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Numerical temperature measurement in far from equilibrium model systems

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We used a spherical piece of a solid crystal as a thermometer to measure the temperature of far from equilibrium model fluids thermostatted by a numerical feedback mechanism. The thermometer, consisting of 135 or 321 small particles, was devised to behave like one of the fluid particles in order to maintain the homogeneity of the dissipative dynamical system. We found the temperature determined by the random velocities in the close-to-equilibrium thermometer to be substantially different from the kinetic temperature of the studied nonequilibrium molecular dynamics models. We discuss the implications of our results.

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The most convenient way to study far from equilibrium systems is to set up a numerical model that correctly describes the microscopic dynamics and mimics the role of the boundaries. In the case of steady state hydrodynamic systems, there is a well-defined methodology for this purpose developed by Hoover [1] and Evans and Morriss [2]. The purely classical nonequilibrium molecular dynamics (NEMD) approach cleverly incorporates fictitious external forces in order to imitate the corresponding boundary effects. In addition to this, a feedback mechanism is used to constrain the kinetic or total internal energy of the fluid to a desired value. The latter technique, termed as *synthetic thermostat*, ensures that there is no real energy flux towards the boundaries, the numerical feedback instantaneously removes the dissipative heat. Thus, the system remains homogeneous and well-defined. These properties make NEMD models as dissipative nonlinear dynamical systems attractive to study.

Although NEMD models are well-defined in terms of their microscopic dynamics, their thermodynamic characteristics are still not fully understood. The familiar concepts of equilibrium thermodynamics such as entropy or temperature obtain different attributes under these conditions. At equilibrium one can identify three different possibilities for temperature definition: the kinetic, the thermodynamic, and the operational temperatures. The kinetic temperature is defined as $T_K \equiv [1/(3N-c)]k\Sigma_{i=1}^{N}(\mathbf{p}_i^2/m_i)$, where $\mathbf{p}_i$ is the random momentum (superimposed on the average, local streaming momentum), c is the number of constraints in the system, and m_i is the mass of particle i. The system consists of N particles and k is Boltzmann's constant. The thermodynamic temperature is defined as $T_T \equiv (\partial U/\partial S)_{N,V}$, where U is the internal energy, V is the volume, and S is the entropy of the system. The definition of the operational temperature, T_O, is, in fact, a measurement instruction: temperatures of two systems in thermal contact are equal if there is no net flow of energy through the common boundary of the systems. While at equilibrium these three definitions represent different aspects of the same state variable, it is not the case away from equilibrium [3–5]. Then it is not surprising that the concept of temperature in nonequilibrium systems is a matter of debate and controversy [6].

In this study we want to quantify the operational temperature, T_O, of several NEMD models by a mechanical thermometer hoping that the results will help in understanding the behavior of real dissipative systems. If the thermometer is a many-body object at equilibrium its random kinetic energy, T_K, measures T_O of the contacting NEMD system. The practical task to be solved is to maintain the equilibrium character of the thermometer despite the contact with its far from equilibrium environment.

Our choice of thermometer is a piece of a solid crystal embedded in the fluid. Cohesive forces of the solid can be strong enough to keep the particles together against the destructive forces of the environment. The size and shape of the solid should, at least approximately, be identical with the size and shape of a fluid particle in order to prevent the thermometer from destroying the homogeneity of the NEMD model. The simplest choice for a particle of the fluid is a soft repulsive sphere. Thus, the thermometer is chosen to be a spherical arrangement of 135 particles carved out from a close-packed, face-centered cubic crystal. Let the diameter of a thermometer particle be σ. Then the outside shell at $r=\sqrt{7}\sigma$ contains 48 particles, which makes the thermometer fairly spherical.

We devised a pairwise additive potential acting between the particles of the thermometer as follows: $\phi_{ss}(r)=\varepsilon[a_1(\sigma/r)^{-6}+a_2(\sigma/r)^{-4}+a_3(\sigma/r)^{-2}+a_4]$. The a_i parameters (128/27, −240/27, 96/27, −11/27) are chosen to produce a minimum at $r=\sigma$ with $\phi(r)=-\varepsilon$, and a maximum at $r=2\sigma$ (which is the cutoff distance for this interaction) with $\phi(r)=0.0$. The fluid-fluid and fluid-solid potentials are identical: $\phi_{ff}(r),\phi_{fs}(r)=\phi_{ss}(r)+\varepsilon$ with a cutoff at $r=\sigma$. The inter-particle distances are calculated as $r_{ij}=[(x_i-x_j)^2+(y_i-y_j)^2+(z_i-z_j)^2]^{1/2}-r_0$. The values of r_0 for the solid-solid, fluid-solid, and fluid-fluid interaction are 0.0, $\sqrt{7}\sigma$, and $2\sqrt{7}\sigma$, respectively. The potential described above provides closely identical size for the fluid particles and the "thermometer." In addition to this, the identical functional form of the interaction helps in speeding up the exchange of energy between the fluid and the solid. To produce significant nonlinear effects one has to use large dissipative fields and, inevitably, large ε's to keep the crystal together. We have no strict *a priori* ideas for the mass of a solid particle. Obviously, the whole crystal should not be lighter than m_f, where m_f is the mass of a fluid particle. Since it is the ε/m_s ratio which determines the frequency of vibrations of the solid, light solid particles mean slow energy exchange. In all that follows the results will be expressed in units of ε, σ, and m_f.

