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Dissipation in monotonic and non-monotonic relaxation to equilibrium

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Using molecular dynamics simulations, we study field free relaxation from a non-uniform initial density, monitored using both density distributions and the dissipation function. When this density gradient is applied to colour labelled particles, the density distribution decays to a sine curve of fundamental wavelength, which then decays conformally towards a uniform distribution. For conformal relaxation, the dissipation function is found to decay towards equilibrium monotonically, consistent with the predictions of the relaxation theorem. When the system is initiated with a more dramatic density gradient, applied to all particles, non-conformal relaxation is seen in both the dissipation function and the Fourier components of the density distribution. At times, the system appears to be moving away from a uniform density distribution. In both cases, the dissipation function satisfies the modified second law inequality, and the dissipation theorem is demonstrated. © *2016 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4941584]

I. INTRODUCTION

There are situations where thermodynamics ceases to be useful. The precise point where this occurs is poorly appreciated and perhaps poorly understood; thermodynamics only works for equilibrium or for systems that can be effectively modelled as being in some equilibrium like state. For example, in the case of transition state theory,[1,2] as frequently used in chemistry, the system must be in quasi-equilibrium, and for linear irreversible thermodynamics, the system must be in local equilibrium.[3] Without any form of equilibrium, thermodynamics fails to define either the entropy or the temperature. Important issues about the limits for the applicability of thermodynamics were given consideration over 100 years ago,[4–8] but seem to have been largely forgotten with the passing of time. Perhaps, the apparent disinterest in this early work is because of an almost complete lack of progress, on extending the range of applicability for thermodynamics, made in the interim. Over the past decade, there has been considerable theoretical progress on the fundamental statistical mechanics of nonequilibrium systems, which has now reached a stage where it may be applied to areas that have previously been solely the domain of thermodynamics. As it turns out, this requires us to change some of our long held views about the nature of the *second law of thermodynamics* around the boundaries of thermodynamics' applicability. To study this, here, we will consider atomic simulations of systems which are relaxing towards equilibrium.

Nonequilibrium states may be broadly classified into three distinct classes.

1. Those that are being driven by some external field or agent and appear to be stationary in time. Such a *nonequilibrium*
steady state is distinct from an equilibrium state because it has a net flow of energy going through the system. The source for this energy flow is the work done by the external field, and the energy is eventually dissipated to the thermal reservoir which regulates the system's temperature.

2. We may have a similar driven nonequilibrium system that is not time independent. Such a system may or may not be periodic, and it could be driven by a time dependent field (i.e., it may be nonautonomous). It could be driven by a time independent field but displays time dependent behaviour due to turbulence. If we were to monitor this latter case in terms of ensemble averages, it may well appear to be in a steady state and could be seen as belonging in the first class above.

3. The system may have had something done to it in the past, but is now left alone and is relaxing towards equilibrium. The time it takes to reach what is deemed to be equilibrium will depend on system details, with glassy systems capable of taking exceedingly long times to relax while ordinary liquids could relax in a small fraction of a second. The time at which a system is first deemed to be in equilibrium will depend on the details of what properties are being measured and to what accuracy.

It is the third of these nonequilibrium classes which we concern ourselves with here, and we will study this by making extensive use of a relatively new quantity and concept, the dissipation function. This third nonequilibrium class is arguably the simplest of the three; it allows us to bring long standing problems about the domain of applicability for thermodynamics[4–8] into sharp focus and allows us to see how the recent dissipation function approach successfully rectifies these issues. By way of introduction, consider a tuning fork (as used to tune musical instruments). If we strike the tuning fork and observe its relaxation, we may observe how it rings due to its two prongs oscillating at a single harmonic frequency.

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This is certainly a thermal system and one we might suppose thermodynamics should apply to. However, thermodynamics concludes that the Helmholtz free energy for such a system must decay monotonically. How may we reconcile the case of an oscillating system or more generally a non-monotonic decay with the second law of thermodynamics? Here, we will show how non-monotonic decays, which are not compatible with traditional thermodynamics, are able to be properly addressed using the dissipation function and the modified second law inequality that the fluctuation theorem based approach produces. Further, we will show how such non-monotonic decays may occur in a simple fluid that is merely relaxing from a nonequilibrium state.

The dissipation function has been shown to be a very useful tool in analysing non-equilibrium systems[9,10] including relaxing systems that are particularly relevant here,[11,12] and it is the central quantity in the Evans-Searles fluctuation theorem,[13,14] the relaxation theorem,[15] a modified version of the second law inequality,[16] and the dissipation theorem.[17,18] Importantly the dissipation function and the modified second law equality that partners it, allow for the possibility of non-monotonic relaxation, which is in sharp distinction to traditional thermodynamics. Further, this modified second law has been derived from the microscopic equations of motion, as opposed to a justification based on consistency with macroscopic observations, in the case of the traditional second law. A dissipation focussed computational study of relaxation has been reported previously for a model of an optically trapped particle, in a system which relaxes non-monotonically towards equilibrium.[19] There has also been an experimental study on the relaxation from the steady state to equilibrium of a vacuum trapped nanoparticle.[20] This study used a form of relative entropy which happens to coincide with the dissipation function. We will extend this area of research by computationally studying the relaxation process from an initial nonequilibrium density gradient in a many particle fluid that is of a prototypical thermodynamic nature and look at monotonic as well as non-monotonic relaxation scenarios. We will study the relaxation process using the dissipation function, as well as other more intuitive measures.

