What is the microscopic formula for temperature?

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March 6, 2026

Consider a system of N particles confined to a volume V held at fixed temperature T. Let $\mathbf{x}$ be a point in our phase space Γ, so that we may write $\mathbf{x} = (p_1, \ldots, p_{3N}, q_1, \ldots, q_{3N})^\top$ in terms of the positions q and momenta p of our N particles. Let $\mathbf{A}(\mathbf{x})$ be an arbitrary vector field defined on our phase space Γ. Denoting the Hamiltonian of our system as $H(\mathbf{x}) = K(\mathbf{p}) + U(\mathbf{q})$, let us examine the following expression:

$$\begin{aligned}\nabla \cdot \left(\mathbf{A}e^{-\beta H}\right) &= (\nabla \cdot \mathbf{A})e^{-\beta H} + \mathbf{A} \cdot \nabla\left(e^{-\beta H}\right) \\ &= (\nabla \cdot \mathbf{A})e^{-\beta H} - \beta(\mathbf{A} \cdot \nabla H)e^{-\beta H}\end{aligned}$$

Here $\nabla = (\ldots, \partial_{p_i}, \ldots, \partial_{q_i}, \ldots)^\top$ is the phase space gradient. Now, we integrate both sides over phase space and divide by the partition function $Z = Z(N, V, \beta)$,

$$\begin{aligned}\frac{1}{Z}\int_\Gamma \nabla \cdot \left(\mathbf{A}e^{-\beta H}\right) \mathrm{d}^{6N}x &= \frac{1}{Z}\int_\Gamma (\nabla \cdot \mathbf{A})e^{-\beta H}\mathrm{d}^{6N}x - \frac{\beta}{Z}\int_\Gamma (\mathbf{A} \cdot \nabla H)e^{-\beta H}\mathrm{d}^{6N}x \\ \frac{1}{Z}\oint_{\partial\Gamma} e^{-\beta H}\mathbf{A} \cdot \hat{\mathbf{n}}\mathrm{d}S &= \langle \nabla \cdot \mathbf{A}\rangle - \beta\langle \mathbf{A} \cdot \nabla H\rangle\end{aligned}$$

On the right hand side, we have employed the definition of the canonical expectation value. On the left hand side we have used the divergence theorem to turn the (hyper-)volume integral into an integral of the flux through the boundary of our phase space, which we will push to infinity. The prefactor of our integrand, $\exp(-\beta H)$, goes to zero as we send any of the $p_i \to \pm\infty$, since the kinetic energy blows up in this case. Since we concern ourselves only with a system of finite volume V, we can safely stipulate that the potential energy blows up outside of the allowable volume, and therefore our integrand also goes to zero if we push any of the q_i to large or small values. Therefore, the left hand side is zero. Rearranging, we then have

$$\boxed{k_\mathrm{B}T = \frac{\langle \mathbf{A} \cdot \nabla H\rangle}{\langle \nabla \cdot \mathbf{A}\rangle}} \tag{1}$$

This is pretty remarkable, because we have said nothing about $\mathbf{A}$. The choice of this vector field is completely arbitrary (up to mathematical niceness, i.e. differentiability, convergence of expectation values, etc.), and so we find that there are infinitely many valid microscopic expressions for temperature in the canonical ensemble: one for each choice of $\mathbf{A}$. Due to the convergence of ensembles in the limit of large N, this expression can also be used for microcanonical systems (constant energy E). In this case it should be noted that rather than being a strict equality, the expression converges to the thermodynamic definition $1/T = (\partial S/\partial E)_{V,N}$ with an $\mathcal{O}(1/N)$ bias term (as shown in ref [2]), though this is true of essentially all formulae for calculating intensive thermodynamic quantities in the microcanonical ensemble.

To show how Eqn. (1) works with a concrete example, let $\mathbf{A}$ be a vector of all zeros except $A_j = p_j/m_j$ (the j^{th} momentum component divided by its corresponding particle mass). $\nabla \cdot \mathbf{A}$ is then simply $1/m_j$. Our Hamiltonian gradient is

$$\begin{aligned}\nabla H &= \nabla\left(\sum_{i=1}^{3N}\frac{p_i^2}{2m_i} + U(\mathbf{q})\right) \\ &= \left(\frac{p_1}{m_1}, \ldots, \frac{p_{3N}}{m_{3N}}, \frac{\partial U}{\partial q_1}, \ldots, \frac{\partial U}{\partial q_{3N}}\right)^\top,\end{aligned}$$

which means that

$$\mathbf{A} \cdot \nabla H = \frac{p_j^2}{m_j^2}.$$

Putting these together, this then says that

$$\left\langle \frac{p_j^2}{m_j} \right\rangle = k_\mathrm{B}T.$$

Adding together three of these for the momentum components of one particle gives us the form more usually seen in intro courses,

$$\left\langle \frac{\mathbf{p}^2}{2m} \right\rangle = \frac{3}{2}k_\mathrm{B}T.$$

Calculating the temperature from this formulation yields the *kinetic temperature*. If your system is in equilibrium this will of course converge to the same value as any of the other possible temperature formulae.

Speaking of, let's look at another temperature formula. Let $\mathbf{A} = \nabla U$. Then

$$\mathbf{A} \cdot \nabla H = \nabla U \cdot (\nabla K + \nabla U) = \underbrace{\nabla U \cdot \nabla K}_{0} + \nabla U \cdot \nabla U = (\nabla U)^2$$

and $\nabla \cdot \mathbf{A} = \nabla^2 U$. Therefore,

$$k_\mathrm{B}T = \frac{\langle (\nabla U)^2 \rangle}{\langle \nabla^2 U \rangle}.$$

This is an interesting expression in that *it does not depend on the momenta*. This expression allows one to calculate the temperature solely from the coordinates and forces. This is called a *configurational temperature*. Again, in equilibrium, this will give the exact same value as the kinetic temperature presented above. As a slightly more concrete example, if we consider a single particle in a 1D harmonic potential, then

$$U(q) = \frac{1}{2}\kappa q^2 \quad \Longrightarrow \quad k_\mathrm{B}T = \kappa \langle q^2 \rangle.$$

So you can get the temperature directly from the variance of the position about the bottom of the well.

At this point, some commentary is warranted. The general formula for $k_\mathrm{B}T$ in Eqn. (1) has been known at least since 1987, as it appears (without proof) in the famous textbook on fluid simulations by Allen and Tildesley[1]. However, it seems that it went relatively unnoticed until the late 1990s, when it was apparently re-discovered and resulted in a flurry of highly-cited papers about the configurational temperature and its applications to Monte Carlo simulations[5, 2, 3, 4]. For historical reasons, many people (and textbooks!) will often quote the kinetic temperature as being *the* microscopic definition of temperature. I am of the opinion that this is *wrong*. It's not simply wrong in a pedantic sense, either. It is critically important to know that temperature can be defined and measured completely independently of particle velocities. In many types of Monte Carlo simulations, velocities are not even calculated! The systems under study still have well-defined temperature. From the persepctive of statistcal mechanics (the theory which connects microscopic descriptions of physical systems to macroscopic thermodynamics), saying a system is held at a fixed temperature T is a statement about the form of the phase space distribution function: it is proportional to $\exp(-H/k_\mathrm{B}T)$. This is an *incredibly* strong statement, and does not put any special emphasis on the kinetic part of the energy.

References

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[5] Hans Henrik Rugh. "Dynamical approach to temperature". In: *Physical review letters* 78.5 (1997), p. 772.