We choose the Sllod (so-called because of its connection to the Doll's tensor algorithm of Hoover [1]) and the color conductivity algorithms as NEMD models [2]. The former method (apart from the synthetic thermostat) is an exact realization of planar Couette flow. It is valid well beyond the linear regime as far as the linear velocity profile is stable. The color flow algorithm is formally identical with the model of a 1-1 molten salt under the impact of a constant electric field. In the case of planar Couette flow, the motion of the crystal can be decomposed into collective and individual movements of the constituent particles. In addition to the center of mass translation, the crystal rotates as a whole without allowing particles to leave their sites. Superimposed on these two obvious collective effects, there can be a subtle pulsation of the sphere. If the position vector of a particle measured from the center of the crystal forms an angle close to $\pi/4$ or $3\pi/4$ with the x axes the impact of the shear field elongates this vector. In the perpendicular directions the shear field induces a contraction. The Sllod equations of motion are as follows [2]:

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m_i} + \mathbf{e}_x \gamma y_i, \qquad \dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{e}_x \gamma \mathbf{p}_{yi} - \alpha \mathbf{p}_i, \tag{1}$$

where e_x is a unit vector, $\mathbf{q}_i$, $\mathbf{p}_i$, $\mathbf{F}_i$, and m_i, are the position, momentum, Newtonian force, and mass of particle i, respectively. The constant shear rate is defined as $\gamma \equiv \partial u_x/\partial y$ and α is the thermostatting multiplier given by the Nosé-Hoover integral feedback formula [1]. Equation (1) describes the motion of the fluid particles. In the case of the particles of the thermometer, there is no thermostat, i.e., the last term of the momentum equation (1) is missing. A further difference is that the streaming terms, [the second terms on the right-hand side of Eq. (1)] act on the particles via the motion of the crystal's center of mass. Thus, y_i is the y coordinate and $\mathbf{p}_{yi}$ is the y momentum of the center of mass. The latter is divided by 135, by the number of solid particles. In the case of the color conductivity algorithm, the standard equation of motions were used [2], with a thermometer particle having no color charge. Fluid particles were thermostatted also with the Nosé-Hoover scheme [1].

We collected data at the number density of $\rho = 0.003\,815$ and $T_K = 1.0$. The thermometer crystal was created in the middle of the simulation box by removing the overlapping fluid particles. This way we ended up with 102 fluid particles plus the thermometer particle. The value of ε was 6.0. This deepness was sufficient to simulate reduced shear rates up to 0.5 without a serious distortion of the sphere. The eigenvalues of the inertia tensor increased less than 5% for the largest shear rate of 0.5, while the difference between the largest (belonging to the eigenvector parallel to z) and the smallest eigenvalues was less then 2%. The lack of significant distortion meant that we could neglect the contribution of the pulsation of the solid sphere on the temperature. (Our pilot calculations also showed that this contribution is below the error bars of our calculations.) We used four different mass values for the thermometer particles: 0.1, 0.2, 1.0, and 5.0. The time step varied between 0.002 and 0.0005 depending on the mass of the thermometer particles. The equations of motion were integrated by a fifth order Gear predictor-corrector algorithm. Averages were collected during 4000–16 000 time units from each state point of the steady state systems.

TABLE I. Details of results for equilibrium and color conductivity [e, average energy of a particle; p_{xx}, $p_{yy} = p_{zz}$ pressure tensor elements; T_x, $T_y = T_z$ kinetic temperature components; $J_x = \sum c_i p_{xi}/m_i$ color current with $c_i = (-1)^i$ and $i = 1,2,\ldots N$] Numbers in parenthesis indicate the uncertainty in units of the last decimal digit. The symbols * and ** refer to the 321-particle thermometer with 102 or 494 fluid particles, respectively.