II. INITIAL CONDITIONS

Our chosen system for studying the relaxation process is a fluid of particles that begins with a non-uniform density distribution. We will model the relaxation of this system with molecular dynamics using a 2-dimensional fluid of Weeks-Chandler-Anderson[21] (WCA) particles with square periodic boundary conditions.[22] Reduced units are used all in terms of the three units: the length unit σ from the WCA potential, the energy unit ϵ from the WCA potential, and the time unit $\sqrt{m\sigma^2/\epsilon}$, where m is the particle mass. The coupled first order ordinary differential equations of motion are solved using the 4th order Runge-Kutta algorithm for coupled 1st order ordinary differential equations with a timestep of 0.001. The density of the 32 particle system is 0.6, the thermostat temperature is set to $T = 1$, and an ensemble of 10^6 trajectories is simulated for each case. The simulation is subjected to a two step process.

1. Initially, the simulation is set up in a perturbed equilibrium. This is done by adding a colour field to the potential of the equilibrium system, which imposes a density gradient (inhomogeneity) across the system. Despite this density gradient, the system is initially in a perturbed equilibrium, with a known canonical distribution function.

2. The colour field is switched off, and the system relaxes towards a homogeneous equilibrium.

The initial set of 10^6 coordinates $\mathbf{\Gamma(q,p)}$ is sampled periodically from a long perturbed equilibrium simulation trajectory. Knowing the initial distribution function is a necessary condition for calculating the form of the dissipation function. A number of different perturbations were used to study different relaxation processes.

III. SINUSOIDAL PERTURBATION—COLOUR FIELD

For simplicity, the first perturbation used to generate a density gradient in the initial system is a sine curve as a function of x position,

$$U_{e,i} = \frac{a}{2} \sin\left(\frac{2\pi x_i}{b_L}\right), \tag{1}$$

where a determines the strength of the applied perturbation and b_L is the length of the periodic cell. Using a smooth continuous perturbation function is convenient because the resulting form for the dissipation function is easier to work with. We studied a gentle relaxation process by using a colour field. The equations of motion used to set up the initial distribution are

$$\dot{\mathbf{q}}_i(t) = \mathbf{p}_i/m, \tag{2}$$

$$\dot{\mathbf{p}}_i(t) = \mathbf{F}_i(t) - \alpha p_{yi}\mathbf{j} + c_i\mathbf{F}_{e,i} - \mu, \tag{3}$$

$$\alpha = \frac{\mathbf{F}_y \cdot \mathbf{p}_y}{\mathbf{p}_y \cdot \mathbf{p}_y}, \tag{4}$$

$$\mu = \left(\sum_{i=0}^{N} c_i\mathbf{F}_{p,i}\right)/N, \tag{5}$$

$$\mathbf{F}_{e,i} = -\frac{\partial U_{g,i}}{\partial x}\mathbf{i}, \tag{6}$$

where $\mathbf{q}_i$ gives the position of the ith particle, $\mathbf{p}_i$ gives the momentum, $\mathbf{p}_y$ is the vector of the y components of the momentum for all of the particles, m is the particle mass, $\mathbf{F}_i$ is the interparticle force on the ith particle, and $c_i = (-1)^i$ is the colour label to control the direction of the perturbation to the potential of each particle. The term μ is added to keep the total momentum of the system to zero. The applied colour field may exert more force to the system as a whole in one direction or another, depending on the position of the particles, and the term, μ, effectively moves the reference frame of the simulation with the system's centre of mass. By using a colour field to set up the initial distribution, there will be a density gradient across the system in both types of particles, while the total density distribution will be relatively uniform, allowing for gentle relaxation dominated by the mixing of particles that only differ in terms of their label. Once the initial distribution has been set up, the system undergoes field free relaxation with an isokinetic thermostat. The equations of motion are

the same as for the setup, but c_i is 0. The thermostat is only applied in the y direction so that any flows in the x direction are not directly effected by it.

