

## Simplified derivation of expression for temperature from energy derivative of entropy

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The internal energy of a thermodynamic system in which only work of expansion or compression is being considered, can be regarded as a function of the internal energy and the volume, so that  $U = U(S, V)$ . Therefore, for any infinitesimal change in  $S$  or  $V$ , the internal energy change is:

$$dU = \left( \frac{\partial U}{\partial S} \right)_V dS + \left( \frac{\partial U}{\partial V} \right)_S dV \quad 1$$

but the first law of thermodynamics gives

$$dU = dQ - dW = TdS - pdV \quad 2$$

where  $Q$  here is the reversible heat transfer that occurs when the infinitesimal transformation is made. These equations together define the thermodynamic temperature as:

$$T = \left( \frac{\partial U}{\partial S} \right)_V \quad 3$$

In the microcanonical ensemble (constant  $U$  and  $V$ ), the equilibrium distribution function is postulated to be uniform over the constant energy surface defined by  $H = U$ , where  $U$  is the value of the internal energy, and  $H$  is a function of  $S$  and  $V$ , or of  $\Gamma$ , the set of positions and momenta of the particles in the system. Mathematically, this statement can be written as:

$$f(\Gamma) = \frac{\delta(H(\Gamma) - U)}{\Omega} \quad 4$$

where the normalisation constant  $\Omega$  given by

$$\Omega = \int \delta(H(\Gamma) - U) d\Gamma \quad 5$$

is called the microcanonical partition function. It represents the phase space volume, weighted by the delta function probability distribution function, occupied by the macroscopic thermodynamic state defined by the values of  $S$  and  $V$ . This physical interpretation is often used when a microcanonical distribution function is pictured as a shell of vanishingly small thickness in phase space (Tolman, Huang). The limiting case, in which the distribution function is a surface in phase space, is sometimes called the surface distribution, to distinguish it from the more common shell picture of the microcanonical distribution (Tolman). In this interpretation, eq. (5) represents the area of the energy surface, rather than the phase space volume.

The entropy is defined in terms of the microcanonical partition function as

$$S = k_B \ln \Omega \quad 6$$

Combining eq (3) and eq(6) we see that the equilibrium thermodynamic temperature can be written as

$$\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_V = k_B \left( \frac{\partial \ln \Omega}{\partial U} \right)_V = \frac{k_B}{\Omega} \left( \frac{\partial \Omega}{\partial U} \right)_V \quad 7$$

The derivative of the partition function is therefore required.

The volume only appears in the limits of integration, and will be assumed to remain constant. Thus, the partial derivative can be written as:

$$\begin{aligned} \frac{\partial \Omega}{\partial U} &= \frac{\partial}{\partial U} \int \delta(H(\Gamma) - U) d\Gamma \\ &= - \int \frac{\partial}{\partial H} \delta(H(\Gamma) - U) d\Gamma \end{aligned} \quad 8$$

The partial derivative can be expressed in terms of a partial derivative with respect to the phase space vector as

$$\frac{\partial}{\partial \Gamma} \delta(H(\Gamma) - U) = \frac{\partial H}{\partial \Gamma} \frac{\partial}{\partial H} \delta(H(\Gamma) - U)$$

If we multiply through by an arbitrary phase variable  $\mathbf{B}(\Gamma)$ , this can be rewritten as

$$\mathbf{B}(\Gamma) \cdot \frac{\partial}{\partial \Gamma} \delta(H(\Gamma) - U) = \mathbf{B}(\Gamma) \cdot \frac{\partial H}{\partial \Gamma} \frac{\partial}{\partial H} \delta(H(\Gamma) - U)$$

which gives the result

$$\frac{\partial}{\partial H} \delta(H(\Gamma) - U) = \frac{\mathbf{B}(\Gamma)}{\mathbf{B}(\Gamma) \cdot \frac{\partial H}{\partial \Gamma}} \frac{\partial}{\partial \Gamma} \delta(H(\Gamma) - U)$$

If we now substitute this into the integral that we wish to evaluate, we obtain

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

which can be integrated by parts. The boundary term is zero, and we obtain

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

Then the final result is

$$\begin{aligned} \frac{1}{k_B T} &= \frac{1}{\Omega} \int \frac{\partial}{\partial \Gamma} \cdot \left[ \frac{\mathbf{B}(\Gamma)}{\mathbf{B}(\Gamma) \cdot \frac{\partial H}{\partial \Gamma}} \right] \delta(H(\Gamma) - U) d\Gamma \\ &= \left\langle \frac{\partial}{\partial \Gamma} \cdot \left[ \frac{\mathbf{B}(\Gamma)}{\mathbf{B}(\Gamma) \cdot \frac{\partial H}{\partial \Gamma}} \right] \right\rangle \end{aligned}$$

This is the microscopic expression for the temperature in the microcanonical ensemble.

### Further notes

The effect of various choices of the vector field  $\mathbf{B}(\Gamma)$  has been discussed by Jepps, Ayton and Evans. Here, it is sufficient to note that the generalized equipartition theorem, the equipartition theorem and the virial theorem all follow from this result.