Color field	0.0	0.5	1.0
e	1.633(4)	1.638(2)	1.641(2)
p_{xx}	0.0427(2)	0.0442(2)	0.0475(3)
p_{yy}	0.0427(2)	0.0438(4)	0.0446(4)
T_x	1.000	1.023(3)	1.140(20)
T_y	1.000	0.989(4)	0.924(10)
J_x	0.0	0.097(3)	0.298(20)
$T_O(m_s=0.1)$	1.06(3)	1.07(2)	0.95(3)
$T_O(m_s=0.2)$	0.99(4)	0.99(2)	0.91(4)
$T_O(m_s=1.0)$	0.99(2)	1.01(2)	0.94(3)
$T_O(m_s=5.0)$	0.99(2)	0.99(2)	0.90(3)
$T_O(m_s=0.2)$*	1.03(3)	1.03(3)	0.93(3)
$T_O(m_s=0.2)$**	1.01(3)	1.02(3)	0.93(3)

We reduced particle positions by the thermometer's center of mass, particle velocities by its average velocity, and determined the angular momentum and the inertia tensor of the thermometer. These two quantities provided the angular velocity vector in the usual way. Subtracting the rotation and the center of mass motion from the velocities of each particle, we identified the random part of their motion which provided the temperature of the thermometer. Temperature values determined for the x, y, and z directions were practically identical. We distinguished the core of the thermometer (approximately 60 particles) from its outer shell by monitoring their temperatures separately. In all cases, the temperature of the core was higher by less than 0.5%. Thus, we can neglect the role of heat conduction inside of the crystal and can accept our thermostat as a close-to-equilibrium, many-particle system. In the case of color conductivity, there is no streaming of the center of mass and no well-defined average rotation of the solid crystal. Still we used the same method to measure the temperature because in the limit of infinitely large number of thermometer particles the reductions described above do not distort the results.

We show equilibrium and color conductivity results in Table I and shear flow results in Table II. Directional temperature ''components'' of the fluid are also shown because for NEMD models these properties also characterize the system. First, we calibrated the solid thermometer by measuring the temperature of the equilibrium fluid thermostatted by the Nosé-Hoover scheme. The discrepancies from 1.0 are beyond the error bars. However, in the absence of the thermostat, we experienced no significant differences from 1.0 using any of the masses. We believe that periodic oscillations of the kinetic temperature governed by the fictive mass of the synthetic thermostat have some impact on the heat transfer between the thermometer and the fluid by interfering with

TABLE II. Details of results for shear flow ($-p_{xy}$ is the xy element of the stress tensor; $T_z=3.0-T_x-T_y$. For further explanation of symbols, see Table I).

Shear rate	0.1	0.2	0.3	0.4	0.5
e	1.650(4)	1.672(4)	1.700(4)	1.707(6)	1.665(10)
p_{xx}	0.0480(3)	0.0553(4)	0.0631(4)	0.0631(10)	0.0440(25)
p_{yy}	0.0479(3)	0.0543(4)	0.0612(4)	0.0630(8)	0.0538(15)
p_{zz}	0.0459(3)	0.0498(4)	0.0538(6)	0.0540(6)	0.0452(15)
$-p_{xy}$	0.0098(3)	0.0179(2)	0.0243(6)	0.0251(6)	0.0172(8)
T_x	1.024(10)	1.035(8)	1.051(4)	1.030(8)	0.935(10)
T_y	0.996(6)	1.008(4)	1.031(4)	1.097(6)	1.219(10)
$T_O(m_s=0.1)$	1.09(3)	1.12(3)	1.31(5)	1.38(5)	1.56(6)
$T_O(m_s=0.2)$	0.99(3)	1.06(3)	1.18(4)	1.28(4)	1.40(5)
$T_O(m_s=1.0)$	1.06(3)	1.11(4)	1.21(4)	1.34(4)	1.42(5)
$T_O(m_s=5.0)$	1.02(3)	1.08(3)	1.20(4)	1.27(4)	1.42(5)
$T_O(m_s=0.2)$*	1.03(3)		1.26(4)		1.53(5)
$T_O(m_s=0.2)$**	1.03(3)		1.28(4)		1.57(6)

the shear-, temperature-, and density-determined average frequency of collisions and with the vibrations in the solid. Characteristic properties of simulated liquids at the same state point and external field did not differ significantly in terms of the different mass of the thermometer. Therefore, we present only their corresponding averages. In fact, these properties could be determined more accurately than the related temperature of the thermometer.

