


Sensitivity of nonequilibrium relaxation to interaction potentials: Timescales of response from Boltzmann's H function

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We investigate, by simulations and analytic theory, the sensitivity of nonequilibrium relaxation to interaction potential and dimensionality by using Boltzmann's H function $H(t)$. We evaluate $H(t)$ for three different intermolecular potentials in all three dimensions and find that the well-known H theorem is valid and that the H function exhibits rather strong sensitivity to all these factors. The relaxation of $H(t)$ is long in one dimension, but short in three dimensions, longer for the Lennard-Jones potential than for the hard spheres. The origin of the ultraslow approach to the equilibrium of $H(t)$ in one-dimensional systems is discussed. Importantly, we obtain a closed-form analytic expression for $H(t)$ using the solution of the Fokker-Planck equation for velocity space probability distribution and compare its predictions with the simulation results. Interestingly, $H(t)$ is found to exhibit a linear response when vastly different initial nonequilibrium conditions are employed. The microscopic origin of this linear response is discussed. The oft-quoted relation of H function with Clausius's entropy theorem is discussed.

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I. INTRODUCTION

One hundred fifty years ago, in 1872, Boltzmann introduced his H function and H theorem, which heralded the birth of statistical mechanics [1–3]. It attempted to address many questions and was successful in some of them. Since Newton's equations are time reversible, the evolution of an initial nonequilibrium state irreversibly to a unique equilibrium state has always been a subject of intense discussions that involve, among other theories, Poincaré's recurrence and Boltzmann's H theorem. The former is resolved by noting the extraordinarily long time for the recurrence in a macroscopic system; the latter continues to be the subject of interest and lively speculation. Boltzmann's H theorem has retained the status of one of the best well-known theorems of statistical mechanics, even though it is fairly restrictive and, in principle, strictly applicable only to a dilute gas [1–3]. However, the H function is general, although it has not been evaluated in many applications.

In its original form, Boltzmann's theorem considers the nonequilibrium function $H(t)$ defined by the following integration [1–5],

$$H(t) = - \int d\mathbf{p} f(\mathbf{p}, t) \ln f(\mathbf{p}, t), \quad (1)$$

where \mathbf{p} is a D -dimensional momentum vector and $f(\mathbf{p}, t)$ is the time-dependent momentum (\mathbf{p}) distribution function.

Note the simplicity of Eq. (1): it does not contain integration over position coordinates. Thus, it is not an average over the full phase space. If we need to make any connection with thermodynamics like entropy, then this point becomes

useful, as we discuss later. Thus, the nonequilibrium state is nonequilibrium with respect to momentum only. In essence, the H function assumes either the system is homogeneous, or the position relaxation is much slower than momentum relaxation.

Boltzmann's H theorem states that if the distribution $f(\mathbf{p}, t)$ satisfies Boltzmann's transport equation, then [1–8]

$$\frac{dH}{dt} \geq 0. \quad (2)$$

The equality sign is satisfied only at equilibrium when the distribution attains the Maxwell form. That is, when $f(\mathbf{p}, t)$ is not an equilibrium distribution, the function H will continuously increase until the equilibrium distribution is reached. Thus, the time dependence of $H(t)$ can be a quantitative measure of the rate of approach of $f(\mathbf{p}, t)$ to equilibrium.

Differentiation of the H function is given by

$$\frac{dH(t)}{dt} = - \int d\mathbf{p} \frac{\partial f(\mathbf{p}, t)}{\partial t} [1 + \ln f(\mathbf{p}, t)]. \quad (3)$$

Since, at equilibrium, $\partial f(\mathbf{p})/\partial t = 0$ for all \mathbf{p} this implies that $\frac{dH}{dt} = 0$.

In the following, we briefly outline a proof of the H theorem. We start with the Boltzmann kinetic (or transport) equation that, in its final form, is written as

$$\left[\frac{\partial}{\partial t} + \frac{\mathbf{p}}{m} \cdot \nabla_{\mathbf{r}} + \mathbf{F} \cdot \nabla_{\mathbf{p}} \right] f^{(1)}(\mathbf{r}, \mathbf{p}, t) = \left(\frac{\partial f^{(1)}}{\partial t} \right)_{\text{coll}}, \quad (4)$$

where \mathbf{F} is the external force acting on a particle. It depends on position only. \mathbf{p} is the momentum of particle with mass m ; $f^{(1)} \equiv f^{(1)}(\mathbf{r}, \mathbf{p}, t)$ is the one-particle distribution function; $\nabla_{\mathbf{r}}$ and $\nabla_{\mathbf{p}}$ are the gradient operators with respect to \mathbf{r} and \mathbf{p} , respectively.