A. Derivation of dissipation function

The dissipation function constitutes the primary tool we will use in studying the relaxation process. It is the central quantity in both the relaxation theorem[15] and the dissipation theorem,[17,18] both of which are applicable to systems relaxing to equilibrium. The form of the dissipation function for our system can be derived from its definition,[12,23]

$$\Omega_t(\mathbf{\Gamma}) \equiv \ln\left(\frac{f(\mathbf{\Gamma},0)}{f(S^t\mathbf{\Gamma},0)}\right) - \int_0^t \Lambda(S^s\mathbf{\Gamma})ds, \quad (7)$$

where Ω_t is the time-integrated dissipation function, $f(\mathbf{\Gamma},0)$ is the phase space density of phase space position $\mathbf{\Gamma}$ at time 0, S^t is the natural time evolution operator, and Λ is the phase space expansion factor. No perturbation is applied to the dynamics during the trajectory, so the phase space expansion factor is determined by the thermostatted dynamics of the system and is given by its usual expression,

$$\Lambda = \frac{\partial}{\partial\mathbf{\Gamma}} \cdot \dot{\mathbf{\Gamma}} = \beta\dot{Q}, \quad (8)$$

where $\beta = 1/k_BT$, k_B is Boltzmann's constant, and $\dot{Q}$ is the rate of change in heat of the system, not including the energy from the perturbation applied to generate the initial distribution. The initial canonical distribution is given by

$$f(\mathbf{\Gamma},0) = \frac{\exp[-\beta H(\mathbf{\Gamma})]}{\int d\mathbf{\Gamma} \exp[-\beta H(\mathbf{\Gamma})]}. \quad (9)$$

The energy of the system, H, can be split up into the energy from particles and particle interactions, H_0, and the energy due to the potential perturbation, $h(\mathbf{\Gamma})$, which determines the initial state,

$$H(\mathbf{\Gamma}) = H_0(\mathbf{\Gamma}) + h(\mathbf{\Gamma}), \quad (10)$$

resulting in the dissipation function being given by

$$\Omega_t = -\beta(h(S^t\mathbf{\Gamma}) - h(\mathbf{\Gamma})). \quad (11)$$

For our system, the potential due to the perturbation is given by Eq. (1), $h(\mathbf{\Gamma}) = \sum_{i=1}^N c_i U_{e,i}(\mathbf{\Gamma})$, and so the resulting expression for the dissipation function is

$$\Omega_t = \beta\frac{a}{2}\left(\sum_{i=1}^N c_i \sin\left(\frac{2\pi x_i(t)}{b_L}\right) - \sum_{i=1}^N c_i \sin\left(\frac{2\pi x_i(0)}{b_L}\right)\right). \quad (12)$$

The streaming derivative,

$$\frac{dg(x(t),t)}{dt} = \frac{\partial g(x(t),t)}{\partial x}\frac{dx(t)}{dt} + \frac{\partial g(x(t),t)}{\partial t}, \quad (13)$$

of this gives us the instantaneous dissipation function,

$$\Omega(S^t\mathbf{\Gamma}) = \frac{\beta a\pi}{mb_L}\left(\sum_{i=1}^N c_i p_{x_i}(t)\cos\left[\frac{2\pi x_i(t)}{b_L}\right]\right). \quad (14)$$

We can monitor the relaxation process by computing the dissipation function for our ensemble of simulations

as they relax and expect the ensemble average of the integrated dissipation function to obey the second law inequality,

$$\langle\bar{\Omega}_t\rangle = \langle\Omega_t\rangle/t > 0. \quad (15)$$

This is different to the traditional second law inequality in two important regards; first, the dissipation function (which is the subject) is a finite time averaged quantity, $\bar{\Omega}_t = -\beta\frac{1}{t}\int_0^t ds\,\dot{h}(S^t\mathbf{\Gamma})$, and second, it is explicitly ensemble averaged and is valid arbitrarily far from equilibrium. In contrast, the traditional second law inequality, $\Delta Q/T > \Delta S$, is supposedly valid in the thermodynamic limit, but leaves both the entropy S and the temperature T undefined, except for special cases where local-equilibrium or quasi-equilibrium arguments may be used. We might assume that the temperature is constant,[24] as would be the case if we used the temperature of the (infinitely large) thermal reservoir.

B. Density profile

We can visualise the initial distribution of the system by creating a histogram of the x positions of the particles from an ensemble of simulations. From this, we can calculate the average particle density in each part of the system, shown in Figure 1. The strength of the perturbing potential is set to $a = 2.5$ for all perturbations.

