

Non-monotonic Relaxation in a Harmonic Well

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Received: 01 January 2017; revised: 12 March 2017; accepted: 15 March 2017; published online: 30 September 2017

Abstract: The dissipation function of Evans and Searles has its origins in describing entropy production, yet it has a straightforward dynamical interpretation as well. The ability to consider either dynamical or thermodynamical contexts deepens our understanding of the dissipation function as a concept, and of numerical results involving the dissipation function. One recent, important application of the dissipation function is in relaxation to equilibrium. Here we look at relaxation in a system of interacting molecules that are confined within a harmonic potential, undergoing Hamiltonian dynamics. We note some similarities, but also important differences, to previous studies. The dissipation function sheds light on the periodic return of our system towards its initial state. We find that intermolecular interactions play a much more significant role in the relaxation toward a non-uniform spatial distribution (induced by a conservative background field) than they do toward a uniform distribution, which is reflected in the strongly non-monotonic relaxation we observe. We also find that the maximum dissipation does not occur in the long-time limit, as one might expect of a relaxation process, but shortly after relaxation begins, beyond which a significant net overall *decrease* in the dissipation function is observed.

Key words: relaxation to equilibrium, dissipation function, equilibrium statistical mechanics, microcanonical ensemble

I. INTRODUCTION

Characterising relaxation to equilibrium remains a significant challenge in the statistical physics of deterministic systems. At the microscopic level we expect equilibrium dynamics to be reversible, but at the macroscopic level, everyday experience encourages an intuition that real thermodynamic systems tend to occupy ‘typical’ microscopic states, and evolve towards them if initialised in ‘atypical’ ones. Part of the challenge lies in reconciling this macroscopic ‘arrow of time’ with microscopic reversibility, but much of it also lies in translating this imprecise notion of typicality and relaxation into a more rigorous conceptualisation [1, 2].

The Boltzmann equation plays a vital role in our understanding of relaxation to equilibrium, describing the evolution of the single-particle distribution function from the microscopic dynamics [3]. Boltzmann’s *Stosszahlansatz* can be characterised (in hindsight) as an assumption of a decay in correlations. Crucially, the resulting collision term admits

the Lyapunov functional that forms the basis of the celebrated H -theorem. From a dynamical perspective, this functional guarantees a globally asymptotically stable solution to Boltzmann’s equation (the Maxwell-Boltzmann distribution), and convergence toward this distribution that is monotonic with respect to $H(t)$.

Boltzmann’s results typify the subtle difficulties here. The *Stosszahlansatz* permits a beautiful result, but it is an imperfect assumption, as has been extensively documented [3]. A few points are worth noting here, however. First is the definition of relaxation with respect to the single-particle distribution function, and the association with a decay in correlations. Second is the use of the function $H(t)$ that quantifies the relaxation process, providing a measure of proximity to the equilibrium distribution. Third is that these results can be considered purely from a dynamical point of view, and in particular without entertaining the vexed question of how H relates to the thermodynamic entropy of the system. Connections between microscopic dynamics and thermody-

dynamic properties are clearly important, but they can confound rather than contribute to our understanding when used without due care. For example, definitions of entropy that are valid for equilibrium ensembles lead to notorious problems when employed to describe relaxation from non-equilibrium states (e.g. the Gibbs entropy is a constant of the motion, so does not relax) [2, 4].

An alternative description to Boltzmann's is required for situations where the *Stosszahlansatz* is not suitable, and to characterise relaxation in situations where it is known to be complex and not trivially monotonic [5, 6]. However, there are few viable alternative approaches. In recent times, the dissipation function of Evans and Searles [7] has proven to be highly insightful in the context of non-equilibrium fluctuations and relaxation [8-10]. Its origins (and indeed its name) arise from thermodynamic considerations, but it has a straightforward dynamical interpretation [11]. Understanding both interpretations helps shed light on the relaxation process in thermodynamic settings: in systems where it is appropriate to do so, one can imbue these results with thermodynamic meaning, but away from such systems, useful dynamical results remain.

However, there are still aspects of the dissipation function and its use in describing relaxation to equilibrium that remain to be properly understood, particularly with respect to monotonicity. We introduce the dissipation function and outline these aspects in section II. To explore these matters, in this manuscript we consider an isolated fluid confined in a harmonic potential. We describe details of the system and its simulation in section III, and the outcomes of these simulations in IV, comparing them to observations in related systems. While our model describes a simple thermodynamic system, we find that its relaxation to equilibrium manifests some striking differences to previous studies [12, 13]. Finally, we draw conclusions in section V.

II. OVERVIEW OF THE DISSIPATION FUNCTION

II. 1. Origins of the dissipation function

The dissipation function arises as the central quantity in the Evans-Searles fluctuation relation [7]:

$$\frac{P(\Omega_{0,t} = A)}{P(\Omega_{0,t} = -A)} = e^A. \quad (1)$$

This relation describes the relative probability of observing trajectory segments in the time interval $[0, t]$ with entropy productions of $\pm A$ in deterministic non-equilibrium systems. The proof of Evans and Searles relies on the association between entropy production and the dissipative power, which in non-equilibrium molecular dynamics (NEMD) simulations is given by the thermostat multiplier

α [14]. This quantity can be expressed in terms of the phase space expansion rate $\Lambda(\Gamma) = \nabla \cdot \dot{\Gamma}$, where Γ denotes the state of the system in the phase space \mathcal{M} , $\dot{\Gamma}$ its rate of change, as determined by the equations of motion, and ∇ the gradient operator in the phase space. The association between entropy and phase space volumes is thus consistent with the equilibrium relationship. However, for non-equilibrium NEMD ensembles, fluctuations in phase volume must be measured relative to the corresponding fluctuations in the equilibrium ensemble, if they are to represent dissipation [7, 11]. This is easily achieved by correcting the phase space expansion term, leading to the so-called integrated dissipation function $\Omega_{0,t}^f(\Gamma)$:

$$\Omega_{0,t}^f(\Gamma) = \frac{f(\Gamma)}{f(S^t\Gamma)} - \int_0^t \Lambda(S^u\Gamma) du \quad (2)$$

where $S^t\Gamma$ is the solution to the equations of motion at time t from initial conditions Γ , and f is the equilibrium distribution. Because the dissipation function has an implicit dependence on the distribution f in its definition, we more properly denote it as $\Omega_{0,t}^f(\Gamma)$. The (un-integrated) dissipation function $\Omega^f(\Gamma)$ can be defined from Eqn. 2, although we will give a simpler interpretation below.