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The collisional term is written as

$$\left(\frac{\partial f^{(1)}}{\partial t}\right)_{\text{coll}} = \iiint d\mathbf{p}_2 d\mathbf{p}'_1 d\mathbf{p}'_2 \delta(\mathbf{P}_f - \mathbf{P}_i) \delta(E_f - E_i) \times |T_{fi}|^2 (f_{1'2'}^{(2)} - f_{12}^{(2)}). \quad (5)$$

Here, \mathbf{P}_i and E_i denote the total momentum and energy before a collision, respectively; \mathbf{P}_f and E_f represent the total momentum and energy after the collision. One can easily identify the energy and momentum constraints. The T matrix gives the transition probability. $f^{(2)} \equiv f^{(2)}(\mathbf{r}, \mathbf{p}_1, \mathbf{p}_2, t)$ is the two-body distribution function. At this stage, we employ the assumption of molecular chaos to express the two-particle distribution function $f^{(2)}$ in terms of the product of two one-particle distribution functions, i.e., $f^{(2)}(\mathbf{r}, \mathbf{p}_1, \mathbf{p}_2, t) \approx f^{(1)}(\mathbf{r}, \mathbf{p}_1, t) f^{(1)}(\mathbf{r}, \mathbf{p}_2, t)$. Here, \mathbf{p}_1 and \mathbf{p}_2 are the momenta of any two particles before a collision, whereas \mathbf{p}'_1 and \mathbf{p}'_2 are the momenta after the collision.

In the absence of any external force, it is consistent to assume that the one-particle distribution function is independent of \mathbf{r} and thus can be denoted by $f(\mathbf{p}, t)$. After certain algebraic manipulations, we are led to the following condition for the time derivative of the H function [4]:

$$\frac{dH}{dt} = -\frac{1}{4} \int d\mathbf{p}_2 d\mathbf{p}'_1 d\mathbf{p}'_2 \delta(\mathbf{P}_f - \mathbf{P}_i) \delta(E_f - E_i) |T_{fi}|^2 \times (f_2^{(1)} f_{1'}^{(1)} - f_2^{(1)} f_1^{(1)}) [\ln(f_2^{(1)} f_1^{(1)}) - \ln(f_2^{(1)} f_{1'}^{(1)})]. \quad (6)$$

The integrand in Eq. (6) is never positive, so the H theorem is satisfied. Thus, in the above derivation, the H theorem is tied to the validity of the Boltzmann kinetic equation.

Despite the formidable character of Eq. (6), a calculation of the H function itself is easy to implement, and its quantitative evaluation can be carried out without any approximation. We first need to obtain or define a nonequilibrium time-dependent momentum distribution function. The simplicity lies in the singlet character of the distribution. Note that the criticism of molecular chaos assumption that is explicit in Eq. (6) is not at all required in the definition of the H function given in Eq. (1). Thus, while it is very difficult to evaluate Eq. (6), Eq. (1) can be evaluated by computer simulations by creating various nonequilibrium momentum distribution functions. As the time-dependent nonequilibrium distribution approaches the Maxwell-Boltzmann velocity distribution, the H function also evolves simultaneously and provides a measure of the nature and timescale of the relaxation. To date, we are aware of only a few explicit evaluations of this function [4,9–12]. This is because initial studies attempted to obtain $H(t)$ through the solution of the Boltzmann kinetic equation, which is hard [4]. There have also been several studies using a generalized Boltzmann (GB) H function defined differently where the following expression has been used [5,13,14]:

$$H_{\text{GB}}(t) = - \int dx P(x, t) \ln \left[\frac{P(x, t)}{P_{\text{eq}}(x)} \right]. \quad (7)$$

This generalized form of Boltzmann's H function serves a similar purpose as the original Boltzmann's H function. Here, $P_{\text{eq}}(x)$ is the equilibrium distribution of a given variable x . The variable “ x ” has often been assumed to be a position variable

or a combination thereof. This is the form advocated in the well-known monograph of Kubo *et al.* [5].

In this work, we shall be concerned with quantitative aspects of nonequilibrium velocity relaxation using the *original H function*. We ask the following questions: (i) What are the timescales of the growth of this function? We imagine that this would be related to the friction or diffusion constant of the gas, but the quantitative dependence is not clear. (ii) One, fortunately, knows the exact solution of the momentum-space Fokker-Planck equation which, even in such a simple case, gives a nontrivial time dependence of the single-particle momentum-space distribution function, $f(\mathbf{p}, t)$. We would like to check the reliability of this description. (iii) What is the range of validity of Boltzmann's H theorem for interacting systems? We ask this question because Boltzmann's entire treatment was for dilute gas, and the H function does not contain any spatial variables. Furthermore, Boltzmann's proof used his kinetic equation, which we know has limited validity. (iv) Does $H(t)$ satisfy linear response? (v) How can we relate this to entropy in a rigorous way, given that the original H function contains only velocity?

In order to understand, examine, and employ the H theorem, it is essential to create a proper nonequilibrium momentum distribution function in an isolated system. We studied several such distribution functions and evaluated $H(t)$ for different three-, two-, and one-dimensional (3D, 2D, and 1D) systems, namely, (i) Lennard-Jones, (ii) soft sphere, and (iii) hard sphere corresponding to initial nonequilibrium velocity distributions. The simulation details have been described in the next section.