C. Relaxation

From our initial distribution, we can monitor the density distribution as the system relaxes. The ensemble was simulated for 5×10^4 time steps over the relaxation process. A sample of density profiles of the system at different points in time is shown in Figure 2. The distribution of green particles (those for which $c_i = -1$) appears to relax to a sine curve, whose amplitude decreases with time. The distribution of red particles
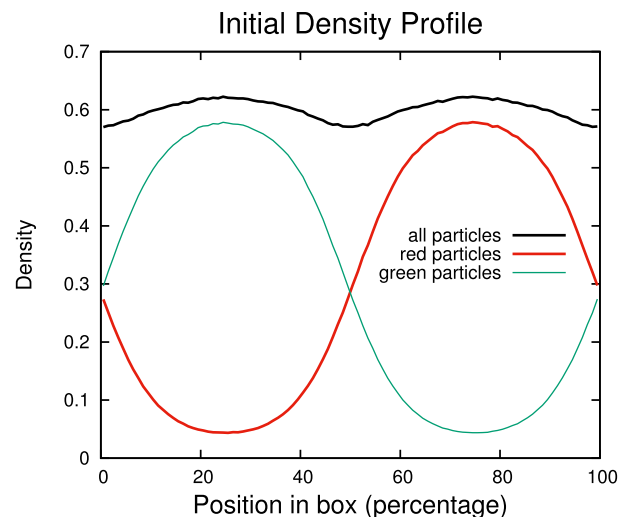

FIG. 1. Average density in the system as a function of x position. A sine potential perturbation was applied to the equations of motion of the particles to generate this distribution, seen in Eq. (6) with $a = 2.5$.
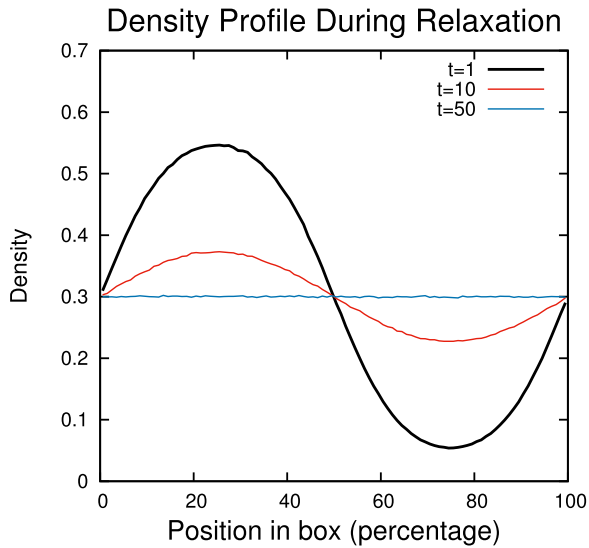
FIG. 2. A sample of density profiles as the system relaxes. The density profile of the green particles is shown.

FIG. 4. Average value of the instantaneous dissipation function, shown as black ticks, calculated along the relaxation process. The integral of the auto-correlation function of the dissipation function is included as yellow triangles to demonstrate the dissipation theorem. Note that the error bars cannot be seen on this scale.

($c_i = 1$, not shown) mirrors the green particle distribution, and the total density relaxes to a uniform distribution quickly.

To quantify our study of the relaxation process, we can perform a least squares fit of these density distribution graphs to a sine curve of fundamental wavelength. That is, we fit the density as a function of position to the equation

$$D = A \sin\left(\frac{2\pi x}{b_L}\right) + \frac{\rho}{2} \qquad (16)$$

to give the amplitude of the sine wave, A, which is plotted against time in Figure 3. We use the density of the green particles, where $c_i = -1$. As expected, the density approaches a uniform distribution as the relaxation time approaches infinity.

We can also monitor the relaxation of the system by calculating the value of the instantaneous dissipation function

throughout the relaxation process, seen in Figure 4. Initially, the average value of the dissipation function is zero because the distribution is even in the momenta, since it is an equilibrium distribution under the potential perturbation. It rises rapidly, before relaxing monotonically towards zero as the system approaches equilibrium. We know from the relaxation theorem, if the deviation function in the distribution relaxes conformally then the average instantaneous dissipation function relaxes to zero monotonically.[15] After a very short initial transient, the density distribution graphs in Figure 2 appear to relax conformally, so this monotonic behaviour of the dissipation function is expected. We can also observe from Figure 4 that since the average of the instantaneous dissipation function is always positive, the integrated dissipation function is always greater than zero, satisfying the second law inequality.

The dissipation theorem[17,18] relates a phase functions average value to its transient correlation function with the instantaneous dissipation function. We can demonstrate the dissipation theorem with this system, using the instantaneous dissipation function as the argument. The dissipation theorem then becomes

$$\langle \Omega(S^t\Gamma) \rangle = \int_0^t \langle \Omega(\Gamma)\Omega(S^s\Gamma) \rangle ds. \qquad (17)$$

