

Configurational temperature for systems with constraints

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A general method is developed for constructing configurational expressions for the temperature of systems with constraints. As an example, this method is applied to molecular systems with bonding constraints, and an explicit formula for the temperature, in terms of only the configurational variables of the system, is derived. This formula is tested against molecular-dynamics simulations for freely jointed Lennard-Jones 8-mer chains and Monte Carlo simulations for a system of diatomic Lennard-Jones molecules.

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I. INTRODUCTION

Until very recently the equilibrium thermodynamic temperature has been calculated almost exclusively using the standard equipartition expression. This expression is, of course, entirely kinetic, involving averages of the peculiar kinetic energy. Recently it has been shown that the temperature of classical atomic systems may be calculated from only configurational information. The so-called configurational temperature, derived by Butler *et al.* [1], based on ideas proposed by Rugh [2] for the functional differentiation of the microcanonical entropy with respect to the internal energy, shows that the thermodynamic temperature may be calculated from averages of the first and second spatial derivatives of the interatomic potential energy. To date, however, expressions for the configurational temperature have been restricted to atomic systems. In the present paper, we show how a configurational temperature may be defined for systems subject to constraints. We propose an explicit configurational expression for the temperature of classical molecular systems subject to holonomic bonding constraints. Such constraints are used frequently in modeling oligomeric and polymeric fluids. We then test these expressions in equilibrium and nonequilibrium simulations of freely jointed Lennard-Jones chains.

II. DYNAMICAL TEMPERATURE FOR SYSTEMS WITH CONSTRAINTS

The entropy S of an isolated system with total energy E and Hamiltonian H is given by

$$S(E) = k_B \ln \int_{\mu C(E)} d\Gamma, \quad (1)$$

where k_B is Boltzmann's constant, and Γ is a phase-space vector of the system. The subscript $\mu C(E)$ on the integral

indicates that the integration is restricted to regions in phase space where the internal energy lies within the bounds $E < H(\Gamma) < E + \delta E$, where $\delta E \ll E$.

The equilibrium thermodynamic temperature T is defined as

$$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_V, \quad (2)$$

where the derivative is taken while holding the total volume V of the system fixed.

We can perform this derivative by displacing the phase points Γ according to

$$\Gamma'_i = \Gamma_i + \mathbf{n}_i(\Gamma) \Delta E, \quad (3)$$

where ΔE is a fixed scalar quantity, and

$$\mathbf{n}_i(\Gamma) = \frac{\sum_j g_{ij}(\Gamma) \partial_j H(\Gamma)}{\sum_{kl} [\partial_k H(\Gamma)] g_{kl}(\Gamma) [\partial_l H(\Gamma)]}, \quad (4)$$

and $\partial_i \equiv \partial / \partial \Gamma_i$. The form of the (metric) matrix $g_{ij}(\Gamma)$ is fairly arbitrary [2]; however, we must ensure that $\sum_{kl} [\partial_k H(\Gamma)] g_{kl}(\Gamma) [\partial_l H(\Gamma)] \neq 0$ for all Γ . Because g_{ij} is not unique, there are many microscopic expressions for the thermodynamic temperature. One such expression is equal, in the thermodynamic limit, to the well-known kinetic temperature [see Eq. (17), below]. At equilibrium, the averages of each of these expressions are all equal.

Because $\sum_i \mathbf{n}_i(\Gamma) \partial_i H(\Gamma) = 1$, the total energy of the system at each of the shifted phase points Γ' is equal to $E + \Delta E + O(\Delta E^2)$. The Jacobian J of the transformation $\Gamma \rightarrow \Gamma'$ is

$$J(\Gamma) = 1 + \Delta E \sum_i \partial_i \mathbf{n}_i(\Gamma) + \dots \quad (5)$$

The entropy of a system with energy $E + \Delta E$ can then be written as

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$$\begin{aligned}
S(E + \Delta E) &= k_B \ln \int_{\mu C(E + \Delta E)} d\Gamma = k_B \ln \int_{\mu C(E)} J(\Gamma) d\Gamma \\
&= S(E) + k_B \sum_i \langle \partial_i \mathbf{n}_i(\Gamma) \rangle \Delta E + \dots
\end{aligned} \quad (6)$$

where the angular brackets denote the average $\langle \dots \rangle = \int_{\mu C(E)} (\dots) d\Gamma / \int_{\mu C(E)} d\Gamma$.