II. SIMULATION DETAILS

We have carried out a series of nonequilibrium molecular dynamic simulations of dilute gases in one, two, and three dimensions in order to study the evolution of the H function. Our model system consists of 10 000 particles in each case. We have carried out these simulations in the microcanonical ensemble (constants N , V , and E) by applying the usual periodic boundary conditions. We choose three different radially symmetric potentials: (a) Lennard-Jones (LJ), (b) soft sphere (SS), and (c) hard sphere (HS) to define the interaction between any two particles. The potential forms are given below:

for Lennard-Jones,

$$U_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (8)$$

for soft-sphere,

$$U_{\text{SS}}(r) = \epsilon \left(\frac{\sigma}{r} \right)^{12}, \quad (9)$$

and, for hard-sphere,

$$U_{\text{HS}}(r) = \infty \quad \text{if } r < \sigma \\ = 0 \quad \text{if } r > \sigma. \quad (10)$$

We have taken the diameter and mass of the particles equal to unity, i.e., $\sigma = 1.0$ and $m = 1.0$. For Lennard-Jones and soft-sphere potentials, we keep the interaction strength $\epsilon = 1.0$. The reduced density ($\rho^* = \frac{Nm}{L^D} \frac{\sigma^D}{m}$) is taken as 0.10 for all the

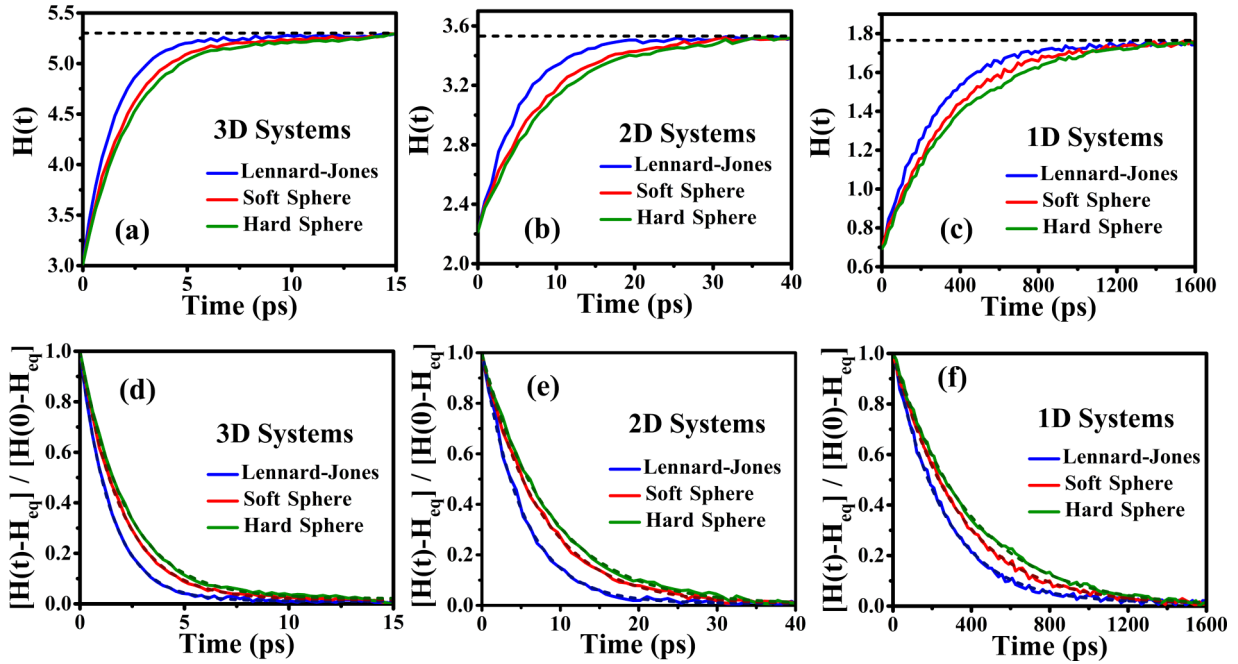


FIG. 1. Time evolution of $H(t)$ obtained via computer simulations for (a) 3D, (b) 2D, and (c) 1D systems of dilute gases (at reduced density $\rho^* = 0.10$, and average reduced temperature, $T^* = 2.0$) interacting with Lennard-Jones [the blue (upper) line], soft-sphere [the red (middle) line], and hard-sphere [the green (lower) line] potentials. In all the cases, the H function increases monotonically and then attains equilibrium at a longer time, which is the equilibrium value at the final temperature, shown by black dashed lines in the figures. Panels (d)–(f) depict time evolution of the normalized $H(t)$ [for the results shown in (a)–(c), respectively] interacting with Lennard-Jones [the blue (lower) line], soft-sphere [the red (middle) line], and hard-sphere [the green (upper) line] potentials. The corresponding dotted lines show the exponential fitting of the normalized $H(t)$. Note the different timescales in each case.

systems, where N is the total number of particles, L is the length of the simulation box, and superscript “ D ” represents the dimensionality of the system.

