

Thermodynamics of homogeneous thermostats for NEMD simulations

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Introduction

Homogeneous non-equilibrium molecular dynamics simulations

e.g. SLLOD Equations of motion

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

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{p}_i \cdot \nabla \mathbf{v}$$

- generate flow specified by the velocity gradient tensor $\nabla \mathbf{v}$
- deformation is homogeneous
- all properties are uniform; single state point
- must be implemented with compatible periodic boundary conditions

For planar shear flow,

$$\nabla \mathbf{v} = \begin{bmatrix} 0 & 0 & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

Work is done on the fluid, and heat is generated by viscous friction:

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

The heat flux is zero because there is no temperature gradient

Instead, homogeneous thermostats have been devised.

Homogeneous thermostats

- homogeneous system, periodic boundary conditions
- no walls, so heat cannot flow out through the walls
- thermostat must also act on the system homogeneously

Common homogeneous thermostats:

- velocity rescaling (does not appear explicitly in the equations of motion)
- Gaussian isokinetic (constrained - differential feedback)
- Nose-Hoover isokinetic (integral feedback)
- DPD thermostat (thermostats relative velocities of pairs of particles)

Isokinetic thermostats

These techniques control the kinetic temperature:

$$T_K = \frac{1}{(3N - N_C)k_B} \sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i}$$

Equations of motion

e.g. Gaussian isokinetic thermostat:

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

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{p}_i \cdot \nabla \mathbf{v} - \alpha \mathbf{p}_i$$

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

What is temperature?

Subject recently revived by Rugh, Jepps and others ...

For a concise review of recent developments:

Powles, Rickayzen and Heyes (Mol. Phys. **103**, 1361 (2005)).

A detailed discussion of the subject of n.e. temperature:

Casas-Vazquez and Jou (Rep. Prog. Phys. 66, 1937 (2003))

Thermodynamic temperature in the microcanonical ensemble

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_V = k_B \left(\frac{\partial \ln \Omega}{\partial U} \right)_V = \frac{k_B}{\Omega} \left(\frac{\partial \Omega}{\partial U} \right)_V$$

The differential change in internal energy can be generated in any direction in $6N$ dimensional phase space by choosing an arbitrary phase space vector **B**:

$$\frac{\partial \Omega}{\partial U} = \int \frac{\partial}{\partial \Gamma} \cdot \left[\frac{\mathbf{B}(\Gamma)}{\mathbf{B}(\Gamma) \cdot \frac{\partial H}{\partial \Gamma}} \right] \delta(H(\Gamma) - U) d\Gamma$$

giving

$$\frac{1}{k_B T} = \left\langle \frac{\partial}{\partial \Gamma} \cdot \left[\frac{\mathbf{B}(\Gamma)}{\mathbf{B}(\Gamma) \cdot \frac{\partial H}{\partial \Gamma}} \right] \right\rangle$$

Different choices of the vector **B** lead to different temperatures.

Kinetic temperature:

$$\mathbf{B}(\Gamma) = \frac{\partial K}{\partial \Gamma} = \left(0, \dots, 0, \frac{\mathbf{p}_1}{m_1}, \dots, \frac{\mathbf{p}_N}{m_N} \right)$$

$$k_B T_K = \frac{1}{3N} \left\langle \sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} \right\rangle$$

Configurational temperature:

$$\mathbf{B}(\Gamma) = \frac{\partial \Phi}{\partial \Gamma} = -(\mathbf{F}_1, \dots, \mathbf{F}_N, 0, \dots, 0)$$

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

Canonical ensemble

Consider the phase space integral

$$\int \frac{\partial}{\partial \Gamma} \cdot (\mathbf{B}(\Gamma) e^{-\beta H}) d\Gamma = \int \frac{\partial}{\partial \Gamma} \cdot \mathbf{B}(\Gamma) e^{-\beta H} d\Gamma - \beta \int \mathbf{B}(\Gamma) \cdot \frac{\partial H}{\partial \Gamma} e^{-\beta H} d\Gamma$$

By Gauss's theorem the lhs can be written as a surface integral

This is zero, because probability is zero at limits of integration

Therefore, the temperature is

$$\frac{1}{k_B T} = \frac{\left\langle \frac{\partial}{\partial \Gamma} \cdot \mathbf{B}(\Gamma) \right\rangle}{\left\langle \mathbf{B}(\Gamma) \cdot \frac{\partial H}{\partial \Gamma} \right\rangle}$$

This differs from microcanonical expression by terms $O(1/N)$.

