

STUDYING NON-EQUILIBRIUM THERMODYNAMICS USING NON-EQUILIBRIUM MOLECULAR DYNAMICS SIMULATIONS

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ABSTRACT

One of the greatest hindrances to the development of theories of non-equilibrium thermodynamics beyond the local equilibrium approximation is the difficulty of formulating definitive experimental tests of the basic concepts. For example, the existence and definition of quantities such as temperature and entropy in far-from-equilibrium systems are extremely difficult questions to directly address by experiment. Of course, this is partially due to the extraordinary success and great range of validity of non-equilibrium thermodynamics in the local-equilibrium approximation. It is usually necessary to create systems under extreme conditions such as shock waves, if we want to see deviations from the local equilibrium approximation, although non-Newtonian fluids also provide some opportunities. Even in these situations, gaining direct experimental access to measurable quantities that can be related to the theory is not simple. Alternatively, non-equilibrium molecular dynamics simulations are an ideal test environment for many concepts in non-equilibrium thermodynamics. Many quantities of interest can be directly computed in molecular dynamics simulations. In this paper, I would like to discuss several ways in which non-equilibrium molecular dynamics simulations can be used to extract detailed information that can contribute to a deeper understanding of non-equilibrium thermodynamics. I will also describe some of the pitfalls of this approach.

INTRODUCTION

Classical non-equilibrium thermodynamics as presented by de Groot and Mazur [1] and others, has been incredibly successful in providing a unified description of an enormous breadth of non-equilibrium phenomena. However, there still remain many non-equilibrium processes that do not fit within the realm of the classical treatment. Some examples include extremely rapid heating and deformation of simple fluids (as found in shock waves, for example), and the deformation of complex materials with large relaxation times (rheology) [2]. Although many successful thermodynamically oriented theories have been developed to describe these phenomena, they are often quite specific to particular materials or processes. Furthermore, there is still disagreement about the basic assumptions underlying these extensions to classical non-equilibrium thermodynamics. Direct comparisons between experimental results and theories often lack the detail needed to test these basic assumptions. For example the concepts of temperature and entropy, which are so important in equilibrium thermodynamics, become controversial when the local equilibrium assumption is violated, but it is very difficult to delineate the range of validity of the local equilibrium assumption experimentally.

Computer simulation methods offer the opportunity to escape some of the constraints of experimental studies. Non-equilibrium molecular dynamics simulation methods have developed rapidly since the late 1970's to the point where the techniques and the theory behind them are now fairly well understood [3]. In molecular dynamics simulations, we have the opportunity to calculate almost all properties of interest while subjecting the sample to a wide variety of different perturbations, some of which could never be achieved in a controlled

way in the laboratory. However, the new pathways opened up by non-equilibrium molecular dynamics simulation techniques also lead us into unknown thermodynamic territory.

In this paper, I will first very briefly summarise the main assumptions of classical non-equilibrium thermodynamics and the ways that they can be generalised. In the second half of the paper, I will discuss two different types of non-equilibrium molecular dynamics simulations in which extensions to classical non-equilibrium thermodynamics are required.

NON-EQUILIBRIUM THERMODYNAMICS

Any brief discussion of non-equilibrium thermodynamics will be necessarily and inevitably incomplete. However, I hope that this will be sufficient to serve as a theoretical framework for the second part of the paper.

Classical non-equilibrium thermodynamics

The two major assumptions made in classical non-equilibrium thermodynamics are the local equilibrium assumption and the assumption that linear (algebraic) constitutive equations are sufficient. The local equilibrium assumption essentially postulates that the local values of fields such as the internal energy, pressure, density and entropy can be expressed entirely in terms of their equations of state using the local values of their independent variables. Thus, we can assume that the local internal energy density is a function of the local entropy, temperature, pressure and mass densities use the first and

second laws of equilibrium thermodynamics to write

$$\rho \frac{du}{dt} = \rho T \frac{ds}{dt} + \frac{p}{\rho} \frac{d\rho}{dt}. \quad (1)$$