The initial configurations (position) for Lennard-Jones and soft-sphere systems were taken from equilibrium simulations in the canonical (NVT) ensemble corresponding to $T^* = 2.0$, whereas for the hard sphere system, initial configurations (position) were taken from equilibrium simulation in the microcanonical (NVE) ensemble. Followed by that, the initial nonequilibrium state is created by taking the amplitude of the velocities of all the particles exactly the same; the magnitude is in accordance with the equipartition theorem corresponding to the reduced temperature $T^* = k_B T / \varepsilon = 2.0$. For 3D and 2D systems, it has been illustrated in the Supplemental Material (Fig. S1) [15] while for the 1D system, it has been shown in Fig. 2(a). This approach allows us to carry out the simulation in the microcanonical (NVE) ensemble.

For Lennard-Jones and soft sphere systems, the equations of motion were integrated using the velocity-Verlet algorithm [16] with a time step $\Delta t^* = 0.001\tau$. The scaled time has been denoted as $\tau = \sigma \sqrt{m/\varepsilon}$. For the hard-sphere system, we have performed event-driven molecular dynamics (EDMD) simulation, which is the standard way of performing hard-particle simulation and extensively documented [17,18]. In this approach, only binary collisions (which is a valid assumption for dilute gases) were employed. Postcollisional velocities were calculated according to mass, diameter, and precollisional velocity information of the colliding pair by satisfying conservation equations of energy and momentum. However,

in order to calculate $H(t)$, we have obtained the distribution of $f(\mathbf{p}, t)$ at a regular time interval, $\Delta t^* = 0.0005\tau$.

Boltzmann’s H function, defined as $H(t) = -\int d\mathbf{p} f(\mathbf{p}, t) \ln f(\mathbf{p}, t)$, is a relatively simple function; however, its evolution for 3D systems is quite complicated as it involves a three-dimensional integral.

In this work, the timescales have been converted from reduced time (t^*) to real time (t) using the relation $t^* = t \sqrt{\frac{\varepsilon}{m\sigma^2}}$, where the values of ε , m , and σ have been taken corresponding to that of an argon atom, i.e., $\varepsilon/k_B = 119.8$ K, $m = 0.03994$ kg/mol, and $\sigma = 3.405 \times 10^{-10}$ m.

III. RESULTS AND DISCUSSION

In Figs. 1(a)–1(c), we show the evolution of $H(t)$ for different systems of dilute gases (at reduced density, $\rho^* = 0.10$ and average reduced temperature, $T^* = 2.0$, which is obtained by a procedure mentioned above) where not only the interaction potential is varied from system to system but also the dimensionality of the systems is changed. We see that in all the cases, the H function sharply increases in a *short time* and subsequently monotonically approaches the equilibrium value (shown by a black dotted line) *at a longer time*, which is the *equilibrium value* at the chosen temperature. Note that the timescales have been converted from reduced unit to real unit (in ps) using the argon parameters. In order to get the relaxation times corresponding to different system, $H(t)$ is fitted with the function $H(t) = H_{eq} + \{[H(0) - H_{eq}] \exp(-t/\tau_H)\}$. In Figs. 1(d)–1(f), we show normalized $H(t)$, defined as