Combining Eqs. (2) and (6), we arrive at

$$\begin{aligned}
\frac{1}{k_B T} &= \sum_i \langle \partial_i \mathbf{n}_i(\Gamma) \rangle \\
&= \sum_{ij} \left\langle \partial_i \left[\frac{g_{ij}(\Gamma) \partial_j H(\Gamma)}{\sum_{kl} [\partial_k H(\Gamma)] g_{kl}(\Gamma) [\partial_l H(\Gamma)]} \right] \right\rangle,
\end{aligned} \quad (7)$$

which is the expression for the dynamical temperature previously derived by Rugh [2]. By choosing $g_{ij}(\Gamma) = 0$ if i or j refers to a momentum variable and is equal to the identity matrix if both i and j refer to coordinate variables, Eq. (7) reduces to the expression for the configurational temperature for a system without constraints, derived by Butler and co-workers [1].

Now we consider a system with a set of K constraints of the general form:

$$G_\alpha(\Gamma) = 0 \quad \text{for } \alpha = 1, 2, \dots, K. \quad (8)$$

The entropy for this system is still given by Eq. (1); however, the integral is further restricted to phase points Γ where the constraints given in Eq. (8) are satisfied.

The derivation of the dynamical temperature for the constrained system is identical to the derivation given above. However, now when we make the transformation $\Gamma \rightarrow \Gamma'$, according to Eqs. (3) and (4), we must ensure that the constraints are satisfied at the new phase points Γ' , given that they are satisfied at the old phase points Γ . By noting that

$$\begin{aligned}
G_\alpha(\Gamma') &= G_\alpha(\Gamma) + \Delta E \sum_i \mathbf{n}_i(\Gamma) \partial_i G_\alpha(\Gamma) + \dots \\
&= \Delta E \sum_i \mathbf{n}_i(\Gamma) \partial_i G_\alpha(\Gamma) + \dots,
\end{aligned} \quad (9)$$

we find that we can satisfy the constraints by choosing the matrix $g_{ij}(\Gamma)$ such that

$$\sum_{ij} [\partial_i H(\Gamma)] g_{ij}(\Gamma) [\partial_j G_\alpha(\Gamma)] = 0 \quad \text{for } \alpha = 1, 2, \dots, K. \quad (10)$$

Therefore, the dynamical temperature of a system with constraints is still given by Eq. (7); however, now there is the additional restriction that $g_{ij}(\Gamma)$ must be chosen to satisfy Eqs. (10). In the next section, we derive an explicit formula for the configurational temperature of a system with molecular bonding constraints.

III. EXAMPLE: BONDING CONSTRAINTS

In this section, we focus on a d -dimensional system of N_{mol} molecules, where molecule i is made up of n_i spherical atoms that are bonded together in a pairwise fashion. The distance between two atoms is constrained to be fixed. For this system, the components of the phase-space vector Γ can be written more explicitly as $\Gamma_{i\alpha a}$, which refers to a position or momentum coordinate of atom α on molecule i . For $a = 1, 2, \dots, d$, $\Gamma_{i\alpha a}$ refers to a positional coordinate; for $a = d+1, d+2, \dots, 2d$, $\Gamma_{i\alpha a}$ refers to a momentum coordinate.

