Definition of temperature in equilibrium and nonequilibrium systems

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We combine the definition of temperature for a Hamiltonian dynamical system with the Hamiltonian representation of a nonequilibrium isokinetic steady state to obtain an expression for the temperature away from equilibrium. Results of numerical simulations, performed to assess the validity of this approach for color field systems, are reported. A strong correlation between the kinetic temperature orthogonal to the color current and the ratio of the averages of two given phase variables is observed. [S1063-651X(99)50101-3]

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In a recent paper by Rugh [1], a method of determining the temperature in a Hamiltonian dynamical system was proposed. It begins with the definition of the entropy S as the (canonically invariant) weighted area of the energy surface Ω [the level set of the Hamiltonian $H(\mathbf{q},\mathbf{p})$], under the assumption that the dynamical system is ergodic in Ω. Defining the temperature $T(E)$ in the usual thermodynamic way through

$$\frac{1}{T(E)} = \frac{dS}{dE}, \tag{1}$$

Rugh defines the phase variable

$$\Psi(\Gamma) = \frac{\partial}{\partial\Gamma} \cdot \left(\frac{\partial H/\partial\Gamma}{(\partial H/\partial\Gamma)\cdot(\partial H/\partial\Gamma)} \right) \quad \text{for all} \ \ \Gamma \equiv (\mathbf{q},\mathbf{p}), \tag{2}$$

whose time average

$$\lim_{t\to\infty} \frac{1}{t} \int_0^t d\tau \Psi(\Gamma(\tau)) = \frac{1}{T(E)} \tag{3}$$

equals the inverse of the thermodynamic temperature $T(E)$ of the system with total energy E. The first numerical results based on this definition of the temperature are beginning to appear [2]. From a physical viewpoint, the phase space derivative with respect to Γ is not dimensionally consistent, therefore we define

$$\frac{\partial}{\partial\Gamma} \equiv \left(a\frac{\partial}{\partial\mathbf{q}}, b\frac{\partial}{\partial\mathbf{p}} \right) = \left(a\frac{\partial}{\partial\mathbf{q}_1},\dots,a\frac{\partial}{\partial\mathbf{q}_N}, b\frac{\partial}{\partial\mathbf{p}_1},\dots,b\frac{\partial}{\partial\mathbf{p}_N} \right), \tag{4}$$

where the prefactors a and b allow us to move to dimensionless units for both coordinates and momenta, and give us the flexibility to weight differently the momentum and coordinate contributions. Consider a d-dimensional system of N particles of unit mass, subjected to conservative forces. The Hamiltonian is

$$H = \frac{1}{2}\sum_{i=1}^{N} \mathbf{p}_i^2 + \phi(\mathbf{q}_1,\dots,\mathbf{q}_N), \tag{5}$$

where $\phi(\mathbf{q}_1,\dots,\mathbf{q}_N)$ is the total potential energy. Then, the phase variable Ψ takes the form

$$\Psi_E = \frac{a^2\displaystyle\sum_{i=1}^{N}\frac{\partial^2\phi}{\partial\mathbf{q}_i^2}+b^2 dN}{a^2\displaystyle\sum_{i=1}^{N}\left(\frac{\partial\phi}{\partial\mathbf{q}_i}\right)^2+b^2\displaystyle\sum_{i=1}^{N}\mathbf{p}_i^2}$$
$$-2\frac{\left(a^4\displaystyle\sum_{i,j=1}^{N}\frac{\partial\phi}{\partial\mathbf{q}_i}\cdot\frac{\partial^2\phi}{\partial\mathbf{q}_i\partial\mathbf{q}_j}\cdot\frac{\partial\phi}{\partial\mathbf{q}_j}+b^4\displaystyle\sum_{i=1}^{N}\mathbf{p}_i^2\right)}{\left[a^2\displaystyle\sum_{i=1}^{N}\left(\frac{\partial\phi}{\partial\mathbf{q}_i}\right)^2+b^2\displaystyle\sum_{i=1}^{N}\mathbf{p}_i^2\right]^2}, \tag{6}$$

where the subscript E indicates that the system is at constant energy. In the limit $a\to 0$, Ψ_E reduces to

$$\Psi_E = \frac{dN}{\displaystyle\sum_{i=1}^{N}\mathbf{p}_i^2} - \frac{2}{\left(\displaystyle\sum_{i=1}^{N}\mathbf{p}_i^2\right)} = \frac{dN-2}{\displaystyle\sum_{i=1}^{N}\mathbf{p}_i^2}, \tag{7}$$

which misses the correct counting of the degrees of freedom. Because of energy conservation, the numerator should have been $dN-1$. If the total linear momentum was also conserved, the numerator should have been $dN-d-1$. Using the information given by the limit $a\to 0$, one may conclude that the first term in Eq. (6) is order $O(1)$, while the second term is order $O(N^{-1})$. This is misleading, since the coefficient of the N^{-1} term is large for $a\approx b$ and cannot be neglected for systems with $N<1000$.