The association with dissipation is reinforced by comparing the transient-time correlation function (TTCF) formula for the evolution of observable values with the dissipation theorem of Evans, Searles and Williams [8]. If we define an observable as the average of a phase function with respect to a distribution, i.e.

$$\langle \mathcal{O} \rangle_f = \int_{\mathcal{M}} f(\Gamma) \mathcal{O}(\Gamma) d\Gamma \quad (3)$$

then the TTCF formalism predicts that, from an initial distribution f_0 , under the influence of an external field \mathbf{F} ,

$$\langle \mathcal{O} \rangle_{f_t} = \langle \mathcal{O} \rangle_{f_0} - \frac{V}{k_B T} \int_0^t \langle (\mathcal{O} \circ S^s) \mathbf{J} \cdot \mathbf{F} \rangle_{f_0} ds \quad (4)$$

for a thermodynamic system with temperature T , volume V , Boltzmann constant k_B , dissipative flux \mathbf{J} , and where the initial distribution f_0 has evolved to f_t at time t . In comparison, we observe from the dissipation theorem that [8]

$$\langle \mathcal{O} \rangle_{f_t} = \langle \mathcal{O} \rangle_{f_0} + \int_0^t \langle (\mathcal{O} \circ S^s) \Omega^{f_0} \rangle_{f_0} ds. \quad (5)$$

From this result we make two observations. We note the connection between Ω^{f_0} and dissipation, but we also recognise that Ω^{f_0} is related in a purely dynamical way to the time evolution of ensemble averages. Indeed, while the TTCF result relies on various assumptions about the thermodynamic

nature of the system, the dissipation theorem has a purely dynamical interpretation, highlighting the connection between the dissipation function and the distribution evolution. This result is not entirely surprising, on reflection: Liouville's theorem shows that the $f_t(S^t\Gamma)$ only differs from $f_0(\Gamma)$ due to fluctuations in phase space volumes, which are precisely the quantities associated with non-equilibrium entropy variation. It follows that one can define $\Omega^{f_t}(\Gamma)$ as a purely dynamical variable, without reference to any thermodynamic interpretation [11]:

$$\frac{\partial f_t(\Gamma)}{\partial t} = f_t(\Gamma)\Omega^{f_t}(\Gamma) \quad (6)$$

This definition is closely connected of the alternative dynamical definition of $\Lambda(\Gamma)$ afforded by Liouville's equation, $df_t(\Gamma)/dt = -f_t(\Gamma)\Lambda(\Gamma)$.

The dynamical approach allows us to generalise some key observations made in the thermodynamic context. For example, the so-called second law inequality $\langle \Omega_{0,t}^f \rangle_f$ [15], proven for ergodically consistent dynamics with initial distributions that are even in the momentum, can be shown to be valid well beyond this limitation. For any invertible (not necessarily time-reversal symmetric) dynamics, where the support of the distribution is conserved, $\langle \Omega_{0,t}^f \rangle_f \geq 0$ can be expressed as a relative entropy, and is therefore non-negative [11]. It follows that this result is not particular to thermodynamic systems, but must always be true for any dynamical system [11].

II. 2. The dissipation function and relaxation

The use of the dissipation function to describe relaxation to equilibrium is a more recent development [10], borne out of the recognition that the only dissipationless distribution is the equilibrium one (i.e. $\langle \Omega^g \rangle_f \equiv 0 \implies g = f$), and that this distribution is unique¹. Under the assumption of a time decay in correlations, the relaxation theorem predicts convergence of an initial distribution function toward the equilibrium distribution [10]. Again, we note the connection between decay in correlations and relaxation to equilibrium, as seen with the H -theorem.

There are other important differences, however. The H -theorem provides a specific quantity against which one may measure convergence to equilibrium, but the corresponding quantity for the relaxation theorem is less clear. In early work, the ensemble-averaged dissipation function $\langle \Omega^{f_0} \rangle_{f_t}$ was interpreted as indicating dissipation, so that its convergence to zero was interpreted as indicating strong convergence of f_0 to the equilibrium distribution f [10]. However, the distribution cannot converge in a strong sense, since it retains information of the initial distribution, in much the way that the Gibbs entropy does. Furthermore, it is not clear that $\langle \Omega^{f_0} \rangle_{f_t}$ can be used to quantify convergence of f_t toward

f , or that it has an unambiguous physical interpretation as dissipation at time t in this context (for more details, see Ref. [11]).

However, much more significant headway can be made by considering weak convergence via the time-evolution equation [11, 16],

$$\langle \mathcal{O} \rangle_{f_t} = \langle \mathcal{O} \rangle_{f_0} + \int_0^t \langle \mathcal{O} \Omega^{f_s} \rangle_{f_s} ds. \quad (7)$$

This result can be interpreted in a purely dynamical sense: if Ω^{f_s} becomes decorrelated from \mathcal{O} as $s \rightarrow \infty$, the quantity $\langle \mathcal{O} \rangle_{f_t}$ will converge. Two subtleties arise at this point. First, for weak convergence in the formal sense, we would require this to hold for any observable. In practice, we usually consider only a limited number of functions of particular thermodynamical interest. It is likely that the relaxation we observe in thermodynamic systems is contingent upon this separation of scales between the degrees of freedom in the system and the number and nature of phase functions whose relaxation we expect to observe [17]. Consequently, we would only require weak convergence with respect to a limited range of thermodynamically-relevant phase functions. As a second subtlety, we might reasonably expect different initial distributions to lead to the same $\langle \mathcal{O} \rangle_{f_t}$ as $t \rightarrow \infty$. This can be achieved through the assumption of T-mixing, which is a condition on the dynamics for any two observables \mathcal{O} and \mathcal{P} , that \mathcal{O} and $\mathcal{P} \circ S^t$ decorrelate as $t \rightarrow \infty$ [11, 16].