All temperatures are equal at equilibrium

- controlling the temperature of any one degree of freedom ensures that the temperatures of all other degrees of freedom are equal to the set value
- all thermostats are then thermodynamically equivalent to $O(1/N)$

But not for systems far from equilibrium

- when strong shear is applied in NEMD simulations, the temperatures of different degrees of freedom may become unequal
- the values of some properties may depend on the thermostat!

Example: string phase and spurious alignment in shearing diatomics

Rotational angular velocity must be calculated correctly for **atomic**

thermostats (Travis, Daivis and Evans JCP 103, 10638 (1995))

Non-linear rheological properties

The response of a fluid to an applied velocity gradient is measured by the pressure tensor.

Steady, planar shear:

$$\mathbf{P}(\dot{\gamma}) = \begin{bmatrix} P_{xx} & P_{xy} & 0 \\ P_{xy} & P_{yy} & 0 \\ 0 & 0 & P_{zz} \end{bmatrix}$$

- viscosity (linear)

- first and second normal stress coefficients (nonlinear):

$$\eta = -\frac{P_{yx}}{\dot{\gamma}} \quad \Psi_1 = \frac{P_{yy} - P_{xx}}{\dot{\gamma}^2} \quad \Psi_2 = \frac{P_{zz} - P_{yy}}{\dot{\gamma}^2}$$

Limiting low shear rate behaviour

To leading order

$$\eta = \eta_0 - \eta_1 \dot{\gamma}^2$$
$$\Psi_1 = \Psi_{1,0} + c \dot{\gamma}^2$$

The viscosity should not depend on the type of thermostat, as long as a temperature is controlled.

The first normal stress coefficient could depend on the thermostat.

Equilibrium calculation of viscosity

Viscosity from stress relaxation modulus (Green-Kubo)

$$\eta_0 = \int_0^{\infty} G(t) dt$$

Equilibrium calculation of the normal stress coefficient

The limiting zero shear rate first normal stress coefficient can also be written as:

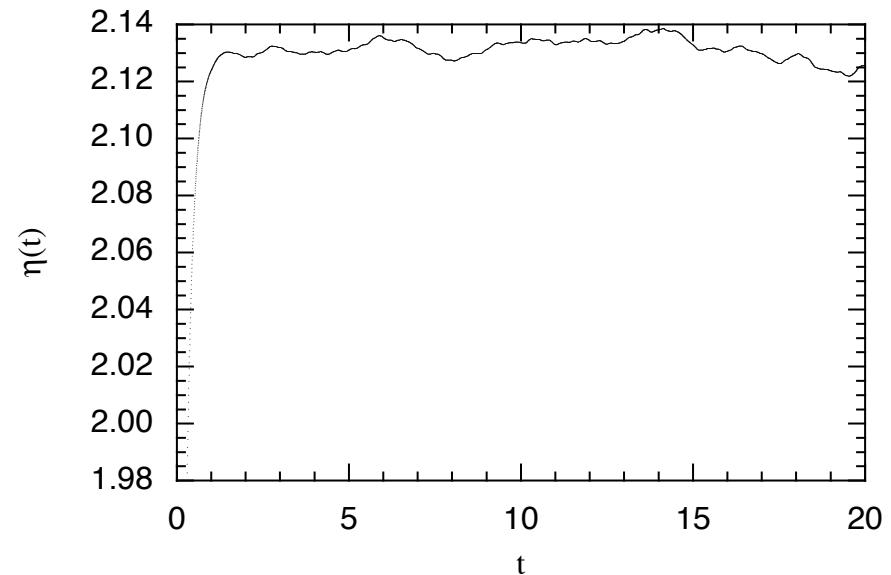
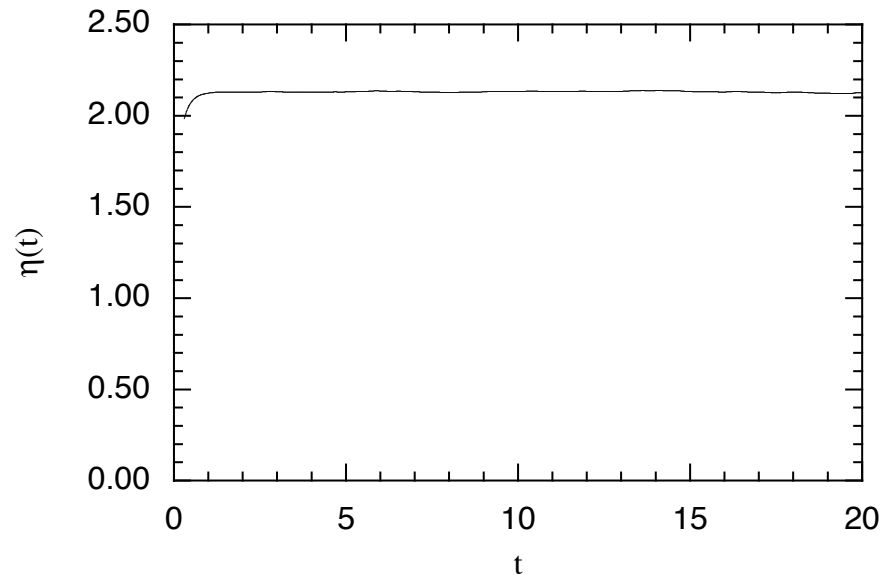
$$\Psi_{1,0} = 2 \int_0^{\infty} tG(t) dt$$