The constraint equations are given by

$$G_\alpha(\Gamma) = (\mathbf{r}_{i\alpha'} - \mathbf{r}_{i\alpha''})^2 - l_\alpha^2 = 0 \quad \text{for } \alpha = 1, 2, \dots, K,$$

$$G_\alpha(\Gamma) = (\mathbf{r}_{i\alpha'} - \mathbf{r}_{i\alpha''}) \cdot (\mathbf{p}_{i\alpha'} - \mathbf{p}_{i\alpha''}) = 0$$

$$\text{for } \alpha = K+1, K+2, \dots, 2K, \quad (11)$$

where K is the number of bonds in the system, l_α is the length of the bond, $\mathbf{r}_{i\alpha'}$ is the position of atom α' in molecule i , and $\mathbf{p}_{i\alpha'}$ is the momentum of atom α' in molecule i . The first set of constraints ensure that the bonds have the appropriate lengths. The second set of constraints ensure that the instantaneous rate of change of the bond lengths is zero.

For these constraints, Eqs. (10) can be satisfied by choosing $g_{ij}(\Gamma) \rightarrow g_{i\alpha' a, j\alpha'' b}(\Gamma)$ such that

$$g_{i\alpha' a, j\alpha'' b}(\Gamma) = \begin{cases} \delta_{ij} \delta_{ab} & \text{if } a \text{ and } b \leq d, \\ 0 & \text{otherwise,} \end{cases} \quad (12)$$

where δ_{ab} is the Kronecker delta. To verify that this choice of $g_{ij}(\Gamma)$ does indeed satisfy Eqs. (10), we substitute Eq. (12) into Eqs. (10) to find

$$\begin{aligned}
&\sum_{i\alpha' a, j\alpha'' b} [\partial_{i\alpha' a} H(\Gamma)] g_{i\alpha' a, j\alpha'' b}(\Gamma) [\partial_{j\alpha'' b} G_\alpha(\Gamma)] \\
&= \sum_{i\alpha' \alpha''} \frac{\partial H(\Gamma)}{\partial \mathbf{r}_{i\alpha'}} \cdot \frac{\partial G_\alpha(\Gamma)}{\partial \mathbf{r}_{i\alpha''}} \\
&= \sum_{i\alpha'} \frac{\partial H(\Gamma)}{\partial \mathbf{r}_{i\alpha'}} \cdot \left(\sum_{\alpha''} \frac{\partial G_\alpha(\Gamma)}{\partial \mathbf{r}_{i\alpha''}} \right) \\
&= 0 \quad \text{for } \alpha = 1, 2, \dots, K,
\end{aligned}$$

where in the last line we have used the fact that $\sum_{\alpha''} \partial G_\alpha(\Gamma) / \partial \mathbf{r}_{i\alpha''} = 0$ for all constraints α [see Eqs. (11)]. Therefore, we find that the constraint equations are indeed satisfied.

With this choice of $g_{ij}(\Gamma)$, Eq. (7) reduces to

$$\begin{aligned}
\frac{1}{k_B T} &= \sum_{i=1}^{N_{mol}} \sum_{\alpha, \alpha'=1}^{n_i} \left\langle \frac{\partial}{\partial \mathbf{r}_{i\alpha}} \cdot \left[\frac{1}{\Delta} \frac{\partial H}{\partial \mathbf{r}_{i\alpha'}} \right] \right\rangle \\
&= \sum_{i=1}^{N_{mol}} \sum_{\alpha, \alpha'=1}^{n_i} \left\langle \frac{1}{\Delta} \frac{\partial}{\partial \mathbf{r}_{i\alpha}} \cdot \frac{\partial H}{\partial \mathbf{r}_{i\alpha'}} \right\rangle + \dots,
\end{aligned} \quad (13)$$

where

$$\Delta = \sum_{i=1}^{N_{mol}} \sum_{\alpha, \alpha'=1}^{n_i} \frac{\partial H}{\partial \mathbf{r}_{i\alpha}} \cdot \frac{\partial H}{\partial \mathbf{r}_{i\alpha'}}. \quad (14)$$

We refer to the temperature defined by Eqs. (13) and (14) as the configurational temperature T_{conf} , because it depends only on the positions of the atoms in the system. Note, in the case $n_i=1$ for all i , this expression reduces to the configurational temperature derived by Butler and coworkers [1].