In Fig. 1 we present the results obtained from constant energy, equilibrium, molecular dynamics simulations of two-dimensional systems of soft spheres of diameter σ, with reduced density $\rho=0.9$, and interaction potential cutoff and shift to zero at $r=1.5\sigma$. We report both the approximate temperature T_1 obtained from Eq. (3), neglecting the second
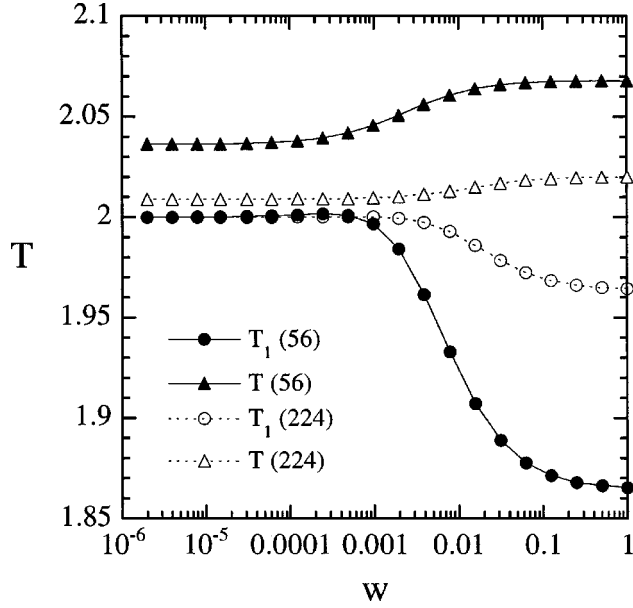
FIG. 1. Temperatures calculated from Eqs. (3) and (6) as a function of the weight $w = a^2$, and of the number of particles N. $T_1(N)$ is the temperature obtained from averaging only the first term in Eq. (6), whereas $T(N)$ is the average of the full expression Ψ_E.
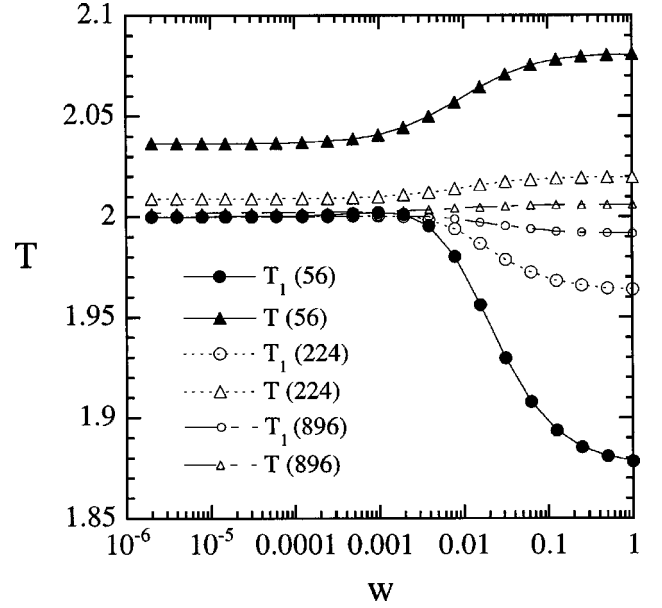

FIG. 2. Temperatures calculated from Eqs. (3) and (16) as a function of the weight $w = a^2$, and of the number of particles N. The density is $\rho = 0.9$ and the kinetic temperature is $T_K = 2.0$. As in Fig. 1, $T_1(N)$ is the approximate temperature obtained from averaging only the first term in Eq. (16), whereas $T(N)$ is the average of the full expression.

term in Eq. (6), and the full result T from Ψ_E, as functions of the number of particles and of the weight $w = a^2$, with $2^{-19} \leq a \leq 1$ and $b = 1$. We observe that T_1 approaches the value of the kinetic temperature, $T_K = 2$ from below, as N grows, while T approaches 2 from above. As a function of w, T is closer than T_1 to the correct value at large w while, for small w, T tends to $2N/(N-1)$ rather than to $T_K = 2$, due to the problem with counting degrees of freedom. We conclude that the dynamic definition of temperature [Eqs. (3) and (6)], as well as T_1, yield the correct values for our equilibrium systems in the thermodynamic limit $N \to \infty$.