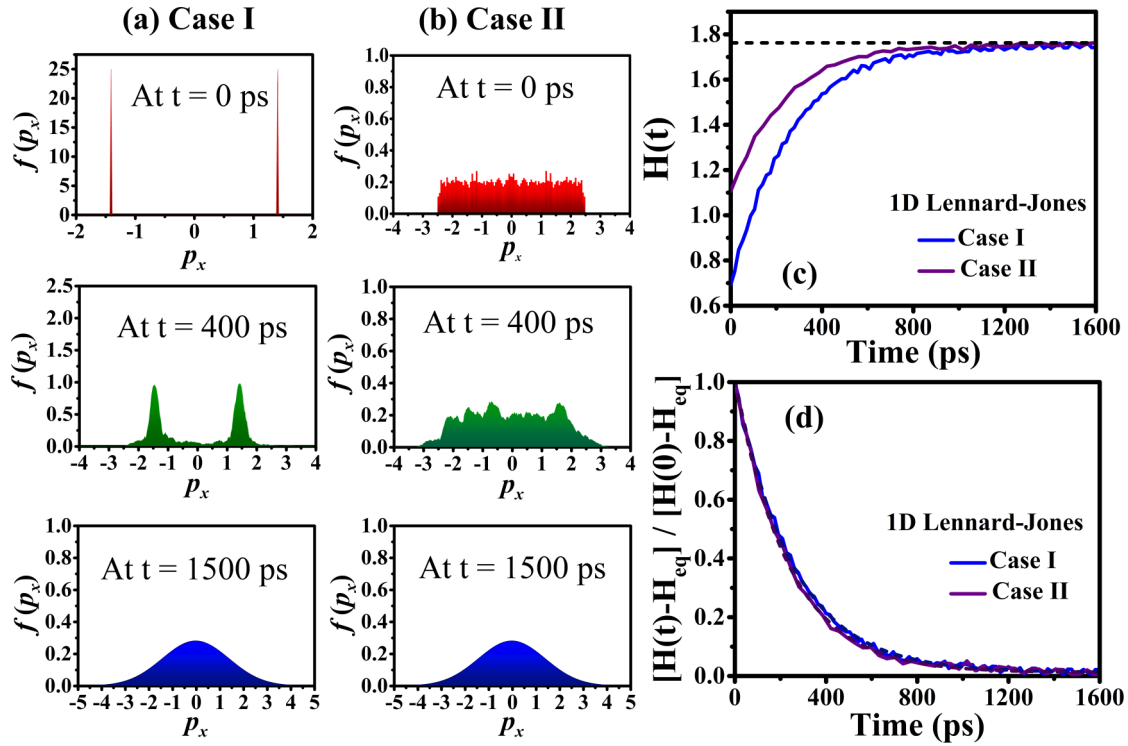


FIG. 2. Evolution of the momentum distribution at different times when initially all particles have (a) the same amplitude of velocity, and (b) random uniform distribution of velocity. (c) Time evolution of the H function for 1D Lennard-Jones systems with two different initial distributions. For case I, it is shown by the blue (lower) line, whereas for case II, it is shown by the purple (upper) line. (d) Time evolution of the normalized H function, showing the validity of linear-response theory. The corresponding dotted lines show the exponential fitting of $H(t)$. The final distribution in each case is Maxwellian and identical.

$[H(t) - H_{eq}]/[H(0) - H_{eq}]$ and its exponential fit. The relaxation times (τ_H) for 3D systems are given in Table I while those of 2D and 1D systems are provided in the Supplemental Material [15].

It is evident from Fig. 1 that the nonequilibrium relaxation function $H(t)$ is sensitive to both potential and dimensionality. For 3D systems, the approach of $H(t)$ to the equilibrium value is the fastest, while for 1D systems, it is the slowest. We also find that in all cases, the relaxation times of the systems interacting via Lennard-Jones potential are faster than those interacting via hard-sphere potential.

The faster relaxation of $H(t)$ for the Lennard-Jones system can be attributed to the longer-range nature of the intermolecular potential between particles as compared to the other two potentials employed in the present study. This allows interaction with a larger number of particles, giving rise to larger fluctuations of the force on the tagged particles. This larger fluctuation of the force gives rise to larger friction than that for the hard-sphere and soft-sphere fluids.

TABLE I. The relaxation times obtained by fitting of the calculated $H(t)$ for three-dimensional systems, with three different interaction potentials.

Systems	τ_H (ps)
Lennard-Jones	1.463 ± 0.052
Soft sphere	1.952 ± 0.034
Hard sphere	2.182 ± 0.043

On the other hand, the behavior of the soft sphere remains similar to hard spheres (with small differences discussed below). This can be partly understood using Barker-Henderson-Weeks-Chandler-Andersen (BHWCA) theories of liquids that allow us to map a soft sphere to a hard sphere system [19–23]. At high temperatures ($T^* = 2$), the effective radius predicted by BHWCA theories of the soft sphere is quite similar to that of the hard sphere. However, this mapping is not perfect when translated to dynamics because friction can still be larger for the soft sphere than the hard sphere, which we indeed find by inverting Einstein’s relation. Another notable difference lies in the ultrashort time where friction experienced in the soft-sphere fluid is less than that for the hard-sphere fluid. This slow relaxation of $H(t)$ for hard-sphere systems deserves further study.

While the validity of Boltzmann’s theorem as the arrow of time was never in doubt at very-low-density gas, quantitative estimates of timescales were not known. This in itself is an interesting issue because as density decreases, collisions become rare, and the rate of approach to equilibrium becomes slow. But the nature and timescales at higher densities remain unexamined. Further, the effect of different initial momentum distributions on the evolution of $H(t)$ remains unaddressed. In order to examine such issues, we have performed simulations with two different initial nonequilibrium momentum distributions [as shown in Figs. 2(a) and 2(b)]. In Fig. 2(c), we show the temporal evolution of $H(t)$ for 1D Lennard-Jones systems with two different initial nonequilibrium conditions. While it seems $H(t)$ shows distinct features in the two cases, the

normalized $H(t)$ exhibits similar behavior [as shown in Fig. 2(d)] with almost the same relaxation times (the relaxation times are given in the Supplemental Material [15]). Besides that, we have checked the validity of the linear response of $H(t)$ in 2D and 3D systems. Thus, it is fair to say that $H(t)$ exhibits a linear response.