$G(t)$ is the linear stress relaxation function, which can be computed in an equilibrium simulation.

(Coleman and Markovitz, Journal of Applied Physics, **35**, 1 (1964))

Results: WCA fluid, $N = 500$, $T = 1.0$, $n = 0.84$

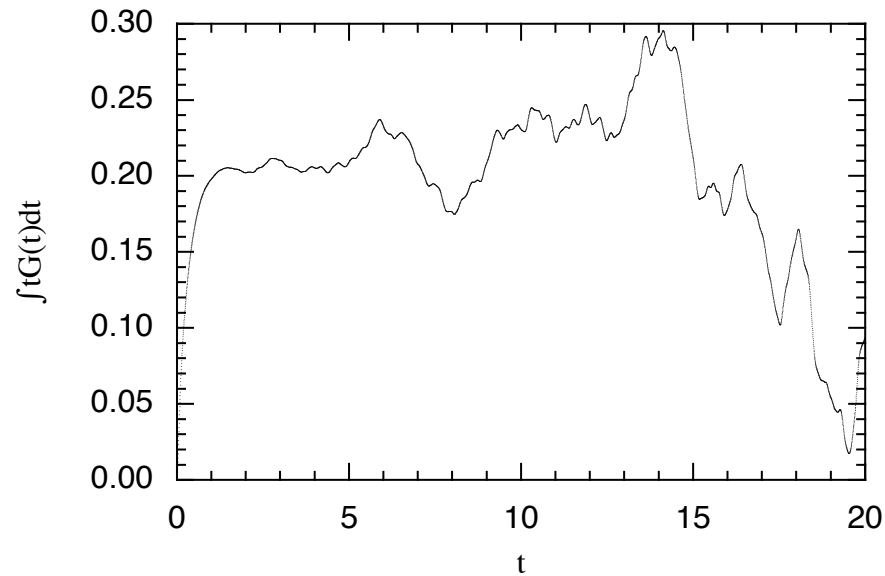
Viscosity



Stress acf integral (equilibrium): $\eta = 2.13 \pm 0.01$

Non-equilibrium – Gaussian isokinetic thermostat

NEMD: $\eta = 2.119 \pm 0.001$



From stress acf:

$$\Psi_{1,0} = 2 \int_0^{\infty} tG(t) dt = 0.40 \pm 0.10$$

NEMD – Gaussian isokinetic thermostat: $\Psi_{1,0} = 0.206 \pm 0.004$

Results disagree! Could this be due to divergence of the different temperatures in the non-equilibrium steady state?

Directional kinetic temperatures

In these computations, the **total kinetic temperature** was kept constant while the shear rate was varied. This is based on a calculation of the kinetic temperature from the sum of the x, y and z kinetic energies.