This says that the time dependence of the internal energy is due entirely due to the time dependence of the (independent variables i.e. the specific entropy and the density) appearing in the Gibbs equation (combined first and second laws of thermodynamics). From energy conservation, we also have

$$\rho \frac{du}{dt} = -\nabla \cdot \mathbf{J}_q - \mathbf{P}^T : \nabla \mathbf{v} \quad (2)$$

and equating eq(1) with eq(2) also using the assumption that the rate of change of the local entropy density is given by

$$\rho \frac{ds}{dt} = -\nabla \cdot \mathbf{J}_s + \sigma \quad (3)$$

we obtain the usual expression for the entropy production (for details, see [1]),

$$\sigma = -\frac{1}{T} (\mathbf{P}^T - p\mathbf{1}) : \nabla \mathbf{v} - \frac{1}{T^2} \mathbf{J}_q \cdot \nabla T \quad (4)$$

where $\mathbf{P}^T - p\mathbf{1}$ is the non-equilibrium part of the pressure tensor. When the part of the entropy production due to stresses is decomposed into its irreducible components, we obtain terms due to the scalar, traceless symmetric and antisymmetric components of the pressure and velocity gradient tensors. At this point in the classical treatment of non-equilibrium thermodynamics, the assumption of linear algebraic constitutive equations is made. The fluxes are assumed to be linear algebraic functions of the thermodynamic forces and we have

$$\Pi = -\eta_V \nabla \cdot \mathbf{v}, \quad \mathbf{P}^{ts} = -2\eta (\nabla \mathbf{v})^{ts}, \quad \mathbf{J}_q = -\lambda \nabla T \quad (5)$$

These equations are valid for isotropic materials in the linear response regime and in the absence of memory and spatial non-locality. In this sense, they are quite restrictive, but they nevertheless describe a wide range of phenomena.

Deviations from local equilibrium

Classical non-equilibrium thermodynamics cannot correctly describe the behaviour of viscoelastic materials, even in a steady state. This is because, even though the viscoelastic constitutive equation (for a Maxwell model material, for example) reduces to Newton's law of viscosity in a steady state, the Gibbs equation must also be modified to account for elastic stored energy. In this sense, the local equilibrium assumption is violated. To account for the stored energy, the work done by stresses must be broken into elastic and viscous components. The decomposition of the work into elastic and viscous components for a general linear viscoelastic material has been discussed in detail previously [4; 5]. Here we will just consider the particularly simple case of a Maxwell model fluid in steady shear.

For a Maxwell model fluid, the shear stress is given by

$$P_{yx} + \tau \frac{dP_{yx}}{dt} = -\eta \dot{\gamma} \quad (6)$$

where $\tau = \eta/G$ is the viscoelastic relaxation time and the work done by the shear stress is

$$\frac{1}{\eta} P_{yx}^2 + \frac{1}{G} P_{yx} \frac{dP_{yx}}{dt} = -\dot{\gamma} P_{yx} \quad (7)$$

where η is the steady shear viscosity and G is the infinite frequency shear modulus. The terms involving these two coefficients naturally separate the work into purely viscous (irreversible) and purely elastic (reversible) contributions. When the system is taken from an equilibrium state into a thermostatted shearing steady state, the integral of the viscous term continues to increase with time, but the integral of the elastic term reaches a value depending on the shear rate (or stress) in the steady state, which becomes constant. Then the change in the total internal energy of the system can be written as the integral of eq(2) over the volume of the system and over time,

$$\Delta U = Q - W_I - W_R = Q_R - W_R \quad (8)$$

where we have defined $Q_R = Q - W_I$ as the reversible heat. This is reminiscent of the "compensated heat" of Clausius, recently discussed in detail again by Eu [6]. In a steady state, the irreversible part of the work is exactly matched by the heat removed from the system by the thermostat, and for this reason, it has been called the "housekeeping heat" [7; 8]. It is interesting to note that since the internal energy is a state function, we expect that the internal energy difference between an equilibrium state and a given shearing steady state should be independent of the path taken. Also, since we are free to take any path into the steady state (provided that it does end in the steady state), we can choose one for which $Q_R = 0$. This is analogous to an adiabatic process in equilibrium thermodynamics, but in this case, it requires a specially tuned thermostat rather than complete thermal insulation.

For the Maxwell model, we can write the reversible work in the steady state as

$$W_R = -\frac{V}{2G} P_{yx}^2 = -\frac{\dot{\gamma}^2 V \eta \tau}{2} \quad (9)$$

This can be expressed in terms of an extensive variable related to the shear rate as

$$W_R = -\frac{\dot{\gamma}^2 V \eta \tau}{2} = -\frac{(\dot{\gamma} V)^2 \eta \tau}{2V} = -\frac{\Gamma^2 \eta \tau}{2V} \quad (10)$$

where the velocity difference Δv is an external macroscopic variable

$$\Gamma = \dot{\gamma} V = \frac{\Delta v}{L} LA = \Delta v A \quad (11)$$

This is similar to the choice made by Sasa [9]. Jou et al. [2] have proposed an extensive variable based on the stress as an alternative macroscopic variable. Choosing a path to the steady state for which the reversible heat and the change in the volume are both zero, we find that the internal energy in the steady state is given by