Another important difference with the H -theorem is that convergence need not be monotonic, in the sense that $\langle \Omega^{f_0} \rangle_{f_t}$ need not converge monotonically to 0 as $t \rightarrow \infty$. Reid *et al.* [12] studied relaxation in a model of a so-called capture experiment [18], where a single particle in a thermal bath is trapped in a laser. The laser is modelled as a harmonic potential: in the relaxation study, the potential strength is changed, and the relaxation in the thermal bath studied. Reid *et al.* found that the relaxation was not monotonic, with $\langle \Omega^{f_0} \rangle_{f_t}$ alternating sign over consecutive t -intervals of similar duration. However, the positive contributions strongly outweighed the negative contributions, and the fluctuations appeared as a relatively small perturbation.

A more recent example of non-monotonic relaxation appears in the work of Petersen *et al.* [13], which is based on the perhaps canonical example of relaxation to equilibrium — free expansion. For technical reasons one cannot study free expansion directly using the dissipation function, but Petersen *et al.* study analogous systems, where two species of otherwise identical particles are initiated with non-uniform distributions in position, and allowed to relax while in thermal equilibrium with an external reservoir. When the initial position distributions comprise low Fourier modes only, the relaxation appears to be monotonic, with

¹ we restrict ourselves here and throughout to distributions that are absolutely continuous with respect to the Lebesgue measure

$\langle \Omega^{f_0} \rangle_{f_t}$ remaining positive out to long times. As higher harmonics are included in the initial position distribution, the variation of $\langle \Omega^{f_0} \rangle_{f_t}$ exhibits gentle monotonicity, with a strongly monotonic initial phase, followed by small fluctuations. It is conceivable that such fluctuations also appear for the lower modes only, but that they are much smaller.

From a theoretical perspective, the meaning of this monotonicity is much less clear. In Boltzmann's work, H must decrease monotonically since it is a Lyapunov function, but as mentioned above $\langle \Omega^{f_0} \rangle_{f_t}$ cannot play such a role [11]. Evans and co-workers identified the condition of *conformal* relaxation as a sufficient condition for monotonic relaxation of $\langle \Omega^{f_0} \rangle_{f_t}$ [10]: if the relaxation could be described as a single-parameter perturbation to the equilibrium distribution function that is even in the momentum, with the parameter decaying to zero (i.e. no perturbation) during the relaxation process, then such relaxation would be monotonic. Unfortunately, such relaxation is not possible [11]. Under the condition of conformal relaxation, the distribution remains even in the momenta for all times, which immediately implies that $\langle \Omega^{f_0} \rangle_{f_t} = 0$ for all times. Relaxation from an even perturbation in the momentum must break this momentum symmetry. It is possible that such symmetry-breaking distributions could exhibit a conformal relaxation, as seen in Petersen *et al.* [13], although this remains to be shown.

III. MODEL DETAILS

In this paper, we consider relaxation in a system that is in some sense of combination of the models discussed above. One can consider the simulations of Petersen *et al.* [13] as relaxation from one initial equilibrated state to another: the states differ by the external potential (which is uniform for the final state). A similar situation occurs in the work of Reid *et al.* [12], where the external potential is only applied to one particle, and is not uniform in either case. In our work, all particles are trapped in an external harmonic field, centred at the origin.

Unlike these previous works, however, we considered a microcanonical ensemble of systems, rather than the canonical-ensemble approach. Also different from these earlier works, and because of this choice, we do not consider relaxation from one equilibrium state to another. In our approach, we construct our initial constant-energy system to have non-microcanonical initial distribution, in order to observe relaxation to equilibrium. To achieve this, we generate initial conditions sampled from the microcanonical ensemble with 'generating' Hamiltonian $\mathcal{H}_{\text{gen}}(\Gamma)$ at energy E , and transform these into initial conditions for a second microcanonical system with 'final' Hamiltonian $\mathcal{H}_{\text{fin}}(\Gamma)$, also at energy E (for convenience). Specifically, we

1. generate a set of initial conditions $\{\Gamma_n\}$ consistent with the microcanonical ensemble $\mathcal{H}_{\text{gen}}(\Gamma_n) = E$;

2. apply a transformation (bijection) to generate the set of initial conditions $\{\Gamma'_n = T(\Gamma_n)\}$ such that $\mathcal{H}_{\text{fin}}(\Gamma'_n) = E$, but which are not distributed microcanonically; and
3. average the dissipation function from this non-microcanonical distribution of initial states as they equilibrate.

In this paper, we will consider Hamiltonians of the form

$$\begin{aligned} \mathcal{H}_\alpha(\mathbf{r}, \mathbf{p}) &= U_\alpha(\mathbf{r}) + \frac{\mathbf{p} \cdot \mathbf{p}}{2m} = \\ &= \sum_{\{ij\}} U_{\text{WCA}}(\mathbf{r}_{ij}) + \sum_{i=1}^N \frac{k_\alpha r_i^2}{2} + \sum_{i=1}^N \frac{p_i^2}{2m} \end{aligned} \quad (8)$$

where α is 'gen' or 'fin'; N represents the number of particles in our 2D system; m represents the mass of each particle; \mathbf{r} and \mathbf{p} represent the vector of all position and momentum coordinates respectively (so that $\Gamma = (\mathbf{r}, \mathbf{p})$); \mathbf{r}_i represents the vector position of the i -th particle, with length r_i ; \mathbf{p}_i represents the momentum of the i -th particle, with length p_i ; r_{ij} represents the separation between particles i and j ; $U_\alpha(\mathbf{r})$ represents the total potential energy for Hamiltonian \mathcal{H}_α , comprising WCA (Weeks-Chandler-Andersen potential) pair-interactions of the form [19]

$$U_{\text{WCA}}(r_{ij}) = \begin{cases} \epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 + 1 \right], & r_{ij} < 2^{1/6} \sigma \\ 0, & r_{ij} \geq 2^{1/6} \sigma \end{cases} \quad (9)$$

for discs of diameter σ and interaction strength ϵ , and a harmonic potential with strength k_α .