The RHS of Eq. (17) is included in Figure 4, and a close agreement is seen between the average of the dissipation function and the integral of the correlation function, demonstrating the dissipation theorem in this relaxing system. The necessary and sufficient condition for relaxation to equilibrium is

$$\int_0^\infty ds\ \langle \Omega(0)\Omega(s) \rangle = 0, \qquad (18)$$

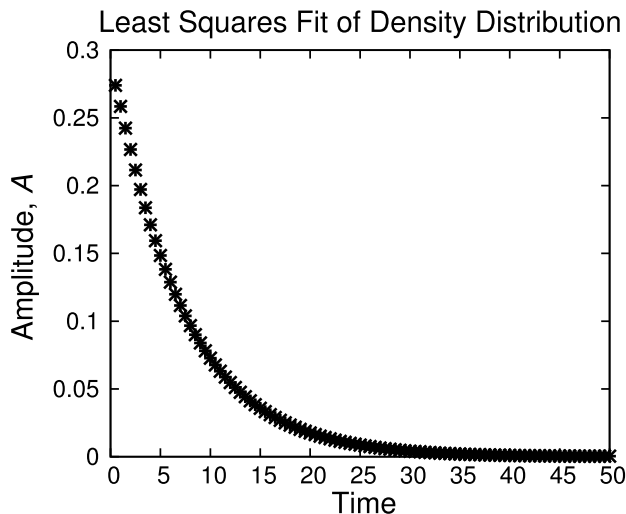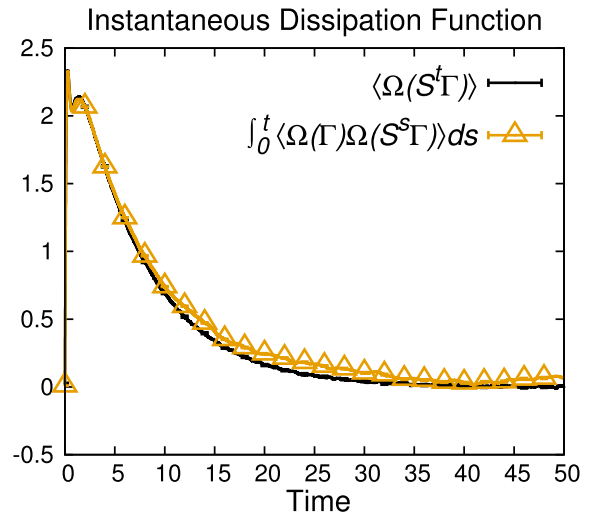which is thus called the *heat death* equation.[10]

FIG. 3. Least squares fit of the density distributions of the green particles to a sine curve with wavelength equal to the box length. The amplitude of the least squares fit is plotted against time as the system relaxes.

IV. MORE COMPLEX POTENTIAL PERTURBATION—COLOUR FIELD

To look at more complex relaxation processes, we can study the relaxation from different perturbing potentials. We start with a sum of two sine functions to generate the initial distribution,

$$U_{e,i} = \frac{a}{2}\left(\sin\left(\frac{2\pi x_i}{b_L}\right) + \sin\left(\frac{4\pi x_i}{b_L}\right)\right). \tag{19}$$

The equations of motion used were the same as in Eqs. (2)-(6), and the instantaneous dissipation function for this system is given by

$$\Omega(S^t\mathbf{\Gamma}) = \frac{\beta a\pi}{mb_L}\left(\sum_{i=1}^{N} c_i p_{x_i}(t)\left(\cos\left[\frac{2\pi x_i(t)}{b_L}\right] + 2\cos\left[\frac{4\pi x_i(t)}{b_L}\right]\right)\right). \tag{20}$$

A. Density profile

The initial distribution can be seen in Figure 5. We can see that the distribution of each colour is complex, and the total density distribution is far from uniform.

B. Relaxation

We let the system relax from the initial distribution in the same way as above. Examples of the density distributions throughout the relaxation process are shown in Figure 6. We can see that the density of green particles remains fairly complex, before apparently relaxing to a sine curve of fundamental wavelength. This sine curve then decays conformally towards a uniform distribution. The dissipation function (not shown) has the same behaviour as the first case.

In order to quantitatively monitor the relaxation, we do a least squares fit of the green particles density distribution to the sum of two sine waves. The density distribution function at each time is fitted to an equation of the form

$$D = A_1 \sin\left(\frac{2\pi x}{b_L}\right) + A_2 \sin\left(\frac{4\pi x}{b_L}\right) + \frac{\rho}{2}. \tag{21}$$

The parameters A_1 and A_2 are plotted against time in Figure 7. We can see that the higher frequency component decays faster. We fitted each series in Figure 7 to an exponential function, $A_1 = 0.225 \exp[-0.142t]$ and $A_2 = 0.259 \exp[-0.574t]$. The amplitude of the second harmonic decays four times as fast as the amplitude of the fundamental. This is the same trend observed by Fourier[25] for temperature gradients. Compared to the fundamental, the peak to the trough distance of the second harmonic is half as far, and the density gradient is twice as steep. This results in the second harmonic decaying four times as fast as the fundamental.