$$U(S, V, \Gamma) = U(S, V, \Gamma = 0) + \frac{\Gamma^2 \eta \tau}{2V} \quad (12)$$

then we have

$$dU = TdS - pdV + \zeta d\Gamma \quad (13)$$

with

$$T = T_0 + \frac{\Gamma^2}{2V} \frac{\partial(\eta\tau)}{\partial S} \quad (14)$$

$$p = p_0 + \frac{\Gamma^2}{2V} \left(\frac{\eta\tau}{V} - \frac{\partial(\eta\tau)}{\partial V} \right) \quad (15)$$

$$\zeta = \frac{\eta\tau\Gamma}{V} \quad (16)$$

These equations show that the thermodynamic temperature and pressure in a shearing steady state must include strain rate dependent corrections. The same conclusion was reached by Jou et al. [2] from a completely different point of view. The resultant Gibbs equation shows that there is a rich set of Maxwell relations that it should be possible to investigate either experimentally or by computer simulation. In fact, some work in this direction has already been carried out, although the treatment in [4; 5] was slightly different from the one presented here.

Another way that local equilibrium can be violated is when certain degrees of freedom are heated and others are cooled, creating an relaxation of internal energy between different degrees of freedom. This immediately violates the assumption of local equilibrium, because at equilibrium, the temperatures of all degrees of freedom are equal. Internal thermal relaxation can be accounted for by proposing separate Gibbs equations for each of the internal energy reservoirs corresponding to the different degrees of freedom. Each of these is assumed to be at equilibrium internally but out of equilibrium with other degrees of freedom. Similar models have been investigated before in the context of plasma physics and NMR for example. They may at first seem unfamiliar, but they are not too different from the local thermodynamic equilibrium models in the sense that the standard local equilibrium models assume that we have spatially separated subsystems that are locally at equilibrium but at different temperatures. This idea has been developed in greater detail in the context of thermostats for non-equilibrium molecular dynamics simulations in [12]. From this, it is found that an additional term in the entropy production due to internal thermal relaxation appears.

Non-equilibrium molecular dynamics (NEMD) simulations exhibit both types of deviation from local equilibrium. Due to the extremely high shear rates generated in these simulations, viscoelastic effects (and also non-linear rheology) are easily observed, even for simple fluids. Also, the homogeneous thermostats that are applied in NEMD simulations remove heat specifically from some degrees of freedom while the dissipation occurs in others. This means that there are internal energy fluxes from the degrees of freedom where dissipation appears to those that are thermostatted. This will be described in more detail in the following section.

NON-EQUILIBRIUM MOLECULAR DYNAMICS SIMULATIONS

There are many different varieties of non-equilibrium molecular dynamics simulation. Some of them are designed to faithfully reproduce experimental conditions by incorporating explicit molecular boundaries by which thermodynamic driving

forces such as velocity and temperature gradients are applied to the fluid between them. These explicit boundary simulations are restricted in size due to computational limitations, making surface effects and inhomogeneity more apparent than they would be for macroscopic systems. In cases where these effects are the main focus of attention, this is an advantage. However, if the bulk macroscopic properties are the focus of interest, it is more convenient to use homogeneous simulations with periodic boundary conditions. In this case, the absence of explicit boundaries means that the thermodynamic forces must be applied through specially formulated external forces which generate the desired thermodynamic fluxes. The details of these homogeneous NEMD algorithms can be found in the literature [3; 11]. Because there are no explicit walls in homogeneous NEMD simulations, dissipated heat cannot be removed from the system by thermal conduction. Instead, additional forces in the equations of motion that do a type of work to remove heat have been developed. These thermostat terms are designed to control the value of a chosen quantity, which may be the internal energy, the kinetic temperature or some other measure of temperature. This raises the important question of the microscopic definition of temperature. At equilibrium, we can derive generalised statistical-mechanical expressions for the temperature directly from the thermodynamic definition of the temperature, but far less is known about the microscopic measures of temperature in far from equilibrium states.

