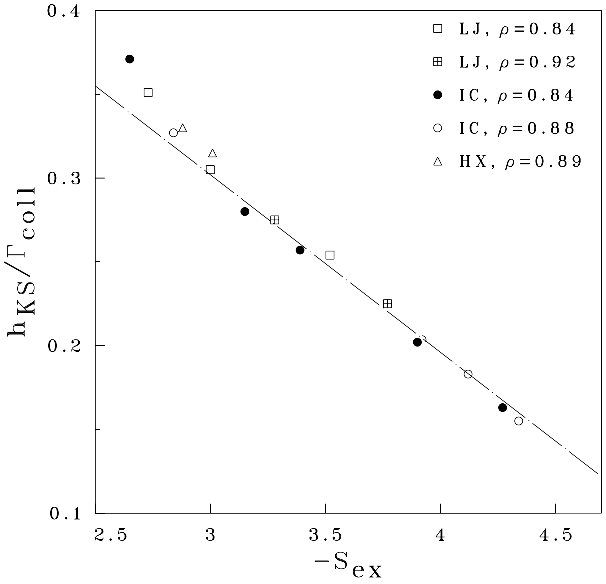

FIG. 2. The Kolmogorov-Sinai entropy, per particle, h_{KS}, scaled by the atomic collision frequency Γ_{coll}, as a function of S_{ex}, the thermodynamic excess entropy. The dashed line indicates the universal scaling relation [Eq. (7)].

The linear relation between the excess entropy and the KS entropy described by Eq. (7) breaks at around $S_{\mathrm{ex}} = -2.5$. Beyond that limit, the pattern of results, while remaining universal, exhibit an appreciable positive deviation from the scaling behavior described by Eq. (7). It is worthwhile to compare this observation with an earlier study [9], whereby the liquids we explore in this simulation have been found to show a universal scaling relation between the diffusion coefficient and the excess entropy. In that study, positive deviation from the universal linear scaling behavior has been observed at the thermodynamic conditions which correspond to the same region of S_{ex} which bounds the linear relation (7). That deviation has been concluded to manifest the crossover from the regime of cage diffusion dynamics, characteristic of the liquid state, to the so-called vortex diffusion observed in lower-density fluids [10]. In the former, atomic transport is constrained by structural relaxations; in the latter, diffusive atomic motions are enhanced by coupling to the transverse current modes [11]. The results presented here indicate that this dynamical transition has a general impact on the phase-space behavior of atomic systems.

It is worthwhile to discuss the results for the HX liquid which represent an interesting case for testing the observed universality of the relation between h_{KS} and S_{ex}. This liquid, in contrast to the other two liquids investigated in this study, has a much less pronounced structure which is manifested by the undersized first peak of the radial distribution function (see Fig. 1). This feature results in a considerable reduction of the collision frequency. Another consequence of the distinctive structure of this liquid is that the absolute value of its excess entropy, at the thermodynamic conditions close to the triple point [18], is anomalously small (see Fig. 2). Nevertheless, the results for this liquid presented in Fig. 2 are in a good agreement with the observed universal pattern.

To rationalize the universal relation between the KS entropy and the excess entropy observed in this simulation, we propose a simple model of relaxation in liquids in the spirit of the Boltzmann approach to kinetic theory. Consider a system of N particles such that, at each step, each particle takes any of $C \gg 1$ accessible positions, in the μ space (i.e., the phase space of the single particle). In order to change the thermodynamic state we assume a structural constraint on the model: each particle position, in the μ space, is closed with the probability p, $0 \leq p \leq 1$. The probability P_i of each configuration i of the system which remains open increases by the factor $(1 - p)^{-N}$. The entropy of the system as a function of p can be written as

$$\begin{aligned} S(p) = -\sum_i P_i \ln P_i &= S(0) + N \ln(1 - p) \\ &= S(0) + N\Delta S\,. \end{aligned} \tag{8}$$

$\Delta S = \ln(1 - p)$ is thus the excess entropy, per particle, of the constrained system measured with respect to the reference system with $p = 0$. Furthermore, in the constrained system, the probability to have a transition to an available new configuration, $W_{i,j}$, is increased by the factor $(1 - p)^{-N}$. Now we approximate the dynamics as a Markov chain; therefore the KS entropy per step is nothing but the Shannon entropy:

$$H(p) = -\sum_i P_i \sum_j W_{ij} \ln W_{ij} \simeq H(0) + N \ln(1 - p)\,. \tag{9}$$

This gives the KS entropy per particle and unit time:

$$h_{\mathrm{KS}}(p) = \frac{1}{N\tau} H(p) = h_{\mathrm{KS}}(0) + \frac{1}{\tau}\Delta S\,, \tag{10}$$

where τ is the physical time interval between two consecutive steps. Assuming that the relevant physical time scale is proportional to the average collision time, we arrive at the Eq. (7), established numerically in the MD simulation experiment.

In this model, the probability of a particle jumping to a new position is proportional to $1 - p = e^{\Delta S}$. Assuming that a particle is displaced by a typical distance at each step, and that these steps are uncorrelated, we get for the diffusion coefficient D the same scaling relation as has been previously observed in MD simulations [9]: $D \propto e^{\Delta S}$. That observation, considered together with Eqs. (7) and (10), allows one to establish a connection between the transport properties of simple liquids and the KS entropy.

A tentative conclusion of this study is that, in equilibrium simple liquids, the KS entropy is determined by the thermodynamic excess entropy and the frequency of atomic collisions. It is important to emphasize that the latter quantity can be directly derived from structural data.

Thus, we obtained strong evidence for a general relationship between the static properties and the dynamical processes in liquids. The thermodynamic entropy may be regarded as a measure of the volume of the region of motion in the phase space which confines the equilibrium dynamics of a system of particles [21]. The observations described in this Letter indicate that the characteristic time scale of the relaxation processes in an equilibrium liquid, which can be related to the rate at which it explores its region of motion in the phase space, is uniquely determined by the volume of that region.

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