V. APPROXIMATE SQUARE WAVE POTENTIAL PERTURBATION APPLIED TO ALL PARTICLES

To study an even more dramatic relaxation process, we can apply an approximate square wave perturbation to
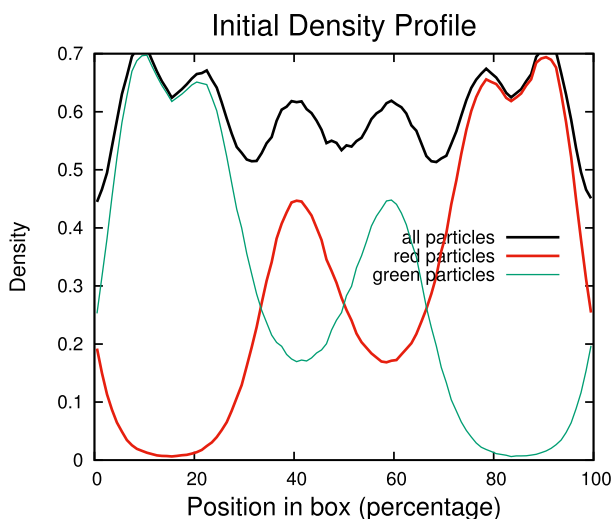

FIG. 5. Distribution generated by perturbing the equations of motion with a potential equal to the sum of two sine curves, Eq. (19). The total density distribution is shown in black, and the two colours shown in red and green.
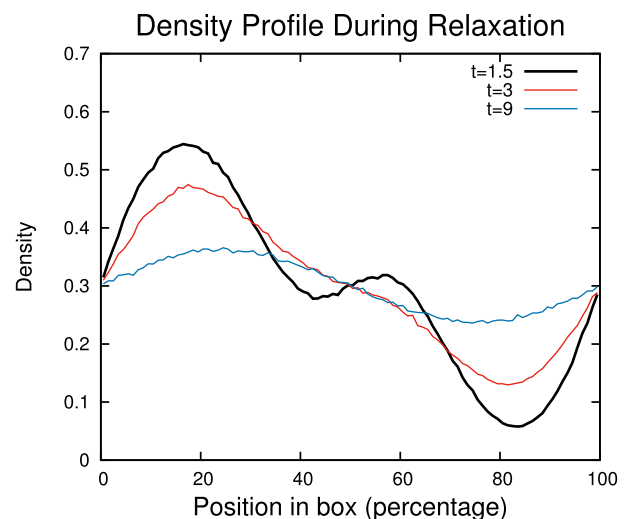

FIG. 6. Relaxation of the system from a distribution generated by a perturbation that was the sum of two sine curves. Density distributions of the green particles are shown for a selection of times along the relaxation process.
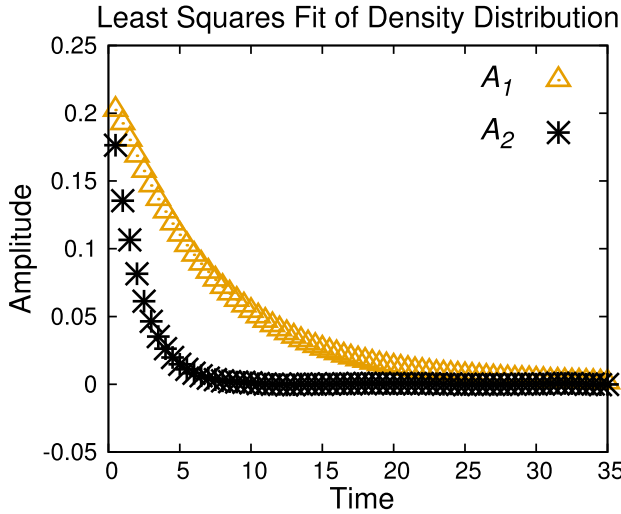
Least Squares Fit of Density Distribution

FIG. 7. A least squares fit of the density distribution of the green particles to the sum of two sine curves, Eq. (21). Both amplitudes are plotted, where A_1 is the amplitude of the sine curve of fundamental wavelength, and A_2 is the amplitude of the shorter wavelength component.

every particle in the system. This was done using a finite number of terms of the Fourier decomposition of a square wave,

$$U_{e,i} = \frac{4a}{\pi} \sum_{n=1,3,5...}^{11} \left(\frac{1}{n} \sin\left(\frac{2\pi n x_i}{b_L} \right) \right), \qquad (22)$$

which is displayed graphically in Figure 8. To apply a single-colour field, we set $c_i = 1$ for all particles in the system, Eq. (3). The instantaneous dissipation function is given by

$$\Omega(S^t \Gamma) = \frac{8\beta a}{m b_L} \left(\sum_{i=1}^{N} p_{x_i}(t) \left(\sum_{n=1,3,5...}^{11} \cos\left(\frac{2\pi n x}{b_L} \right) \right) \right). \qquad (23)$$
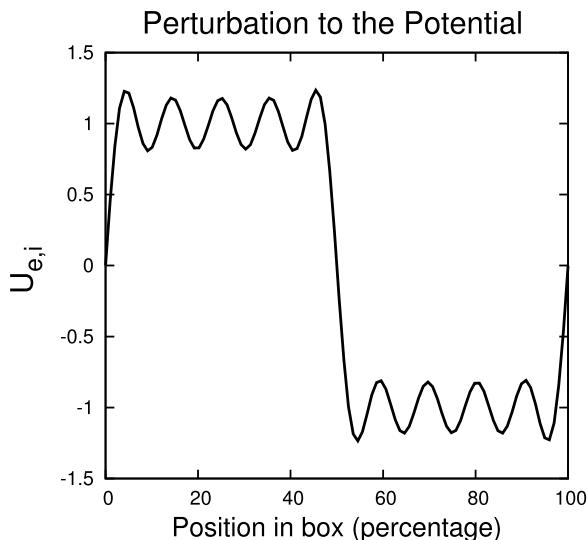
Perturbation to the Potential