Homogeneous shear

The equations of motion that are commonly used to generate a homogeneous velocity gradient are called the SLLOD equations of motion

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \mathbf{r}_i \cdot \nabla \mathbf{v} \quad (17)$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{p}_i \cdot \nabla \mathbf{v} - \alpha \mathbf{p}_i \quad (18)$$

which generate shear flow when we set the velocity gradient as

$$\nabla \mathbf{v} = \begin{bmatrix} 0 & 0 & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (19)$$

where $\dot{\gamma}$ is the shear rate. The work done by stresses calculated from the microscopic expression for the rate of change of the internal energy exactly matches eq(2) when these equations are applied. These equations of motion include a thermostat through the last term of the momentum equation of motion. The thermostat coefficient α in this case acts to keeps the kinetic temperature fixed, where the kinetic temperature is given by

$$T_K = \frac{1}{(3N - N_C) k_B} \left\langle \sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} \right\rangle. \quad (20)$$

N is the number of particles in the system and N_C is the number of constrained degrees of freedom. Note that the momentum appearing in this expression is the thermal part of the momentum, as defined by the position equation of motion, eq(17). Then we

have

$$\alpha = \frac{\sum_{i=1}^N \mathbf{p}_i \cdot (\mathbf{F}_i - \mathbf{p}_i \cdot \nabla \mathbf{v}) / m_i}{\sum_{i=1}^N \mathbf{p}_i^2 / m_i} \quad (21)$$

Eq(20) is not the only microscopic expression for the temperature that is available to us. For example, the configurational temperature, which only depends on the positions of the particles, is given by

$$k_B T_C = \frac{\left\langle \sum_{i=1}^N \left(\frac{\partial \Phi}{\partial \mathbf{r}_i} \right)^2 \right\rangle}{\left\langle \sum_{i=1}^N \frac{\partial^2 \Phi}{\partial \mathbf{r}_i^2} \right\rangle}. \quad (22)$$

where Φ is the total intermolecular potential energy of the system. At equilibrium the kinetic and configurational temperatures are equal.

We have used the SLLOD equations of motion to calculate the viscosity and first normal stress coefficient of a simple liquid undergoing shear flow in the presence of different types of thermostat [12]. Previous work has shown that as the strain rate is increased, the kinetic and configurational temperatures diverge from each other. Furthermore, it is also observed that the kinetic temperatures calculated from the different cartesian components of the thermal momentum diverge from each other as the strain rate is increased. Similarly, the configurational temperatures calculated from the different cartesian components of the force also begin to differ as the shear rate increases. This difference can be eliminated by constraining each independent cartesian kinetic and configurational temperature to the same set value with thermostats of increasing complexity (for details see [12]). It is interesting to observe that in each case, the limiting zero shear rate viscosity of the system (a linear transport coefficient) was the same within the statistical uncertainty. But the first normal stress coefficient, which is a second order property, changed dramatically under the influence of different thermostats. The value obtained also differed from the value found from the stress relaxation function evaluated at equilibrium, using the Coleman-Markovitz equation

$$\Psi_{1,0} = 2 \int_0^\infty t G(t) dt. \quad (23)$$

It has previously been shown that the first normal stress coefficient is related to the elastic energy stored in a shearing fluid [5].

The limiting zero shear rate values of viscosity and first normal stress coefficient for different thermostats are shown in Table 1. All of the values for the first normal stress coefficient differ from the value obtained from eq(23), which is evaluated at equilibrium. This provides strong evidence that the thermodynamic considerations discussed in the first section of this paper must be taken into account when analysing non-equilibrium molecular dynamics simulation results. In particular, we must question the use of microscopic expressions for temperature derived from the equilibrium distribution function to describe the state of systems that are in shearing steady states, particularly

Table 1. Zero shear rate viscosities and first normal stress coefficients calculated by NEMD for various thermostats.

temperatures fixed	η_0	error	$\Psi_{1,0}$	error
T_K	2.119	0.001	0.206	0.004
T_C	2.118	0.002	0.193	0.009
$T_{K\alpha}, \alpha = x, y, z$	2.124	0.006	0.27	0.03
$T_{C\alpha}, \alpha = x, y, z$	2.115	0.002	0.205	0.009
$T_{K\alpha}, T_{C\alpha}, \alpha = x, y, z$	2.120	0.003	0.24	0.02

when we consider non-linear properties such as the first normal stress coefficient. We must also account for temperature inhomogeneity between different degrees of freedom due to the action of the homogeneous thermostats employed in NEMD simulations. Work in this direction is currently under way.