The major result of these calculations is the *significant difference* between the kinetic temperature of the nonequilibrium thermostatted fluid and the kinetic temperature of the thermometer. There can be no doubt that in NEMD models *the operational temperature is not identical with the kinetic temperature*.

We have already mentioned the ε-related limitations of creating large, easy-to-measure nonequilibrium effects in our model. Unfortunately, there are other limitations as well. Driving NEMD systems to extreme external field values might cause a change in their dynamics. This can be observed for the color conductivity with the external field of 1.0, and for the two higher shear rates, 0.4 and 0.5. For both NEMD models the motion of fluid particles becomes more ordered than it was at lower fields. At high shear rates the fluid gets ordered, particles with identical y coordinates form channels (this is the cause of the name ''string phase'') and these channels travel as collective entities during the flow. In the case of color conductivity, the situation is similar, most of the color is carried in channels. The random kinetic energy accumulates along the field direction. Particles perform intensive vibrations in the x direction but are less likely to leave their channels in the other two directions. It seems that the thermometer measures this out of channel motion as T_0. (We performed additional calculations which supported this assumption.) This is the reason of the surprising operational temperature decline for the high color field. In the case of shear flow, the increase of T_0 with the field is monotonic. The string formation, indicated by Table I, has no impact on this trend.

These changes in the dynamics prevent us from accurately determining the relationship between the *increase* of T_0 and the dissipation of the system. Nevertheless, it is a reasonable assumption to suggest a linear relationship between these two quantities in terms of increasing external fields as long as the system and thermostat set up is identical. This is in accordance with the results of Ref. [5]. As can be seen in the tables, different particle masses in the thermometer lead to different T_0 values. Since the random kinetic energy of the thermometer might be a function of the heat conductivity between the fluid and the solid (see our discussion later), the existence of such a difference cannot be excluded. However, we think that for this simple system it cannot be very significant. It is more likely that, in addition to numerical uncertainties, the interference of the synthetic thermostat might be responsible for these temperature differences as we alluded to above.

We performed additional calculations with a thermometer containing 321 small particles. (This arrangement has 72 particles on the surface.) We rescaled the size (and the pair-potential inside the thermometer) of the small particles by a factor of $\sqrt{7/13}$ in order to keep the same circumstances in the fluid as before. (The fluid-thermometer interaction remained the same.) The calculations reported at the end of Tables I and II used $m_s=0.2$. The fluid contained 102 or 494 fluid particles in equilibrium and under the impact of several external field values. The results are in agreement with the rest of the calculations. We also performed calculations with larger and smaller ε's. In the former cases, we had slow energy exchange, while in the latter cases, values below 3.0–4.0 could not keep the crystal together for high shear rates. Our studies at low densities and in a two-dimensional fluid indicated that these calculations are disadvantageous because of the small frequency of collisions and the hexagonal shape of the thermometer, respectively. Nevertheless, these results did not indicate any change in the qualitative behavior reported in the tables.

We will now make a few remarks concerning the implications of the results. First, properties of thermal balance between systems with different dissipation per mass may not guarantee the uniformity of the temperature in steady states far from equilibrium. Let $\dot{Q}$ be the average rate of dissipation of our fluid phase. Then $\dot{Q}=\dot{Q}_R+\dot{Q}_T$, where $\dot{Q}_R$ denotes the heat removed by the synthetic thermostat and $\dot{Q}_T$ is the energy transfer to the thermometer. After reaching the steady state the energy transfer from the thermometer to the fluid cancels $\dot{Q}_T$. The driving force of this reverse current is the larger kinetic temperature of the thermometer. Our results indicates that the temperature difference is a function of the dissipative process. However, this difference depends also on the thermal conductivity of the boundaries. Then, it is reasonable to assume that, in general, the kinetic temperature will be a function of Navier-Stokes transport coefficients characteristic of the particular setup of the system. In the case of several nonequilibrium systems being in thermal contact, thermal conductivities of phases and phase boundaries together with the relative dissipations of these phases will determine the resulting map of kinetic temperatures.

Second, the three definitions of temperature in NEMD models thermostatted with instantaneous feedback mechanisms can give substantially different values outside the linear regime. While the thermodynamic temperature seems to be smaller [3,4], the operational temperature is larger than the kinetic one. It seems very likely that the kinetic temperature of NEMD models is a wrong candidate for the role one can expect from a temperaturelike quantity [7]. We believe that the operational temperature as measured by our thermometer provides a good grasp of these problems and together with other promising approaches [7,8] can help clarify the picture both for NEMD models and real systems.

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