FIG. 8. Approximate square wave used to perturb the equations of motion to generate the initial distribution (where the amplitude is determined by $a = 1$).
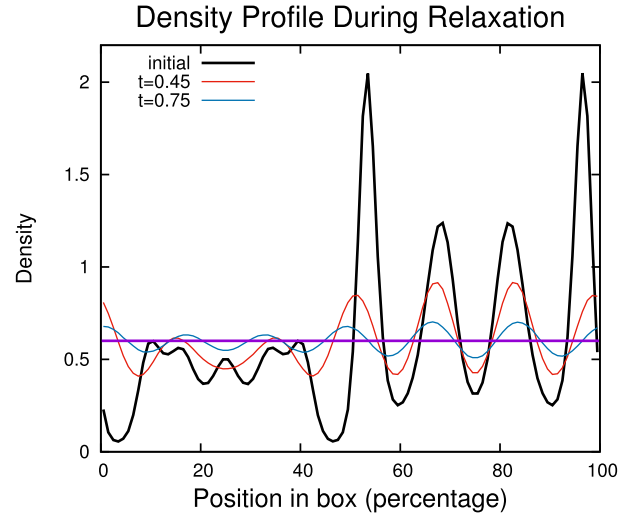
Density Profile During Relaxation

FIG. 9. Density distributions of the system initially and as it relaxes. The purple line shows the average density within the system.

A. Non-monotonic relaxation

This single-colour field perturbation results in a large density gradient across the system and a very non-uniform initial distribution, seen in Figure 9.

The relaxation of the density distribution in time is fairly complex, also seen in Figure 9. The easiest way to monitor the distribution quantitatively is to preform a discrete Fourier transform (DFT) on each distribution, and then plot each component with time. The DFT fits the density distribution to an equation of the form

$$D = \sum_{i=1}^{N} A_i \sin\left(\frac{2i\pi x}{b_L} \right) + B_i \cos\left(\frac{2i\pi x}{b_L} \right). \qquad (24)$$

A few key components can be seen in Figure 10. A particularly interesting component, the first sine component, A_1, is plotted separately in Figure 11. We can see that it displays non-monotonic relaxation; as the amplitude approaches zero, it "bounces," passing through zero a number
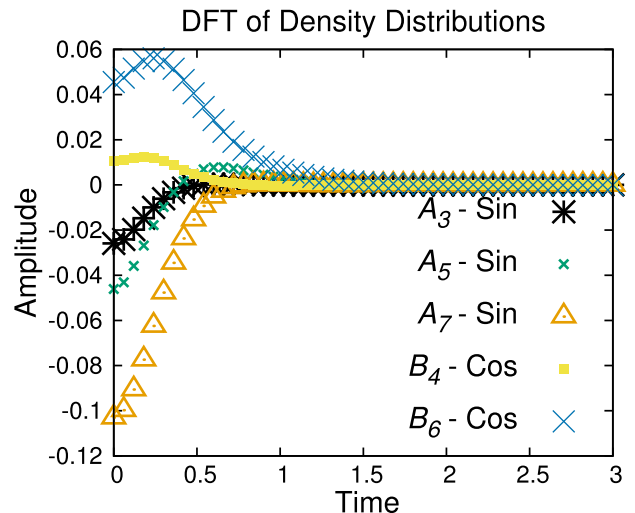
DFT of Density Distributions

FIG. 10. A selection of components of the discrete Fourier transform of the density distribution throughout the relaxation process.
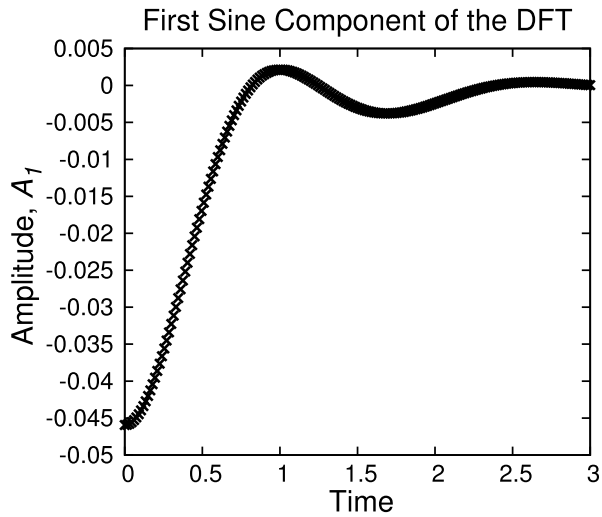
FIG. 11. Amplitude of the first sine component of the discrete Fourier transform as the system relaxes with time.

of times before finally relaxing to it. This means that at times, the density is moving away from a uniform distribution.