Consider the possibility of extending the dynamic definition of temperature, given by Eqs. (2) and (3) to nonequilibrium stationary states. Indeed, it has recently been shown that the Gaussian isokinetic (GIK) equations of motion for systems, in which the forces are derivable from a potential ϕ can be written in Hamiltonian form [3]. This means that Eqs. (2) and (3) can be used to define a temperature for such nonequilibrium systems, despite the presence of the nonholonomic constraint

$$K = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2} = \frac{dNT}{2} = \text{const}, \tag{8}$$

where K is the kinetic energy of a d-dimensional system of N particles with unit mass. For such a system in a color field ε [4], the equations of motion for the canonical coordinates $\Gamma \equiv (\mathbf{q}, \pi)$ can be obtained from the Hamiltonian

$$H_\beta(\mathbf{q}, \pi) = \frac{1}{2} e^{(\beta+1)\phi/2K} \sum_{i=1}^{N} \pi_i^2 - K e^{(\beta-1)\phi/2K}, \tag{9}$$

where β is a parameter introduced for greater generality, and

$$\phi = \phi^{\text{int}} + \phi^{\text{ext}} = \phi^{\text{int}} - \varepsilon \sum_{i=1}^{N} c_i x_i \tag{10}$$

is the total potential energy (including internal and external fields). In fact, denoting the temporal variable by λ, we get

$$\frac{d}{d\lambda} \mathbf{q}_i = e^{(\beta+1)\phi/2K} \pi_i, \tag{11a}$$

$$\frac{d}{d\lambda} \pi_i = \mathbf{F}_i \frac{1}{4K} \left[\beta \left(\sum_i \mathbf{p}_i^2 - 2K \right) \right.$$
$$\left. + \left(\sum_i \mathbf{p}_i^2 + 2K \right) \right] e^{(\beta-1)\phi/2K}, \tag{11b}$$

where $\mathbf{F}_i = -\partial \phi / \partial \mathbf{q} = \mathbf{F}^{\text{int}} + \varepsilon c_i \hat{\mathbf{i}}$ is the total force on particle i. Then, connecting canonical (π_i) and physical ($\mathbf{p}_i$) momenta by $\pi_i e^{\phi/2K} = \mathbf{p}_i$, and rescaling the time as $e^{\beta\phi/2\hat{K}} = dt/d\lambda$, we obtain

$$\frac{d}{dt} \mathbf{q}_i = \mathbf{p}_i, \tag{12a}$$

$$\frac{d}{dt} \mathbf{p}_i = \mathbf{F}_i \frac{1}{4K} \left[\beta \left(\sum_i \mathbf{p}_i^2 - 2K \right) + \left(\sum_i \mathbf{p}_i^2 + 2K \right) \right] - \alpha \mathbf{p}_i, \tag{12b}$$

where α is the thermostatting multiplier. Taking initial conditions that satisfy the isokinetic constraint, Eq. (12b) reduces to the usual GIK equation of motion for the physical momentum: $d\mathbf{p}_i/dt = \mathbf{F}_i - \alpha\mathbf{p}_i$, which then preserves the constraint [Eq. (8)]. This model reduces to an isokinetic equilibrium one when $\phi^{\text{ext}} = 0$.

Choosing $\beta = 0$, so that the canonical and physical time variables are the same, we now differentiate $H_{\beta=0}$ to construct the function Ψ of Eq. (2). The gradient yields

$$\frac{\partial}{\partial\Gamma} H_{\beta=0}(\mathbf{q},\pi) = \left[\frac{\partial\phi}{\partial\mathbf{q}_i}\frac{a}{2}\left(\frac{e^{\phi/\hat{K}}}{2\hat{K}}\sum_{i=1}^{N}\pi_i^2 + 1\right)\right.$$

$$\left. \times e^{-\phi/2\hat{K}}, be^{\phi/2\hat{K}}\pi_i\right] \tag{13}$$

at all times. Differentiating once more, and using initial conditions and parameters that lead to the GIK equations, and substituting into Eq. (2), we get