We regard the results presented in Fig. 2 as quite striking. The initial nonequilibrium distributions are quite different. The difference persists at intermediate times. Yet, the normalized $H(t)$ behaves in a *nearly identical fashion* in the two cases. We do not have a full answer for this behavior, but it certainly arises from the form of $H(t)$. We can understand partially from the fact that $p \ln p$ is a relatively weak function of p . This result needs further analysis.

We now turn to an important point. The H function and entropy have been associated with each other from the beginning because both define a direction of time. Clausius's statement asserts that the entropy of an isolated system can only increase with time. In fact, for a one-component ideal gas, one can derive a simple relation between the two [4,24–26]. For a 3D ideal gas at equilibrium, the velocity distribution is Maxwellian, and one can easily evaluate the H function at equilibrium to obtain

$$H_{\text{eq}} = -\ln\left(\frac{1}{2\pi mk_B T}\right)^{3/2} + \frac{3}{2}. \quad (11)$$

We can obtain the entropy per particle of an ideal gas from the Sackur-Tetrode equation,

$$S^{id} = k_B \ln(2\pi mk_B T)^{3/2} + k_B \ln V + \frac{5}{2}. \quad (12)$$

Thus, we obtain the following relation,

$$S^{id} = k_B H_{\text{eq}} + \text{constant}, \quad (13)$$

at constant volume V . There is an “ $\ln V$ ” term absorbed in the “constant” factor of Eq. (13).

As both the functions increase as an initial nonequilibrium state evolves to essentially the same values in the equilibrium state, it is natural to look for a relationship between H and S , even as a function of time. However, there has been *no convincing proof* that such a relation should indeed exist. The only exact statement we can make is that both can serve as the arrow of time. A strictly valid definition for time-dependent entropy is not available. One can attempt to define evolving entropy of a subsystem that is in contact with a bath that is governed by faster dynamics. For example, we can change the temperature of the system in a controlled manner, slowly, such that one can define entropy in the intermediate states. However, that remains problematic because $H(t)$, on the other hand, is defined for an isolated system.

We first consider the case when the value of $H(t)$ is only slightly different than the equilibrium value, i.e., when $f(\mathbf{p}, t)$ is close to Maxwell distribution. Let us define $\delta f(\mathbf{p}, t) = f(\mathbf{p}, t) - f_M(\mathbf{p})$. The above analysis suggests that we can attempt a stochastic approach. We now use the Fokker-Planck equation in the momentum space for $f(\mathbf{p}, t)$, given by [5,27]

$$\frac{\partial \delta f(\mathbf{p}, t)}{\partial t} = \zeta \left(\frac{\partial}{\partial \mathbf{p}} \left[\frac{\mathbf{p}}{m} + \langle E \rangle \frac{\partial}{\partial \mathbf{p}} \right] \right) \delta f(\mathbf{p}, t), \quad (14)$$

where $\langle E \rangle$ is the average energy and $\partial/\partial \mathbf{p}$ is the D -dimensional gradient in momentum space.

In three dimensions, the above equation has the solution

$$f(\mathbf{p}, t) = \frac{1}{\{2\pi mk_B T[1 - \Gamma^2(t)]\}^{3/2}} \exp(-[\mathbf{p} - \mathbf{p}_0 \Gamma(t)]^2 / \{2mk_B T[1 - \Gamma^2(t)]\}), \quad (15)$$

where $\Gamma(t) = e^{-\zeta t}$. Fortunately, we can obtain a closed-form analytic expression for $H(t)$ (in three dimensions) using the Fokker-Planck equation for the momentum-space probability distribution as follows (a detailed description is given in the Supplemental Material [15]):

$$H(t) = -\frac{3}{2} \ln \left(\frac{1}{2\pi mk_B T[1 - \exp(-2\zeta t)]} \right) + \frac{3}{2}. \quad (16)$$

The above expression can be generalized to the D -dimensional case (as discussed in the Supplemental Material [15]). We can see that this form already predicts the rapid rise of the H function followed by the attainment of the equilibrium. Thus, the Fokker-Planck equation can capture the time dependence of $H(t)$ through the distribution function $f(p, t)$. The solution needs the input of the friction, which we obtained via the integration of the velocity autocorrelation function (VACF) [at equilibrium]. The normalized velocity autocorrelation functions for 3D and 2D Lennard-Jones systems are shown in the Supplemental Material [15]. We calculated the value of friction (ζ) from the self-diffusion coefficient (D_s) using Einstein's relation $D_s = k_B T/\zeta$ and put it into Eq. (16) to obtain $H(t)$.