The Hamiltonians $\mathcal{H}_{\text{gen}}(\Gamma)$ and $\mathcal{H}_{\text{fin}}(\Gamma)$ correspond to different choices in the strength k of the confining harmonic potential. In this work, we consider two cases of discrete changes to k : $k_{\text{fin}} = 0.95k_{\text{gen}}$ or $0.8k_{\text{gen}}$. In order for the total energy $\mathcal{H}_{\text{gen}}(\Gamma) = \mathcal{H}_{\text{fin}}(\Gamma') = E$ to be preserved upon the switch in Hamiltonians, the transformation $\Gamma' = T(\Gamma)$ rescales the momenta \mathbf{p} by the required factor (which we denote $\kappa(\mathbf{r})$):

$$\begin{aligned} T(\Gamma) = \Gamma' &= (\mathbf{r}', \mathbf{p}') = \\ &= (\mathbf{r}, \sqrt{\frac{E - U_{\text{fin}}(\mathbf{r})}{E - U_{\text{gen}}(\mathbf{r})}} \mathbf{p}) = (\mathbf{r}, \kappa(\mathbf{r})\mathbf{p}). \end{aligned} \quad (10)$$

Since $\mathcal{H}_{\text{fin}}(\Gamma) < \mathcal{H}_{\text{gen}}(\Gamma)$, this is possible almost everywhere in \mathcal{M} .

Choosing the microcanonical ensemble significantly impacts on the derivation of the dissipation function, and, to our

knowledge, this is the first attempt to calculate the dissipation function for microcanonical systems. Since the Hamiltonian dynamics preserves phase space volume, $\Lambda(\Gamma) \equiv 0$, reducing the expression for the dissipation function to

$$\Omega_{0,t}^f = \ln \frac{f(\Gamma)}{f(S^t\Gamma)}. \quad (11)$$

If we consider the equilibrium shell ensemble, comprising points whose energies lie between E and $E + dE$, the distribution function $f(\Gamma) = 1/\mathcal{V}$ (where \mathcal{V} represents the volume of the shell ensemble in the phase space) is preserved by the dynamics, so $f(S^t\Gamma) = f(\Gamma) = 1/\mathcal{V}$ and $\Omega \equiv 0$. This result is consistent with the equal *a priori* probability distribution associated with the microcanonical ensemble, which we would expect to be dissipationless.

However, our simulations are performed in the surface ensemble where E is fixed rather than lying between bounds. The surface ensemble can be considered as the projection of an infinitesimal shell ensemble onto the lower surface of constant energy E . Consequently, probability densities on this surface, $\sigma_f(\Gamma)$, must be weighted by the local thickness of the energy shell, which is proportional to the inverse of the length of the gradient vector, i.e.

$$\sigma_f(\Gamma) = \frac{f(\Gamma)}{\|\nabla\mathcal{H}(\Gamma)\|}. \quad (12)$$

We can therefore express the dissipation function in these terms, as

$$\Omega_{0,t}^f = \ln \frac{\sigma_f(\Gamma)\|\nabla\mathcal{H}(\Gamma)\|}{\sigma_f(S^t\Gamma)\|\nabla\mathcal{H}(S^t\Gamma)\|}. \quad (13)$$

To calculate the dissipation function for our relaxation process, we must determine the initial distribution $g(\Gamma')$ of our transformed initial conditions. Here we will develop the expression for the surface density $\sigma_g(\Gamma')$, which combined with Eqn. 13 can be used to determine the dissipation function:

$$\Omega_{0,t}^g = \ln \frac{\sigma_g(\Gamma')\|\nabla\mathcal{H}_{\text{fin}}(\Gamma')\|}{\sigma_g(S^t\Gamma')\|\nabla\mathcal{H}_{\text{fin}}(S^t\Gamma')\|}. \quad (14)$$

The surface density is calculated in two steps. First, we must determine the surface density from the initial untransformed ensemble. Second, we must determine the effect of the transformation $T(\Gamma)$ on this surface density, which is the inverse of the rescaling in the surface due to the transformation (if the transformation doubles the surface size, the resulting surface density must be halved). The scaling of the surface must be the ratio of the Jacobian, representing the

scaling of the local *volume*, to the change in surface thickness, the dimension normal to the surface.

From Eqn. 12, the surface density for Γ in the initial, untransformed ensemble is given by $1/\|\nabla\mathcal{H}_{\text{gen}}(\Gamma)\|$. The Jacobian of the transformation $T(\Gamma)$, which only transforms the momenta \mathbf{p} , is easily calculated as $\kappa(\mathbf{r})^{3N}$. The surface thickness of the generating surface is $\|\nabla\mathcal{H}_{\text{gen}}(\Gamma)\|$, and the surface thickness of the final surface is $\|\nabla\mathcal{H}_{\text{fin}}(\Gamma')\|$. Thus, the relative change in surface area due to the transformation $T(\Gamma)$ is

$$\kappa(\mathbf{r})^{3N} \frac{\|\nabla\mathcal{H}_{\text{gen}}(\Gamma)\|}{\|\nabla\mathcal{H}_{\text{fin}}(\Gamma')\|}. \quad (15)$$

Inverting this quantity gives us the rescaling required to determine the final surface density at Γ' :

$$\sigma(\Gamma') = \kappa(\mathbf{r})^{-3N} \frac{\|\nabla\mathcal{H}_{\text{fin}}(\Gamma')\|}{\|\nabla\mathcal{H}_{\text{gen}}(\Gamma)\|^2} \quad (16)$$

and therefore the quantity required in the numerator and denominator of Eqn. 14 is given by

$$\begin{aligned} \sigma(\Gamma')\|\nabla\mathcal{H}_{\text{fin}}(\Gamma')\| &= \kappa(\mathbf{r})^{-3N} \frac{\|\nabla\mathcal{H}_{\text{fin}}(\Gamma')\|^2}{\|\nabla\mathcal{H}_{\text{gen}}(\Gamma)\|^2} \\ &= \kappa(\mathbf{r})^{-3N} \frac{|\nabla U_{\text{fin}}(\mathbf{r})|^2 + \kappa(\mathbf{r})\frac{|\mathbf{p}|^2}{m^2}}{|\nabla U_{\text{gen}}(\mathbf{r})|^2 + \frac{|\mathbf{p}|^2}{m^2}}. \end{aligned} \quad (18)$$

If $U_{\text{fin}} = U_{\text{gen}}$, both numerator and denominator are identically unity, so the dissipation function is zero everywhere, as expected. Given the complexity of the expression, we do not calculate the instantaneous phase-averaged dissipation function $\langle\Omega^{f_0}\rangle_{f_t}$ analytically, but determine it numerically.