The expression we have given for the configurational temperature is not unique, and by choosing different forms for $g_{ij}(\mathbf{\Gamma})$ one can obtain different expressions for T_{conf} . The only restrictions on the form of $g_{ij}(\mathbf{\Gamma})$ are that Eqs. (10) must be satisfied and that $\sum_{kl} [\partial_k H(\mathbf{\Gamma})] g_{kl}(\mathbf{\Gamma}) [\partial_l H(\mathbf{\Gamma})] \neq 0$ for all $\mathbf{\Gamma}$.

IV. COMPARISON WITH COMPUTER SIMULATIONS

In order to verify the formula for the configurational temperature, we perform computer simulations for $d=3$ dimensional systems of Lennard-Jones atoms with bonding constraints. The atoms interact through the Lennard-Jones potential

$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (15)$$

where r is the distance between atoms. The length between two bonded atoms is rigidly fixed at σ . The total configurational energy Φ of the system is

$$\Phi = \frac{1}{2} \sum_{i,j=1}^{N_{mol}} \sum_{\alpha, \alpha'=1}^{n_m} u(|\mathbf{r}_{i\alpha, j\alpha'}|), \quad (16)$$

where n_m is the (fixed) number of atoms per molecule, $\mathbf{r}_{i\alpha, j\alpha'} = \mathbf{r}_{i\alpha} - \mathbf{r}_{j\alpha'}$, and $\mathbf{r}_{i\alpha}$ is the position of atom α of molecule i .

Molecular-dynamics simulations were conducted on systems of linear Lennard-Jones chains, each consisting of $n_m = 8$ freely jointed atoms per chain. We employ the molecular version of the SLLD algorithm [3] given by Edberg, Morriss, and Evans [4,5] combined with a Gaussian thermostat for the molecular kinetic temperature T_{kin} , defined as

$$\sum_{i=1}^{N_{mol}} \frac{\mathbf{P}_i \cdot \mathbf{P}_i}{2n_m m} = \frac{3(N_{mol}-1)}{2} k_B T_{kin}, \quad (17)$$

where \mathbf{P}_i is the total momentum of molecule i , N_{mol} is the total number of chains in the system, and m is the mass of each atom. In the SLLD algorithm, a constant strain rate is applied to the system by employing the usual *sliding brick* periodic boundary conditions [3] along with the following equations of motion:

$$\dot{\mathbf{r}}_{i\alpha} = \frac{\mathbf{P}_{i\alpha}}{m} + \mathbf{e}_x \gamma y_i, \quad (18)$$

$$\dot{\mathbf{p}}_{i\alpha} = \mathbf{F}_{i\alpha}^N + \mathbf{F}_{i\alpha}^C - \frac{1}{n_m} \mathbf{e}_x \gamma P_{yi} - \frac{1}{n_m} \zeta \mathbf{P}_i, \quad (19)$$

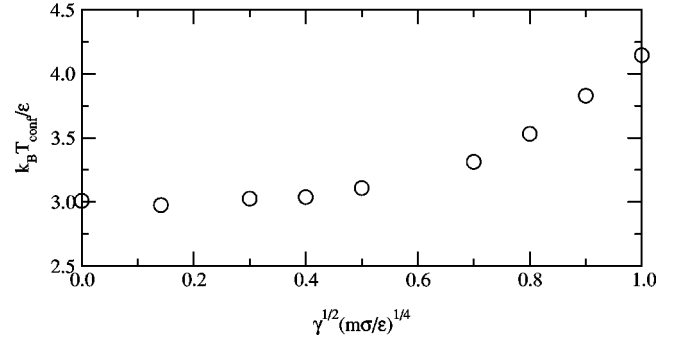


FIG. 1. NEMD simulation results for freely jointed Lennard-Jones 8-mer chains at $k_B T_{kin}/\epsilon=3$ and a total monomer density of $\rho\sigma^3=0.7$.