In Fig. 3, we compare the results obtained via simulation and Eq. (16) for 3D and 2D systems. In the case of 3D systems, we find that the Fokker-Planck equation provides a reasonable description (except at very short time) for Lennard-Jones and soft-sphere systems but fails for hard-sphere systems. The Fokker-Planck equation, unfortunately, is Markovian, so it fails to reproduce the correct short-time description, and as $t \rightarrow 0$, $H(t)$ predicted by Eq. (16) diverges. We further observe that the Fokker-Planck equation based description of $H(t)$ fails for 2D systems and also for 1D systems. This failure needs further study.

Earlier studies in 1D have pointed out the anomalous nature of particle displacements in one dimension [28–32]. In Fig. 4(a), we plot the trajectories of six adjacent particles for the 1D Lennard-Jones system at $T^* = 2.0$ and $\rho^* = 0.10$. We find that the adjacent particles in 1D show *highly correlated motion*. This highly correlated motion of adjacent particles in one dimension has already been observed experimentally by Leiderer and co-workers [33]. The correlated motion of the adjacent particles gives rise to transient longitudinal flow. In Fig. 4(b), we plot the normalized velocity autocorrelation function (VACF) of a 1D Lennard-Jones system at $T^* = 2.0$ and $\rho^* = 0.10, 0.20, 0.40, 0.60, 0.80$, and 0.95 , respectively. This shows the effect of density on the velocity autocorrelation function in 1D. For low to intermediate densities, a slow long-time decay of velocity autocorrelation function has been observed. At high densities, a negative region in velocity autocorrelation arises due to backscattering.

The breakdown of the Fokker-Planck equation in one- and two-dimensional systems can be quite instructive. We attribute

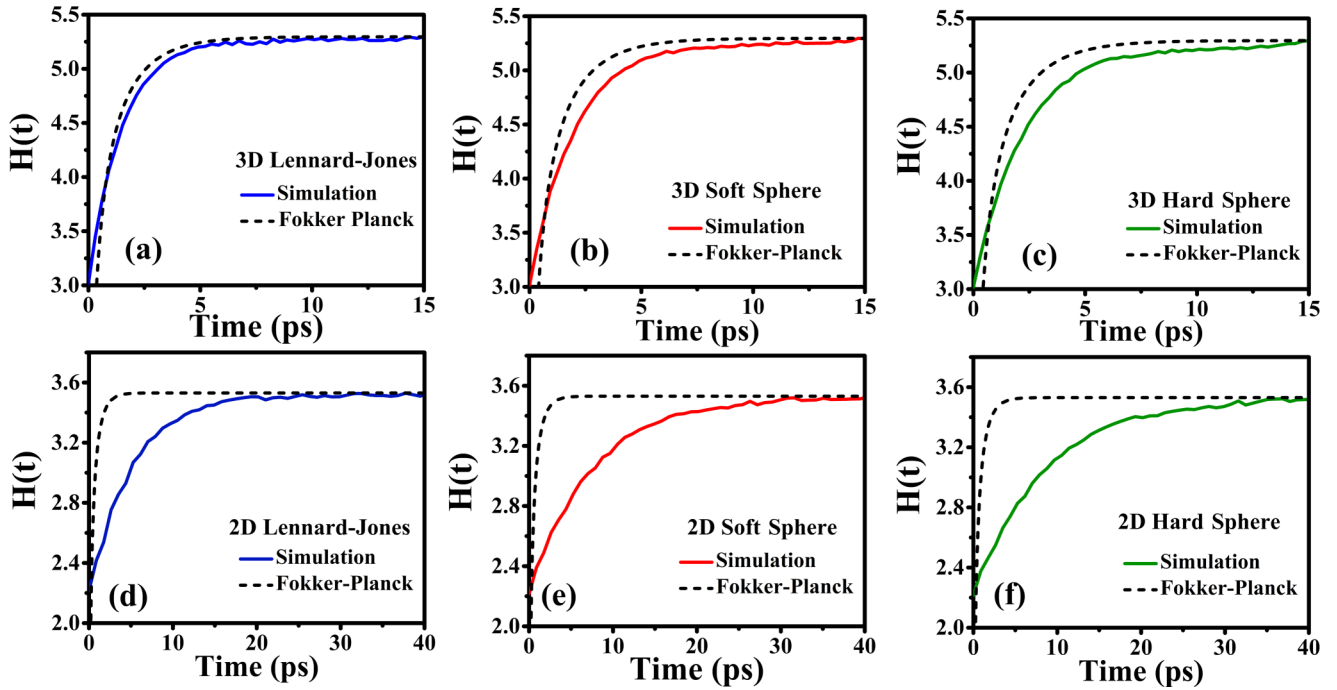


FIG. 3. The comparison of $H(t)$ obtained via computer simulation with the analytical solution from the Fokker-Planck equation for 3D and 2D systems. We employ Eq. (16) to obtain the predicted variation of $H(t)$, with ζ obtained from simulation.

this failure to the existence of correlated motions leading to pronounced memory effects even at low densities, particularly in one-dimensional systems. Thus, the Markovian Fokker-Planck equation needs to be replaced by the non-Markovian equation [34,35]. The Markovian description used here gives rise to a too large value of friction at short times.