In order to facilitate comparison with earlier work, we chose states whose physical characteristics (temperature, density, number of particles, dimension) are similar to those in Petersen *et al.* [13]. Our simulations comprise a two-dimensional fluid of 64 WCA particles, confined by the external harmonic potential centred at the origin. The simulation uses 4th order Runge-Kutta integration to solve the equations of motion, with each step having time length 0.001 reduced units (i.e. the unit system in which $\epsilon = \sigma = k_B = m = 1$). We chose $k_{\text{gen}} = 0.024$, and set E to various values in the range 290–475, so that the temperature and density (estimated from an effective system volume based on the radial density profile) of the particles was close to that in Petersen *et al* [13].

The simulations were performed by first initialising particles according to a Gaussian distribution in position and momentum, total energy E . The system was allowed to equilibrate over 2×10^6 steps, after which a daughter trajectory

was spawned every 4×10^5 to 5×10^5 steps. For each of the daughter trajectories, the field was rescaled at $t = 0$ by a factor of 0.95 or 0.8, and the kinetic energy rescaled to ensure that the total energy was held at E ; then the daughter trajectory was run. The dissipation function for each daughter was calculated every 100 steps, and this value averaged across all daughters to obtain the ensemble average. The evolution of the potential and kinetic energies, and radial distributions, was also recorded and averaged for each daughter, to shed light on the approach to equilibrium.

IV. RESULTS AND DISCUSSION

In Figure 1, we show the integrated ($\langle \Omega_{0,t}^{f_0} \rangle_{f_0}$) and instantaneous ($\langle \Omega_{0,t}^{f_0} \rangle_{f_t}$) dissipation functions, and the potential energy, for the relaxation process described above. The initial states are generated using the \mathcal{H}_{gen} , with $k_{\text{gen}} = 0.024$, with their momenta rescaled to maintain the same total energy for the daughter trajectories when the strength of the harmonic potential is changed to $k_{\text{fin}} = 0.95k_{\text{gen}}$ (left panel) or $k_{\text{fin}} = 0.8k_{\text{gen}}$ (right panel). The results shown are the averaged outcomes of 7,400 realisations.

We can see an immediate difference with the earlier systems that have been studied. In the work of Reid *et al.* [12] and Petersen *et al.* [13], the dissipation function was either overdamped or gently underdamped, converging toward a limit after a handful of oscillations at most. Here, the convergence is far from monotonic — it is significantly underdamped, taking much longer to converge than in these earlier works. When $k_{\text{fin}} = 0.95k_{\text{gen}}$, it is not entirely clear after 1000 time units that the system is equilibrating, although longer simulations indicate the gradual relaxation of macroscopic system properties (such as the potential energy). When $k_{\text{fin}} = 0.8k_{\text{gen}}$, the decay is more pronounced, but still clearly continuing beyond 1000 time units. In Petersen *et al.* [13], the time to decay for a system at similar temperature and density was 50 time units: in Reid *et al.* [12], it was of the order of 5–10 time units.

The period of the oscillations in the dissipation function matches the half-period of oscillation in a harmonic well with potential $\frac{1}{2}kr^2$,

$$T = \frac{\pi\sqrt{m}}{\sqrt{k}} = \frac{\pi}{\sqrt{0.95 \times 0.024}} \approx 20.8 \quad \text{or} \quad (19)$$

$$\frac{\pi}{\sqrt{0.8 \times 0.024}} \approx 22.7.$$

This suggests that the oscillatory nature of the dissipation function arises from the oscillatory dynamics in the system, and that relaxation can only occur if this oscillatory process is perturbed. Related to this, we note that the first oscillations in both systems virtually return $\langle \Omega_{0,t}^{f_0} \rangle_{f_0}$ to zero. This is an important observation, because while $\langle \Omega_{0,t}^{f_0} \rangle_{f_0}$ is not a

metric between f_t and f_0 (it lacks the necessary symmetry property), it still gives a measure of the closeness of f_t to f_0 (although not of either distribution to the invariant, equilibrium distribution). Consequently, $\langle \Omega_{0,t}^{f_0} \rangle_{f_0} \rightarrow 0$ implies that $\sup |f_t(\Gamma) - f_0(\Gamma)| \rightarrow 0$, so small values of $\langle \Omega_{0,t}^{f_0} \rangle_{f_0}$ imply proximity of f_t to f_0 , in a way that can be made rigorous.

Here, it suffices to note the implication that the system is periodically returning to a distribution that is exceedingly close to its starting distribution. This must be true, simultaneously, of *all* the daughter simulations — otherwise, the mean value across the daughters would not be zero. This suggests that the intermolecular interactions are critical, but only weakly influence the system in facilitating relaxation to equilibrium. Only after many periods do the interactions permit the system to lose memory of its original distribution in the march to equilibrium.

To establish the importance of the interactions, we ran simulations with different values of ϵ and σ . We found that changes in ϵ had little impact on the convergence to equilibrium, while changes to σ had a much more significant impact. In Figure 2, we show the integrated and instantaneous dissipation functions, and the potential energy, for the same relaxation processes described above, but with $\sigma = 4$ (rather than $\sigma = 1$). Results are shown for the average over 12,600 realisations. It is clear that the more frequent interaction between molecules has a significant influence on convergence time (and, from our observations, the energetics of those collisions as determined by ϵ played little role).

Surprisingly, even though the collisions have a more immediate effect on the relaxation, and despite the number of simulations collated, the oscillatory nature of the relaxation process lasts a considerable time. One might expect the collisions to lead to decorrelation in the phase of individual oscillations, but this is not particularly evident. This is possibly because particles are much more likely to collide in the central, more densely occupied region, and at this point the phases through their oscillations of the colliding particles are similar. Collisions with the likelihood to disrupt the overall oscillatory response are less likely.

This can also be seen in the potential energies, whose fluctuations demonstrate a striking similarity to the fluctuations in the integrated dissipation function, as can be seen from Figures 1 and 2. This arises despite the highly complicated form of the latter, and is possibly due to dominance by the factor $\kappa(\mathbf{r})^{3N}$, which has a direct relation to the potential energy. While the integrated dissipation function and potential energy do not linearly scale precisely on top of one another, the behaviours are clearly closely matched. The persisting oscillations in the potential energy can perhaps be more directly supported by the greater likelihood that collisions occur between molecules at similar phases in their oscillations: the apparent relationship between potential energy and integrated dissipation function supports our observations for the latter's behaviour.