Figure 12 displays the calculated dissipation function of the system, which also shows non-monotonic relaxation. The points where the instantaneous dissipation function is zero correspond to the stationary points in the first component of the density distribution; there is instantaneously, approximately, no change in the distribution. While the instantaneous dissipation function is not always positive in this system, the integrated dissipation function, also plotted in Figure 12, is always greater than zero. This is consistent with the second law inequality.

We can use the dissipation function to demonstrate the dissipation theorem in this system, and again, we see
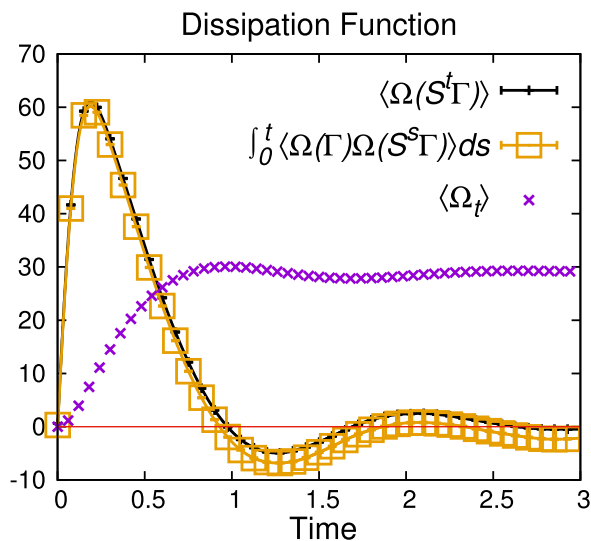

FIG. 12. Value of the instantaneous dissipation function as the system relaxes towards equilibrium, displayed as black tics. The form of the dissipation function is given in Eq. (23). An average dissipation of zero is marked by the red line. The integral of the autocorrelation function is shown in yellow squares. The ensemble average of the integrated dissipation function is plotted with purple crosses. Note that the error bars cannot be seen on this scale.

a good agreement between the average and the integrated autocorrelation function, also plotted in Figure 12.

VI. CONCLUSION

Field free relaxation was studied in systems relaxing from a non-uniform initial density, monitored using both density distributions and the dissipation function. When this density gradient was in terms of colour labeled particles the density distribution decayed to a sine curve of fundamental wavelength, which then after a very short initial transient, decayed conformally towards a uniform distribution. After the short transient, the dissipation function decayed towards equilibrium monotonically, consistent with the predictions of the relaxation theorem for a conformally relaxing system. When the system was initiated with a more dramatic density gradient, applied to all particles, non-conformal relaxation was seen in both the dissipation function and the Fourier components of the density distribution. At times, the system appeared to be moving away from a uniform density distribution. In both cases, the dissipation function based second law inequality (as derived from the fluctuation theorem) was satisfied, and the computational results were consistent with the dissipation theorem.

The observed non-monotonic decay is in sharp distinction with traditional macroscopic thermodynamics. Under this scenario, the relevant quantity (for the NVT systems under focus here) would be the Helmholtz free energy,

$$A = U - TS,$$

where U is the internal energy and T is assumed to be the temperature of the thermal reservoir, which is constant. A relaxing system has no work done on it (by construction) and so $\Delta Q = \Delta U$. The second law inequality, $\Delta S > \Delta Q/T$, is supposed to be applicable (arguably incorrectly) to a relaxing system at any instant in time and for any time interval where the system is relaxing, which leads us directly to

$$\frac{dA}{dt} < 0.$$

This is the precise argument that is used in traditional thermodynamics to conclude that A must be a minimum at equilibrium for a NVT system, *e.g.,* see page 125 of Kondepudi and Prigogine.[24] Obviously, this also precludes a system from non-monotonic decay, but in the present paper, we have shown explicitly how a thermal system, which is widely believed to be one that thermodynamics should apply to, is able to decay non-monotonically. In sharp distinction, the dissipation function based on our second law inequality, Eq. (15), does allow for non-monotonic decay and is observed to hold for all of the cases studied here.

One might wonder what would happen if we were to monitor the Helmholtz free energy directly during the relaxation. Unfortunately, this cannot be done because traditional thermodynamics does not define the entropy or the temperature of a nonequilibrium system. As the traditional Clausius inequality points out, away from equilibrium, the

entropy is not a state function. This in turn implies that the temperature is not well defined for irreversible processes, Refs. 4–8.

ACKNOWLEDGMENTS

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