We can define the **directional kinetic temperatures** by

$$T_{Kx} = \frac{1}{(N-2)k_B} \sum_{i=1}^N \frac{p_{ix}^2}{m_i}$$

$$T_{Ky} = \frac{1}{(N-2)k_B} \sum_{i=1}^N \frac{p_{iy}^2}{m_i}$$

$$T_{Kz} = \frac{1}{(N-2)k_B} \sum_{i=1}^N \frac{p_{iz}^2}{m_i}$$

Directional kinetic thermostats

Using a directional kinetic thermostat, the directional kinetic temperatures can be kept constant. The equations of motion are then:

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

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{p}_i \cdot \nabla \mathbf{v} - \alpha_x p_{ix} \mathbf{i} - \alpha_y p_{iy} \mathbf{j} - \alpha_z p_{iz} \mathbf{k}$$

$$\alpha_x = \frac{\sum_{i=1}^N p_{ix} (F_{ix} - (\mathbf{p}_i \cdot \nabla \mathbf{v})_x) / m_i}{\sum_{i=1}^N p_{ix}^2 / m_i}$$

with similar equations for α_y and α_z .

Directional kinetic thermostat results

Viscosity:

$$\eta_0 = 2.124 \pm 0.006$$

Within uncertainties of the equilibrium and NEMD results with the kinetic thermostat.

First normal stress coefficient:

$$\Psi_{1,0} = 0.27 \pm 0.02$$

This can be compared with the previous results at equilibrium:

$$\Psi_{1,0} = 0.40 \pm 0.10$$

and with the isotropic kinetic thermostat:

$$\Psi_{1,0} = 0.206 \pm 0.004$$

Configurational thermostat

The configurational temperature can be controlled using a generalization of the Nose-Hoover thermostat devised by Braga and Travis (Braga and Travis, J. Chem. Phys. **123**, 134101 (2005)).

The equations of motion are:

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \mathbf{r}_i \cdot \nabla \mathbf{v} + \zeta \mathbf{F}_i$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{p}_i \cdot \nabla \mathbf{v}$$

$$\dot{\zeta} = \frac{1}{Q_\zeta} \left(\sum_{i=1}^N \left(\frac{\partial \Phi}{\partial \mathbf{r}_i} \right)^2 - k_B T \sum_{i=1}^N \frac{\partial^2 \Phi}{\partial \mathbf{r}_i^2} \right)$$

Directional configurational thermostats

Using a directional configurational thermostat, each of the directional configurational temperatures can be kept constant.

These temperatures are defined as:

$$k_B T_{Cx} = \frac{\left\langle \sum_{i=1}^N \left(\frac{\partial \Phi}{\partial x_i} \right)^2 \right\rangle}{\left\langle \sum_{i=1}^N \frac{\partial^2 \Phi}{\partial x_i^2} \right\rangle}$$

Directional configurational thermostats

Using the Braga-Travis thermostat, the equations of motion are then:

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \mathbf{r}_i \cdot \nabla \mathbf{v} + \zeta_x F_{ix} \mathbf{i} + \zeta_y F_{iy} \mathbf{j} + \zeta_z F_{iz} \mathbf{k}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{p}_i \cdot \nabla \mathbf{v}$$

$$\dot{\zeta}_x = \frac{1}{Q_\zeta} \left(\sum_{i=1}^N \left(\frac{\partial \Phi}{\partial x_i} \right)^2 - k_B T \sum_{i=1}^N \frac{\partial^2 \Phi}{\partial x_i^2} \right)$$

$$\dot{\zeta}_y = \frac{1}{Q_\zeta} \left(\sum_{i=1}^N \left(\frac{\partial \Phi}{\partial y_i} \right)^2 - k_B T \sum_{i=1}^N \frac{\partial^2 \Phi}{\partial y_i^2} \right)$$

$$\dot{\zeta}_z = \frac{1}{Q_\zeta} \left(\sum_{i=1}^N \left(\frac{\partial \Phi}{\partial z_i} \right)^2 - k_B T \sum_{i=1}^N \frac{\partial^2 \Phi}{\partial z_i^2} \right)$$

Summary of results

type	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
$T_{Kx,y,z}$	2.124	0.006	0.27	0.03
$T_{Cx,y,z}$	2.115	0.002	0.205	0.009
$T_{Kx,y,z}$ & $T_{Cx,y,z}$	2.120	0.003	0.24	0.02

Summary

- Two main problems that need to be resolved
- First, these definitions of temperature use the equilibrium distribution function
- These may differ when the n.e. distribution function is used
- Temperature is a thermodynamic quantity – needs a macroscopic framework for definition
- We clearly also have to account for thermal relaxation between different degrees of freedom