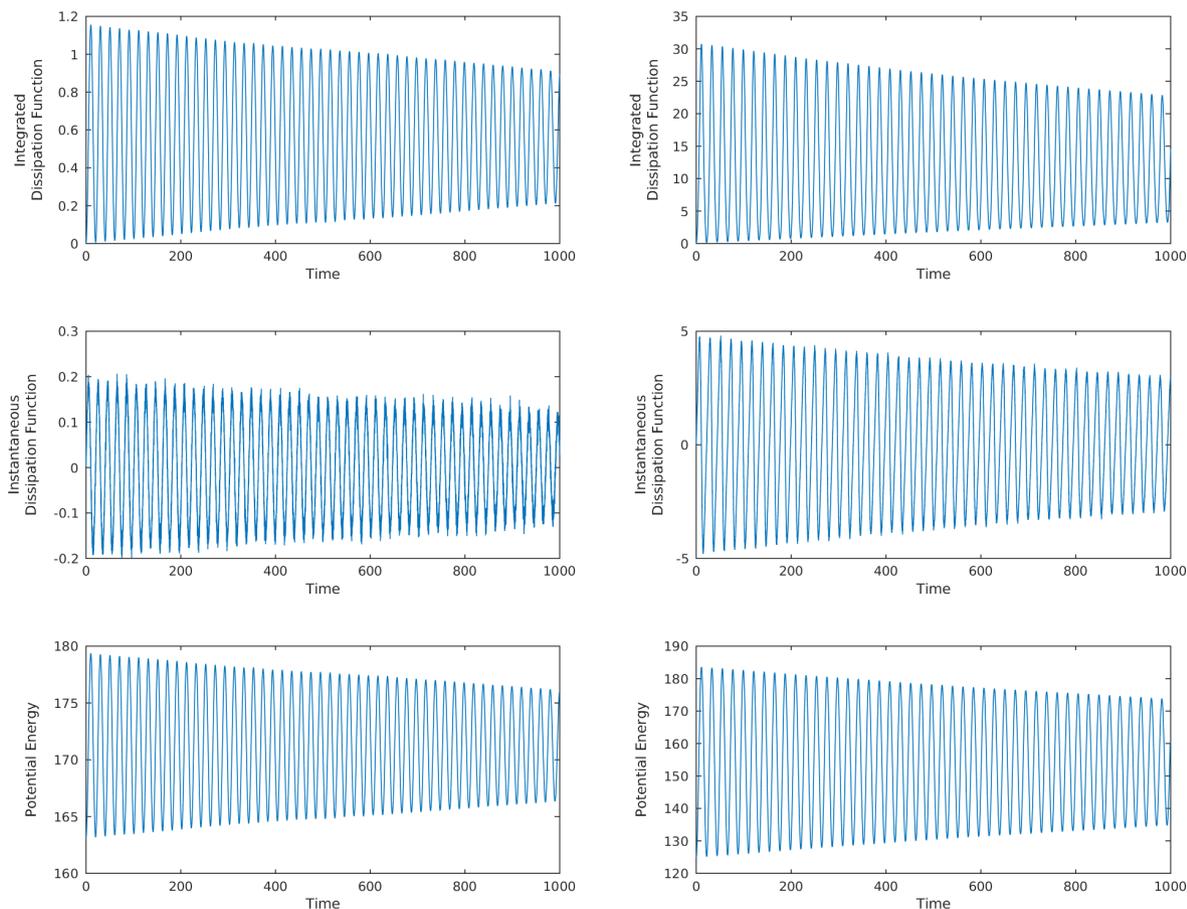


Fig. 1. Integrated (top panels) and instantaneous (middle panels) values of the dissipation function, and potential energy (bottom panels) for relaxation from a non-microcanonical distribution of states generated using a harmonic well with $k_{\text{gen}} = 0.024$. The relaxation dynamics has identical Hamiltonian, but with $k_{\text{fin}} = 0.95k_{\text{gen}}$ (left panel) and $k_{\text{fin}} = 0.8k_{\text{gen}}$ (right panel). In all cases, $\sigma = 1$

An important consequence is that relaxation in this system could never occur if there were no interactions. The dynamics in each individual daughter trajectory would instantly be typical of the dynamics in the target system — for each individual system no relaxation would be required. However, as an ensemble of systems, the distribution of properties would not match the microcanonical distribution. The dissipation function reflects the fact that the ensemble does not relax, but does not reflect the fact that individual systems immediately exhibit typical dynamics, because by its definition the dissipation function shows the evolution of the average *across an evolving distribution*, but makes no comment on how this relates to the behaviour in individual systems.

This shows a qualitative difference in the relaxation to a uniform distribution in periodic boundary conditions. Even

if there were no interactions between molecules, periodic boundary conditions would permit almost every initial condition to produce a decorrelation between $\mathbf{x}(0)$ and $\mathbf{x}(t)$ at long times, and the consequent decay in $\langle \Omega^{f_0} \rangle_{f_t}$. Molecular interactions merely accelerate this process, but are unnecessary for the relaxation process to occur. Only under very special conditions would each trajectory return to its initial state after a fixed time.