$$\mathbf{F}_{i\alpha}^N = - \frac{\partial \Phi}{\partial \mathbf{r}_{i\alpha}}, \quad (20)$$

where $\mathbf{p}_{i\alpha}$ is the momentum of atom α of molecule i , $n_m = 8$ is the number of atoms per molecule, \mathbf{e}_x is a unit vector directed in the positive x direction, y_i is the y coordinate of the center-of-mass of molecule i , and γ is the strain rate. The vector $\mathbf{F}_{i\alpha}^N$ is the force on atom α of molecule i due to non-bonding interactions, and $\mathbf{F}_{i\alpha}^C$ is the force due to bonding constraints (see Refs. [6] and [3]). The explicit form of $\mathbf{F}_{i\alpha}^C$ is given in the Appendix. The multiplier ζ for the molecular thermostat is given by

$$\zeta = \frac{\sum_{i=1}^{N_{mol}} (\mathbf{F}_i \cdot \mathbf{P}_i - \gamma P_{xi} P_{yi})}{\sum_{i=1}^{N_{mol}} \mathbf{P}_i \cdot \mathbf{P}_i}, \quad (21)$$

where $\mathbf{F}_i = \sum_{\alpha=1}^{n_m} (\mathbf{F}_{i\alpha}^N + \mathbf{F}_{i\alpha}^C)$.

We performed simulations for the Lennard-Jones chain system under various applied strain rates γ , with $k_B T_{kin}/\epsilon = 3$ and at a total monomer density of $\rho\sigma^3=0.7$. Each simulation consisted of a total of 256 molecules (2048 atoms), and a cutoff of 3σ was used. To integrate the equations of motion, the fourth-order Gear predictor-corrector algorithm was used with a time step $\Delta t = 0.001 (m\sigma^2/\epsilon)^{1/2}$. In addition, we have incorporated a continuous proportional feedback mechanism [7] to cancel drift in the bond length constraints.

For each set of conditions, an equilibration period of $t = 5(m\sigma^2/\epsilon)^{1/2}$ was employed, and the properties were collected over a production run of $t = 50(m\sigma^2/\epsilon)^{1/2}$. The results of the simulations are summarized in Fig. 1, where γ is the strain rate. At zero strain rate, the configurational temperature is equal to the kinetic temperature. This verifies the fact that when a system is in thermodynamic equilibrium, the average configurational temperature equals the average kinetic temperature, even when holonomic constraints are present. However, as the strain rate increases, the configurational temperature increases monotonically with the strain rate, when the kinetic temperature is kept fixed. Thus, although there are many expressions for the (unique) equilibrium thermodynamic temperature, away from equilibrium, these expressions have distinct, unequal values.

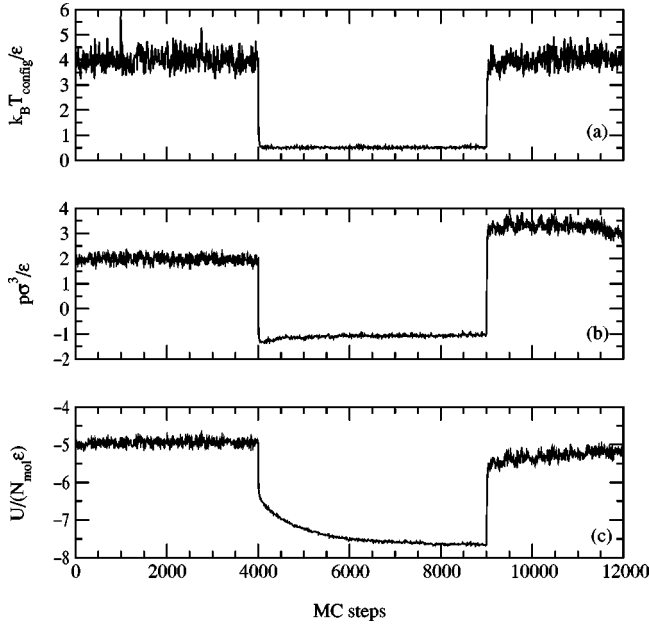


FIG. 2. Monte Carlo simulation for diatomic Lennard-Jones fluid at a total monomer density of $\rho\sigma^3=0.5$: (a) configurational temperature, (b) pressure, and (c) interaction energy. The configurational temperature rapidly attains its equilibrium value in comparison with the pressure and the interaction energy.