Thermodynamics of n.e. steady states:

Equilibrium: internal energy is a function of S , V (fixed N)

$$dU = TdS - pdV$$

NEMD simulations show that:

$$U = U(T, V, \dot{\gamma})$$

Evans and Hanley (Phys. Lett. **80A**, 175 (1980)) suggested

$$dU = TdS - pdV + \zeta d\dot{\gamma}$$

Questions:

- it leads to a Maxwell relation

$$\frac{\partial^2 A}{\partial V \partial \dot{\gamma}} = \left(\frac{\partial \zeta}{\partial V} \right)_{T, \dot{\gamma}} = - \left(\frac{\partial p}{\partial \dot{\gamma}} \right)_{T, V}$$

which is violated (Daivis, J. Non-Newtonian Fluid Mech. **152**, 120 (2008))

- computationally, p is assumed to be $p = (1/3)\text{Tr}(\mathbf{P})$

- thermodynamically,
$$p = \left(\frac{\partial U}{\partial V} \right)_{S, \dot{\gamma}}$$

- U should be expressed as a function of extensive variables, but $\dot{\gamma}$ is not extensive
- it does not account for temperature inhomogeneity between degrees of freedom

A way forward: extensions of thermodynamics

e.g.

D. Jou, J. Casas-Vazquez and M. Criado-Sancho, Thermodynamics of fluids under flow, 2nd ed. 2011

Account for non-zero fluxes (shear stress, heat flux etc.)

However, these would have to be modified to apply to NEMD thermostats.

Must include internal thermal relaxation!!

(Daivis and Jou, Continuum Mech. Thermodyn. 24, 37 (2011))

Example: kinetic-potential relaxation

Internal energy balance – can be derived microscopically

$$\frac{dU_K}{dt} = -\frac{dQ_K}{dt} - VP_{yx}^K \dot{\gamma} - \frac{dR}{dt}$$
$$\frac{dU_\Phi}{dt} = -\frac{dQ_\Phi}{dt} - VP_{yx}^\Phi \dot{\gamma} + \frac{dR}{dt}$$

Extended Gibbs equations – postulated

$$dU_K = T_K dS_K - p_K dV - \zeta_K d(VP_{yx}^K)$$

$$dU_\Phi = T_\Phi dS_\Phi - p_\Phi dV - \zeta_\Phi d(VP_{yx}^\Phi)$$

Rate of energy transfer between degrees of freedom

$$\frac{dR}{dt} = \kappa \left(\frac{1}{T_\Phi} - \frac{1}{T_K} \right)$$

Useful for modelling shock waves (Holian, Hoover ...)

Conclusions

- Extended formulations of thermodynamics are needed
- Various extensions exist, but they need to be tested
- Definitive answers not yet available

Remaining problems

Existing extended thermodynamics treatments are limited

- Maxwell model (linear) viscoelastic fluids
- assumption of internal equilibrium within a heat bath (validity?)

Existence of n.e. thermodynamic temperature?

Alternative approach (boundary thermostat):

Integrate the internal energy balance equation:

- take a homogeneous system from an equilibrium state to a shearing steady state
- use a strain rate history that can establish a steady state

Then

$$\Delta U = Q - W$$

where

$$Q = -\lim_{t \rightarrow \infty} \int_0^t \left(\oint \mathbf{J}_q \cdot d\mathbf{A} \right) ds$$

and

$$W = -\lim_{t \rightarrow \infty} \int_0^t V P_{yx}(s) \dot{\gamma}(s) ds$$

Division of mechanical work into reversible (elastic) and irreversible (viscous) components

Example: Maxwell model viscoelastic liquid

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

Rate at which work is done on the fluid:

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

First term is purely dissipative and the second is purely elastic.

The integral of the elastic term is independent of the strain history provided that the final state is a steady state.

(Daivis, JCP 118, 11111 (2003), JNNFM 152, 120 (2008))

Total work done:

$$W = W_R + W_I$$

So we can write

$$\begin{aligned}\Delta U &= (Q - W_I) - W_R \\ &= Q_R - W_R\end{aligned}$$

where Q_R is a type of “compensated heat”.

Consider a process in which the system is brought into a shearing steady state while keeping (S,V) constant.

Then, e.g. for a Maxwell fluid

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

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

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

(introduced by Sasa with different reasoning).

The internal energy in the steady state is:

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