By contrast, the harmonic potential does precisely this: in the absence of other influences, the system would return to its initial state periodically, and the dissipation function would therefore be periodic. Molecular interactions are essential in this case for relaxation to equilibrium, and the nature of the interactions plays a critical role in the nature of the relaxation. Weaker interactions lead to very slow relaxation. However, our systems have been chosen so that the fre-

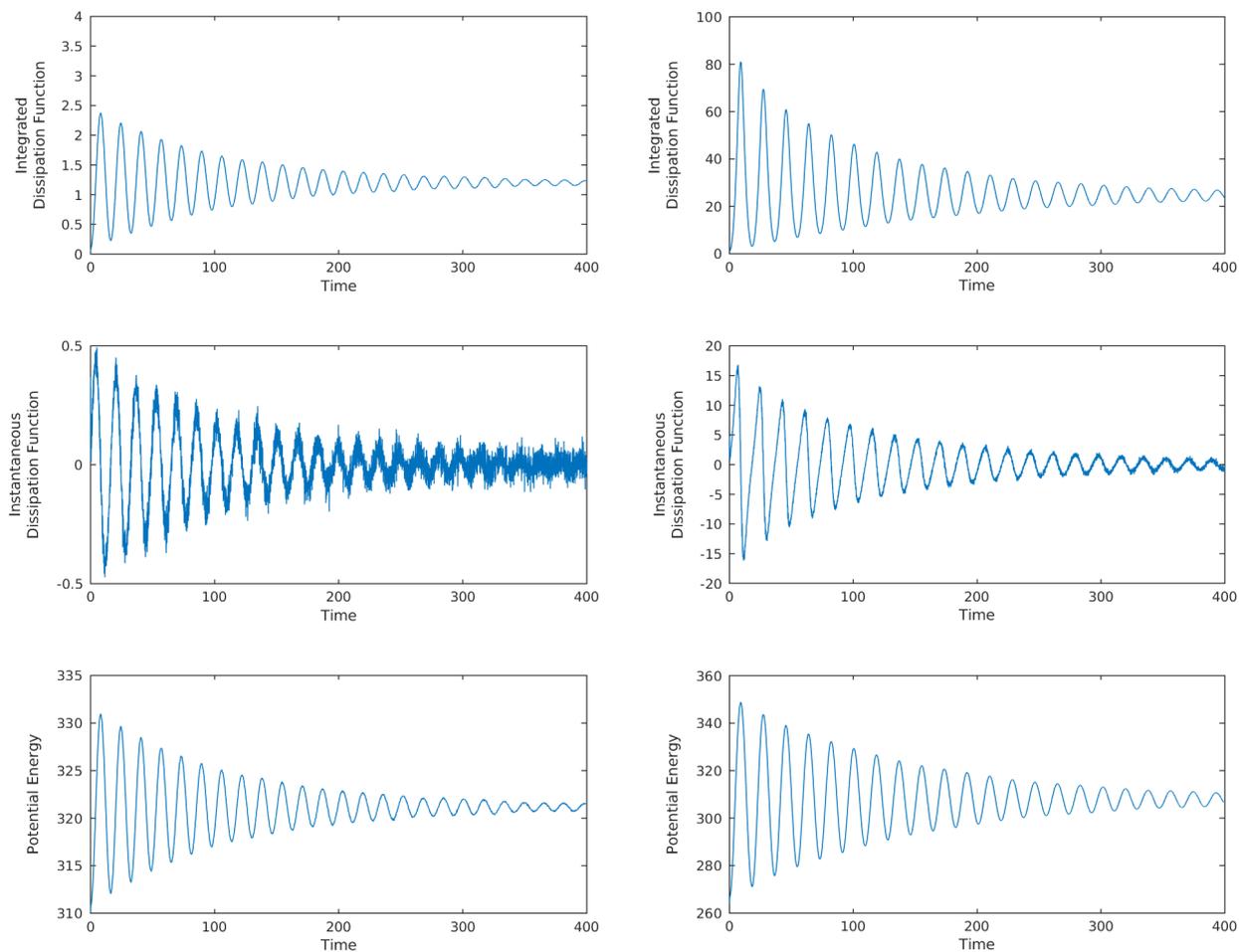


Fig. 2. Integrated (top panels) and instantaneous (middle panels) values of the dissipation function, and potential energy (bottom panels) for relaxation from a non-microcanonical distribution of states generated using a harmonic well with $k_{\text{gen}} = 0.024$. The relaxation dynamics has identical Hamiltonian, but with $k_{\text{fin}} = 0.95k_{\text{gen}}$ (left panel) and $k_{\text{fin}} = 0.8k_{\text{gen}}$ (right panel). In all cases, $\sigma = 4$

quency and intensity of intermolecular interactions should be similar to those of Petersen *et al.* [13], indicating that the nature of the potential energy landscape (including the nature of the boundary) plays a pivotal role here in the relaxation process.

Indeed, the choice of harmonic potential exacerbates this distinction. The fact that all oscillators in a harmonic potential have the same period implies that the entire system returns to the original state periodically. Arbitrary potential wells do not share this property, and would lead to a mixing on a time scale related to the distribution of oscillation periods.

We note that the initial fluctuations in the integrated dissipation function are much smaller in the systems that are closer to the equilibrium distribution initially (i.e. when

$k_{\text{fin}} = 0.95k_{\text{gen}}$) than in the systems that start further from the equilibrium distribution (i.e. when $k_{\text{fin}} = 0.8k_{\text{gen}}$). Thus, the variation in the dissipation function here is indicative of the greater variation (larger relative entropies) between the initial and final distribution functions. The decaying size of these fluctuations as the integrated dissipation function converges to its limit value is also consistent with the approach to a final, equilibrium distribution. As mentioned above, we would expect these fluctuations to ultimately decay to zero after many iterations, although it is not clear on what time scale this can be expected.

We also note a further distinction between our results and those previously. In earlier work, the integrated dissipation function appears to reach its maximum in the long-time limit, suggesting that the excursions into negative val-

ues of the instantaneous dissipation function are dominated by subsequent positive contributions. Here, this is clearly not the case. The first peak attained by the integrated dissipation function appears to be the maximum: the subsequent relaxation contributes a net negative change. Given that the key contributions to the relaxation process — the intermolecular interactions — occur predominantly beyond this peak, it is not clear what physical interpretation regarding dissipation might be given to this observation.