In order to determine the ability of the configurational temperature to respond to sudden changes in the “equilibrium” temperature, we performed an NVT Monte Carlo (MC) simulation of a rapid quench for a system of 864 diatomic Lennard-Jones molecules (1728 atoms) with bond length σ .

The simulation was started from a configuration previously equilibrated at $k_B T/\epsilon=4$ and a monomer density of $\rho\sigma^3=0.5$. The simulation was run at $k_B T/\epsilon=4$ for a period of 4000 MC steps, where an MC step consists of 864 attempted rotation-translation moves. At step 4000, the temperature was reduced to $k_B T/\epsilon=0.5$, where it remained for 5000 MC steps. Then, the temperature was returned to $k_B T/\epsilon=4$ for the remainder of the simulation.

Figure 2 shows the evolution of the (a) instantaneous configurational temperature $k_B T_{conf}/\epsilon$ [see Eq. (13)], (b) the pressure $p\sigma^3/\epsilon$, and (c) the interaction energy per molecule $U/(N_{mol}\epsilon)$. The configurational temperature T_{conf} rapidly responds to the temperature changes, attaining its equilibrium value much more quickly than the pressure or the interaction energy. Similar behavior has been observed for $d=2$ dimensional systems of Lennard-Jones atoms [1].

V. CONCLUSIONS

We have derived a completely configurational expression for the equilibrium thermodynamic temperature of systems subject to holonomic constraints. We have verified that at equilibrium this new “configurational temperature” is equal to the thermodynamic temperature, which is conventionally given by the kinetic temperature [see Eq. (17)].

Away from equilibrium, these different expressions for the temperature have distinct average values. There seems to be no good reason for preferring one expression for the tem-

perature over the others. They are each temperaturelike phase functions. In general, it seems that if the kinetic temperature is held fixed, the nonequilibrium value of the configurational temperature will be a monotonic increasing function of the strain rate. We expect that the converse might also be true, namely, if the configurational temperature is held fixed, then the kinetic temperature should be a monotonic increasing function of the strain rate.

In spite of the fact that we can legitimately expect each of these temperatures to be equal only at equilibrium, computer simulations show that, in temperature quenches, the values of the kinetic and configurational temperature equilibrate far more quickly than do other properties (e.g., pressure or energy).

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APPENDIX: CONSTRAINT FORCES

The force on atom α of molecule i due to the bonding constraints is given by

$$\mathbf{F}_{i\alpha}^C = \sum_{\alpha'=1}^{n_m-1} M_{\alpha\alpha'} \lambda_{\alpha'} (\mathbf{r}_{i\alpha'} - \mathbf{r}_{i\alpha'+1}), \quad (\text{A1})$$

where the matrix \mathbf{M} is given by

$$\mathbf{M} = \begin{pmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & -1 \end{pmatrix} \quad (\text{A2})$$

for linear freely jointed 8-mer chains. The vector $\boldsymbol{\lambda}$ is given by the solution of the equation

$$-\sum_{\alpha'=1}^{n_m-1} L_{\alpha\alpha'} \lambda_{\alpha'} = (\mathbf{r}_{i,\alpha} - \mathbf{r}_{i,\alpha+1}) \cdot (\mathbf{F}_{i,\alpha}^N - \mathbf{F}_{i,\alpha+1}^N) + (\mathbf{p}_{i,\alpha} - \mathbf{p}_{i,\alpha+1})^2, \quad (\text{A3})$$

where the matrix \mathbf{L} is given by

$$\mathbf{L} = \begin{pmatrix} 2 & -1 & 0 & 0 & 0 & 0 & 0 \\ -1 & 2 & -1 & 0 & 0 & 0 & 0 \\ 0 & -1 & 2 & -1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 2 & -1 & 0 & 0 \\ 0 & 0 & 0 & -1 & 2 & -1 & 0 \\ 0 & 0 & 0 & 0 & -1 & 2 & -1 \\ 0 & 0 & 0 & 0 & 0 & -1 & 2 \end{pmatrix}. \quad (\text{A4})$$

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