Let us again turn to the relationship of $H(t)$ with entropy. By Boltzmann's formula, entropy is given by the logarithm of the total number of states. We can evaluate the entropy if we assume that the distribution changes infinitesimally slowly, say, at $\zeta \sim 0$. In that limit, we can calculate the total number of states and hence the entropy. That is, we need to calculate the number of configurations Ω corresponding to a given slowly evolving momentum-space distribution function.

It is interesting to inquire about the range of validity of the H theorem. From its original proof by Boltzmann using his transport equation, it is not clear that the theorem remains valid at higher densities. We verified the validity of the H theorem at $\rho^* = 0.20$ and 0.30 (in Sec. S3 of the Supplemental Material [15]). However, note that the relation between the H function and entropy may not hold at high densities because the total entropy is increasingly dominated by intermolecular correlations as the density is increased progressively.

The sensitivity of $H(t)$ to the interaction potential, of course, reflects the *sensitivity of the relaxation of $f(p,t)$* . The difference between Lennard-Jones and hard-sphere systems has been examined earlier with the Enskog approximation [36]. This is an interesting aspect we believe deserves further

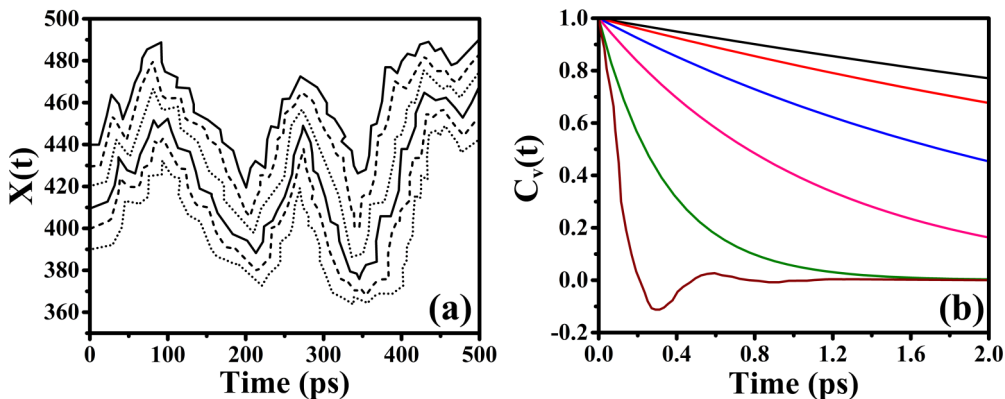


FIG. 4. (a) Trajectories of six adjacent particles obtained from molecular dynamics simulation of 1D Lennard-Jones system at $T^* = 2.0$ and $\rho^* = 0.10$. It is to be noted that the adjacent particles show highly correlated motion. (b) The normalized velocity autocorrelation function (VACF) of a 1D Lennard-Jones system at $T^* = 2.0$. The lines from top to bottom represent the system with $\rho^* = 0.10, 0.20, 0.40, 0.60, 0.80,$ and 0.95 , respectively. Note the slow decay of the VACF at low densities.

examination. It represents at least partly the dependence on the range of potential. This agrees with the much slower relaxation in one dimension where the number of nearest neighbors is limited.

IV. CONCLUDING REMARKS

As remarked earlier, there appears to be surprisingly less study of $H(t)$. The present study provides a detailed understanding of Boltzmann's H theorem, which is one of the most celebrated theorems of science and paved the way for developing nonequilibrium statistical mechanics. We find in every case Boltzmann's H theorem is verified. We also find dimension- and interaction-potentialdependent timescales which for a density of $\rho^* = 0.10$ ranges from a few picoseconds in three dimensions to several hundred picoseconds in one dimension. We find that the evolution of the H function in the case of Lennard-Jones potential is quite different from that of hard-sphere potential. We also remark here that the approach of equilibrium in 1D is substantially slower than that in 2D and 3D. The sensitivity of $H(t)$ on the potential and dimensionality of the system should help to understand many basic aspects of nonequilibrium phenomena. It would be fascinating to employ it in many areas, such as

plasma physics and active matter [12,37,38]. Finally, the failure of the Fokker-Planck description points to the importance of non-Markovian or memory effects due to correlations. It is thus no surprise that the time dependence of $H(t)$ is influenced by the interaction potential.

The function $H(t)$ continues to evoke interest endlessly. We have already mentioned Kubo's generalization. Perhaps the most important aspect is that it can provide crucial information about the relaxation of a nonequilibrium system.

We have verified numerically that the basic nature of Boltzmann's H function $H(t)$ remains unaltered at higher densities, as discussed in the Supplemental Material [15]. At such high density, Kubo's form of the H function seems more appropriate and provides a better description of relaxation [5], although its relationship with entropy remains unclear.

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