$$\Psi_K = e^{\phi/2K}\frac{a^2e^{-\phi/K}\sum_{i=1}^{N}\frac{\partial^2\phi}{\partial\mathbf{q}^2} + b^2dN}{a^2e^{-\phi/K}\sum_{i=1}^{N}\left(\frac{\partial\phi}{\partial\mathbf{q}_i}\right)^2 + 2b^2K} - 2e^{\phi/2K}\frac{a^4e^{-2\phi/K}\sum_{i,j=1}^{N}\left(\frac{\partial\phi}{\partial\mathbf{q}_i}\cdot\frac{\partial^2\phi}{\partial\mathbf{q}_i\partial\mathbf{q}_j}\cdot\frac{\partial\phi}{\partial\mathbf{q}_j}\right) + 2a^2b^2e^{-\phi/K}\sum_{i=1}^{N}\left(\frac{\partial\phi}{\partial\mathbf{q}_i}\right)^2 + 2b^4K}{\left[a^2e^{-\phi/K}\sum_{i=1}^{N}\left(\frac{\partial\phi}{\partial\mathbf{q}_i}\right)^2 + 2b^2K\right]^2}, \tag{14}$$

where the subscript K indicates that the system is at constant kinetic energy. If we consider the limit $a \to 0$, and substitute the first term of Eq. (14) into Eq. (3), we get

$$\frac{1}{T_1} = \langle e^{\phi/2K}\rangle\frac{1}{T_K}, \tag{15}$$

where $T_K = 2K/dN$ is the fixed value of the kinetic temperature. Now, the zero of the potential cannot influence the value of the temperature, hence, we may replace ϕ by $\varphi = \phi - \phi_0$, with $\phi_0 = 2K\ln\langle e^{\phi/2K}\rangle$, obtaining $\langle e^{\varphi/2K}\rangle = 1$ and $1/T_1 = 1/T_K$. Also, Ψ_K can be written as

$$\Psi_K = e^{\varphi/2K}\frac{a'^2e^{-\varphi/K}\sum_{i=1}^{N}\frac{\partial^2\phi}{\partial\mathbf{q}_i^2} + b^2dN}{a'^2e^{-\varphi/K}\sum_{i=1}^{N}\left(\frac{\partial\phi}{\partial\mathbf{q}_i}\right)^2 + 2b^2K} - 2e^{\varphi/2K}\frac{a'^4e^{-2\varphi/K}\sum_{i,j=1}^{N}\left(\frac{\partial\phi}{\partial\mathbf{q}_i}\cdot\frac{\partial^2\phi}{\partial\mathbf{q}_i\partial\mathbf{q}_j}\cdot\frac{\partial\phi}{\partial\mathbf{q}_j}\right) + 2a'^2b^2e^{-\varphi/K}\sum_{i=1}^{N}\left(\frac{\partial\phi}{\partial\mathbf{q}_i}\right)^2 + 2b^4K}{\left[a'^2e^{-\varphi/K}\sum_{i=1}^{N}\left(\frac{\partial\phi}{\partial\mathbf{q}_i}\right)^2 + 2b^2K\right]^2}, \tag{16}$$

where we have introduced the modified weight $a' = ae^{-\phi_0/2K}$. Therefore, in the numerical simulations, it suffices to choose values of a and b, and to calculate the average of the right-hand side (RHS) of Eq. (14) and $e^{\phi/2K}$, in order to obtain the results corresponding to a'.

In Fig. 2 we present the results obtained from GIK simulations of systems of two-dimensional soft spheres at density $\rho = 0.9$ and zero color potential ϕ^{ext}. Again the weights are obtained by setting $b = 1$ and varying a. The results are very similar in character to those obtained from the constant energy simulations described above, showing the same kind of convergence, both with N and with w to the desired value of $T_K = 2.0$.

If $\phi^{\text{ext}} \neq 0$, the system evolves to a nonequilibrium steady state with a nonzero average dissipation. Moreover, it has been shown that this system has a transition from homogeneous flow to a separated state, in which particles of each color collect together and flow at a faster rate [5]. The value of color field ε_s, for which the separation transition occurs, depends on the density and on the system size, therefore, comparing systems with same ε and different N does not

necessarily compare equivalent state points. Equation (16), combined with Eq. (3), can now be used to define a nonequilibrium temperature. We calculated this temperature and compared the results with those obtained by other means (Fig. 3).