Inhomogeneous shear

Extensions to classical non-equilibrium thermodynamics are also required for the analysis of results from inhomogeneous NEMD simulations. As an example, we will consider simulations that model the flow of a nanoparticle suspension through a narrow slit pore [13]. In these simulations, a binary solution of simple spherical particles is sandwiched between two planar molecular walls and an external field is applied to the fluid to generate Poiseuille flow. The equations of motion for the fluid are

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} \quad (24)$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{F}_e m_i \quad (25)$$

where \mathbf{F}_e is the external field. Here, \mathbf{p}_i represents the laboratory frame momentum, not the thermal momentum. More details of the simulation technique can be found in [13; 14]. When a sufficiently low external field is applied to the fluid, we obtain a quadratic velocity profile, as predicted by the classical Navier-Stokes equations. Fig. 1 shows the velocity profile for a model colloidal fluid with an external field of $F_e = 0.0001$. The fluid consists of a solution of larger particles in an explicit solvent. The solute to solvent mass ratio is 10, the solute to solvent diameter ratio is 2.2254 and the mass fraction of colloid is 0.2939. The reduced temperature is equal to 1.0. The predicted velocity profile, using the viscosity calculated from independent homogeneous simulations at equilibrium using the Green-Kubo relation, is in excellent agreement with the simulation results within the error bars which are approximately the size of the plot symbols. In a similar way, we can calculate the kinetic temperature profile for the shearing fluid, as shown in Fig. 2. The surprising result here is that, even though the flow is slow enough for the Navier-Stokes equation for the velocity profile to apply very precisely, the temperature profile cannot be predicted using Fourier's law of heat conduction. It might be thought that by using Fourier's law, we have neglected the coupling of the heat flux to the concentration gradient (in other words, the Dufour effect). However, we have calculated all of the relevant transport coefficients and find that this term is negligible in comparison to the other effects. On the other hand, we do find that the additional quadratic term in the temperature

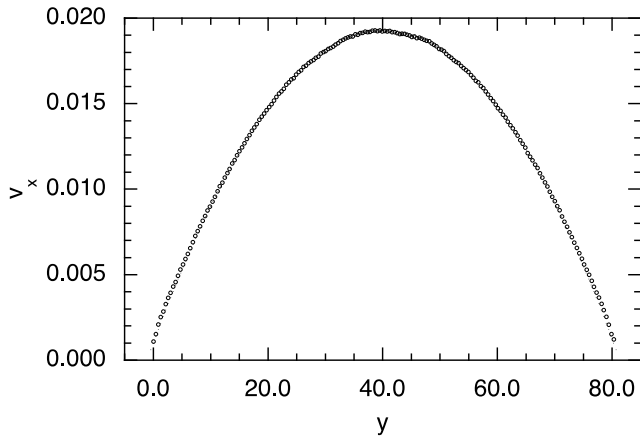


Figure 1. Velocity profile for a model colloid in planar Poiseuille flow.

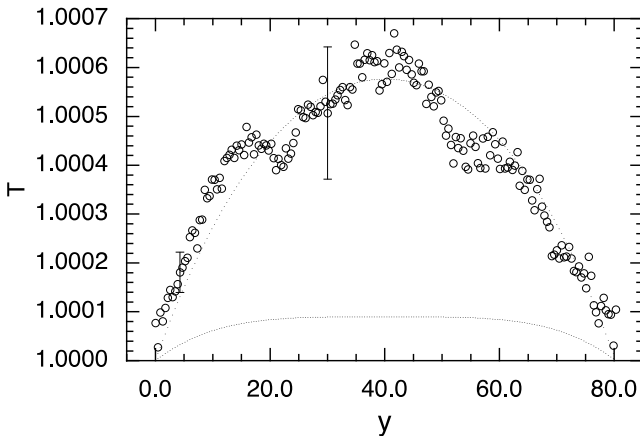


Figure 2. Temperature profile for a model colloid in planar Poiseuille flow. The solid line is the prediction of Fourier's Law and the dashed line is Fourier's Law supplemented with a nonlinear coupling to the strain rate.

profile is consistent with coupling to the strain rate. The heat flux is then given by

$$J_{qy} = -\lambda \frac{\partial T}{\partial y} - \xi \dot{\gamma} \frac{\partial \dot{\gamma}}{\partial y} \quad (26)$$

This coupling has been observed before in simulations of single component fluids [15; 16]. Further analysis of the coupling shows that it is only observable for very narrow channels - exactly the case that our non-equilibrium molecular dynamics simulations are restricted to, by computational limitations on the system size.

CONCLUSION

In this paper, we have shown how two quite different types of non-equilibrium molecular dynamics simulation cannot be described by classical non-equilibrium thermodynamics. It seems that the extensions that are required in order to have a consistent thermodynamic explanation of non-equilibrium molecular dynamics simulation results include the modification of the Gibbs equation to include a term due to the storage of elastic energy for viscoelastic fluids, a microscopic definition of temperature that can be used for shearing steady states, a proper account of

the effects of homogeneous thermostats in producing thermal relaxation between different degrees of freedom, and allowance for non-linear strain rate coupling in the constitutive equation for the heat flux. Clearly, non-equilibrium molecular dynamics simulations provide a fertile testing ground for extended theories of non-equilibrium thermodynamics.

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