Finally, we contrast our results with the decay in Fourier modes observed by Petersen *et al.* [13]. As discussed earlier, Petersen *et al.* found that initial perturbations involving only lower Fourier modes decayed monotonically, while initial perturbations involving higher modes exhibited a more complex, non-monotonic decay. It appears that the lower-mode perturbation relaxes in accordance with the diffusion equation, with coefficients for the different harmonics decay exponentially as predicted by the separated solutions to the diffusion equation. Given the similar nature of the intermolecular interactions between this system and our own, one might have anticipated that a similar decay might be observed for relaxation in the harmonic potential. Relaxation from an initial single-variable spatial distribution $\rho(x)$ in a non-uniform potential landscape can be described using the Smoluchowski equation [20]

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= \frac{1}{m\gamma} \left[\frac{\partial}{\partial x} U'(x) + k_B T \frac{\partial^2}{\partial x^2} \right] \rho \\ &= \frac{1}{m\gamma} \frac{\partial}{\partial x} [U'(x)\rho] + \frac{k_B T}{m\gamma} \frac{\partial^2 \rho}{\partial x^2}. \end{aligned} \quad (20)$$

Here, γ represents the frictional forces between molecules, which are assumed to play a central role in the overdamped response of molecules to the forces they experience (from the external potential, captured in the first term on the right hand side of Eqn. 20, or from neighbouring particles, captured in the second, diffusion term). However, the origin of the diffusive relaxation in the simulations in Petersen *et al.* [13], for the given density and temperature, is not determined by the strength of intermolecular interactions. It is closer to the origins of diffusion in systems of non-interacting particles in a rectangular box with periodic boundary conditions, which is due to the almost-everywhere ergodic trajectories of single particles. This is consistent with the rate of decay of the slowest Fourier modes in their work: the half-life of the coefficient decay is approximately one-quarter the half-period of oscillations in our system.

For our system, however, the Smoluchowski equation cannot apply, because there is no linear response, mediated by intermolecular collisions, to the forces on molecules. If it were to apply, one should be able to describe the resulting dynamics using the Smoluchowski equation in two dimensions, where $U(r) = \frac{1}{2}kr^2$ is our confining harmonic potential. The solution can be obtained through various means,

including separation of variables [20]: in one dimension, the separated spatial solutions $\phi_n(x)$ and time solutions $\tau_n(t)$ are

$$\begin{aligned} \phi_n(x) &= e^{-kx^2/2k_B T} H_n \left(\sqrt{\frac{k}{2k_B T}} x \right) \\ \tau_n(x) &= e^{-nkt/m\gamma} \quad n = 0, 1, 2, \dots \end{aligned} \quad (21)$$

where the $H_n(x)$ are the orthogonal (physicists') Hermite polynomials. In two dimensions, the separated solutions take the form

$$\phi_n(x)\phi_m(y)\tau_{n+m}(t) \quad n, m = 0, 1, 2, \dots \quad (22)$$

We note immediately that these solutions have a time dependence that is an exponential decay: solutions matching our observed dynamics cannot arise from the Smoluchowski equation. Indeed, decay from an initial distribution with a different k leads to a smooth transition between Gaussian distributions (as can be seen by expressing the initial conditions as a linear combination of the $\phi_n(x)\phi_m(y)$, and observing the decay to the final distribution). It is clear from Figures 1 and 2 that our solution arises from a significant underdamped response, in which case a second-order term $\frac{\partial^2 \rho}{\partial t^2}$ should also feature in the description of the dynamics Eqn. 20, to describe the response we have observed.

V. CONCLUSION

The theoretical basis supporting NEMD provides a strong connection between entropy production and changes in phase space volume, and the dissipation function of Evans and Searles provides a means of describing entropy production through its relationship with phase space contraction and the relevant equilibrium distribution function. However, Liouville's equation provides a close association between changes in phase space volume and the evolution of probability distributions. While entropy is clearly a thermodynamic concept, the evolution of probability distributions can be considered in much broader dynamical contexts. In such contexts, the dissipation function has a more general interpretation, and having both a thermodynamical and a dynamical interpretation provides clearer insight into results involving this function, both in the general theory and specific to numerical observations.

While the role of Boltzmann's H -function in describing relaxation is clear, the physical interpretation of the integrated dissipation function $\langle \Omega_{0,t}^{f_0} \rangle_{f_0}$ is less so. It provides some measure of closeness between f_0 and f_t , as a relative entropy, but is technically not a metric because it does not enjoy a symmetry property. Furthermore, convergence of $\langle \Omega_{0,t}^{f_0} \rangle_{f_0}$ to some limit does not guarantee, in and of itself, convergence of f_t to some invariant measure. For this to be

the case, we must establish the further condition of T-mixing. It is also not clear how to interpret $\langle \Omega_{0,t}^{f_0} \rangle_{f_0}$ or $\langle \Omega^{f_0} \rangle_{f_t}$ as a measure of convergence toward or away from equilibrium. Whenever $\langle \Omega^{f_0} \rangle_{f_t} < 0$, as occurs during non-monotonic relaxation, there must be some $t - \delta < s < t$ for small δ such that $\langle \Omega^{f_s} \rangle_{f_t} > 0$, but we cannot consider the system at time t to be simultaneously moving toward *and* away from equilibrium. Despite such currently unresolved difficulties, however, the dissipation function has provided a new and fruitful theoretical underpinning for our understanding of relaxation processes.

To our knowledge, the work presented here gives the first demonstration of explicit calculations of the dissipation function to show relaxation under Hamiltonian dynamics, rather than in the canonical ensemble. Starting from a non-equilibrium distribution, we considered the relaxation of WCA discs in a confining harmonic potential. Unlike previous studies, we observed strongly persisting non-monotonic relaxation. This persistence appears to be peculiar to our choice of confining potential, wherein each molecule has the same period of oscillation in the absence of intermolecular collisions. The weak intermolecular interactions perturb this process only slowly. The use of $\langle \Omega_{0,t}^{f_0} \rangle_{f_0}$ as a measure of the separation of f_0 and f_t is clearly demonstrated in the recurrence to near-zero values of $\langle \Omega_{0,t}^{f_0} \rangle_{f_0}$ for values of t coinciding with the oscillatory period of our potential. Furthermore, we note that our choice of system parameters was guided by the aim of generating similar intermolecular interactions to those of Petersen *et al.*, but in those systems relaxation can be strongly monotonic. This reflects a special characteristic of relaxation to uniform potentials, which cannot arise in our system: the non-uniform potential induces a strongly underdamped response to the field. Finally, we note that, unlike in previous work, the maximum integrated dissipation does not occur in the long-time limit, but at the first peak, after which there is a net decrease in the integrated dissipation function. Here, again, a consistent physical interpretation with the relaxation process is not clear. From our work, we see that the dissipation function continues to provide useful insights into relaxation to equilibrium, but that there remain questions regarding the interpretation of various general and numerical results.

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