At $N = 56$ and $a^2 = 1$, the temperature T, calculated using Eqs. (3) and (16) is dominated by the potential contributions. The result 2.07 (assuming errors of at least 1%) is rather close to the fixed kinetic value $T_K = 2.0$, and to the orthogonal kinetic temperature, defined by $\Sigma p_{i,y}^2 = dNT_y$, which is $T_y = 1.994$. For $N = 224$ and $a^2 = 1$, the temperature T is 1.98, which is in even better agreement with the corresponding $T_y = 1.966$. At $N = 896$, T is 1.93, which is a little lower than $T_y = 1.954$. We conclude that the temperature defined by Eq. (16) agrees with the orthogonal part of the kinetic temperature, i.e., the part that is unaffected by the streaming motion. It would appear that Eq. (16) is a reasonable starting point for a definition of the temperature away from equilibrium. During these simulations, the value of T_y appeared to be strongly correlated to the quantity
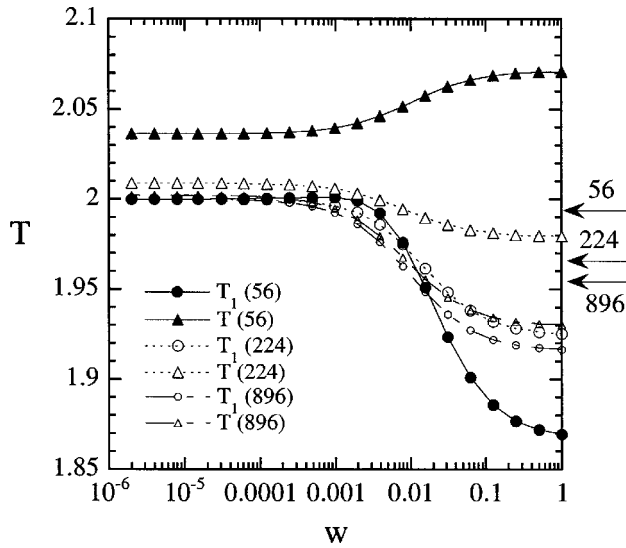
FIG. 3. Temperatures calculated from Eq. (16) as a function of the weight $w = a^2$, and of the number of particles N. The density is $\rho = 0.9$, the kinetic temperature is $T_K = 2.0$, and $\varepsilon = 1.0$. $T_1(N)$ is the temperature obtained from averaging only the first term in Eq. (16), whereas $T(N)$ is the average of the full expression. The arrows on the RHS mark the average values of the kinetic temperature orthogonal to the flow T_y, for the system sizes indicated.

$$X = \frac{\left\langle \sum_{i=1}^{N} (\partial^2 \phi / \partial \mathbf{q}^2) \right\rangle}{\left\langle \sum_{i=1}^{N} \left(\partial \phi / \partial \mathbf{q}_i \right)^2 \right\rangle}, \qquad (17)$$

in a way that is quite robust to changes in the density, field, and system size. Although this expression is similar to the first term in Eq. (16), the ratio of averages should not equal the average of the ratios in general and, at present, we have no theoretical justification for this observation. In Fig. 4, we
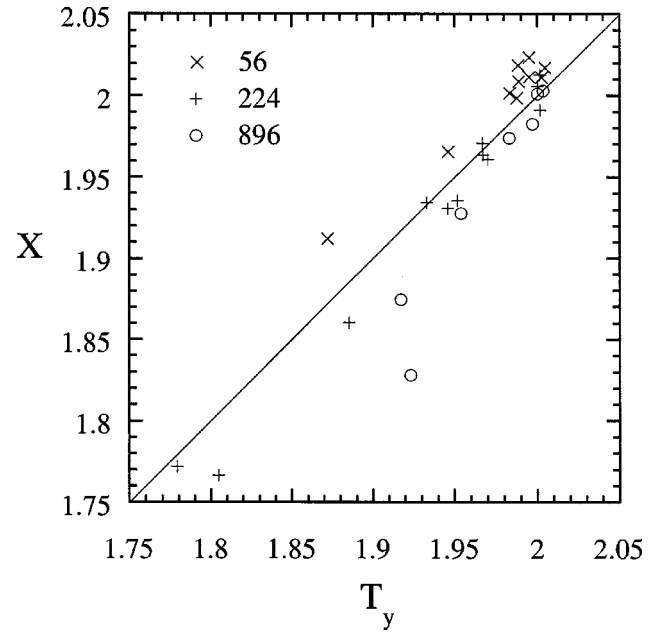

FIG. 4. Correlation between the ratio X of two average quantities, and the orthogonal temperature T_y, which is close to the average of the ratio of the same quantities. The markedly outlying points are low density, high color field states, in which some separation of the two colored species may have occurred.

present a plot of X against the orthogonal temperature T_y, as obtained in our simulations; the straight line represents the relation $X = T_y$.

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