It is convenient to simplify this further. Applying the phase space gradient operator to the fraction in the brackets gives us

$$\frac{\partial}{\partial \Gamma} \cdot \left[ \frac{\mathbf{B}(\Gamma)}{\mathbf{B}(\Gamma) \cdot \frac{\partial H}{\partial \Gamma}} \right] = \frac{\frac{\partial}{\partial \Gamma} \cdot \mathbf{B}(\Gamma)}{\mathbf{B}(\Gamma) \cdot \frac{\partial H}{\partial \Gamma}} + \mathbf{B}(\Gamma) \cdot \frac{\partial}{\partial \Gamma} \left( \frac{1}{\mathbf{B}(\Gamma) \cdot \frac{\partial H}{\partial \Gamma}} \right)$$

and

$$\frac{\partial}{\partial \Gamma} \left( \frac{1}{\mathbf{B}(\Gamma) \cdot \frac{\partial H}{\partial \Gamma}} \right) = - \frac{1}{\left( \mathbf{B}(\Gamma) \cdot \frac{\partial H}{\partial \Gamma} \right)^2} \left( \frac{\partial \mathbf{B}(\Gamma)}{\partial \Gamma} \cdot \frac{\partial H}{\partial \Gamma} + \frac{\partial^2 H}{\partial \Gamma \partial \Gamma} \cdot \mathbf{B}(\Gamma) \right)$$

The derivatives of the Hamiltonian are:

$$\begin{aligned} \frac{\partial H}{\partial \Gamma} &= \frac{\partial}{\partial \Gamma} (K + \Phi) \\ &= \left( \frac{\partial \Phi}{\partial \mathbf{r}_1}, \dots, \frac{\partial \Phi}{\partial \mathbf{r}_N}, \frac{\partial K}{\partial \mathbf{p}_1}, \dots, \frac{\partial K}{\partial \mathbf{p}_N} \right) \\ &= \left( \mathbf{F}_1, \dots, \mathbf{F}_N, \frac{\mathbf{p}_1}{m_1}, \dots, \frac{\mathbf{p}_N}{m_N} \right) \end{aligned}$$

and

$$\frac{\partial^2 H}{\partial \Gamma \partial \Gamma} = \begin{bmatrix} \left( \frac{\partial \mathbf{F}_j}{\partial \mathbf{r}_i} \right) & \dots & 0 \\ \dots & \dots & \dots \\ 0 & \dots & \left( \frac{1}{m_j} \frac{\partial \mathbf{p}_j}{\partial \mathbf{p}_i} \right) \end{bmatrix}$$

which is a matrix consisting of an upper left block with second derivatives of the potential energy and a lower right block which is diagonal, containing the second derivatives of the kinetic energy. Note that we have adopted the convenient notation of writing each entry as a vector so that the number of rows and columns are both  $2N$ . Of course, the full phase space is  $6N$  dimensional because each position or momentum vector has three Cartesian components.

Now we consider the following special choices for  $\mathbf{B}(\Gamma)$ . If we choose

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

then

$$\frac{\partial \mathbf{B}(\Gamma)}{\partial \Gamma} = \begin{bmatrix} 0 & \dots & 0 \\ \dots & \dots & \dots \\ 0 & \dots & \left( \frac{1}{m_j} \frac{\partial \mathbf{p}_j}{\partial \mathbf{p}_i} \right) \end{bmatrix}$$

which is a lower right diagonal block matrix consisting of the mass-weighted unit tensor. Then the terms in the expression for the temperature are:

$$\begin{aligned}\frac{\partial}{\partial \Gamma} \cdot \mathbf{B}(\Gamma) &= \sum \frac{3}{m_i} \\ \mathbf{B}(\Gamma) \cdot \frac{\partial H}{\partial \Gamma} &= \sum \frac{\mathbf{p}_i^2}{m_i^2} \\ \mathbf{B}(\Gamma) \cdot \frac{\partial \mathbf{B}(\Gamma)}{\partial \Gamma} \cdot \frac{\partial H}{\partial \Gamma} &= \sum \frac{\mathbf{p}_i^2}{m_i^2} \\ \mathbf{B}(\Gamma) \cdot \frac{\partial^2 H}{\partial \Gamma \partial \Gamma} \cdot \mathbf{B}(\Gamma) &= \sum \frac{\mathbf{p}_i^2}{m_i^2}\end{aligned}$$

And the final expression for the kinetic temperature is

$$\frac{1}{k_B T} = \left\langle \frac{\partial}{\partial \Gamma} \cdot \left[ \frac{\mathbf{B}(\Gamma)}{\mathbf{B}(\Gamma) \cdot \frac{\partial H}{\partial \Gamma}} \right] \right\rangle = \frac{\sum \frac{3}{m_i} - 2}{\left\langle \sum \frac{\mathbf{p}_i^2}{m_i^2} \right\rangle}$$

A second choice of interest is

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

This results in the following:

$$\frac{\partial \mathbf{B}(\Gamma)}{\partial \Gamma} = - \begin{bmatrix} \left( \frac{\partial \mathbf{F}_j}{\partial \mathbf{r}_i} \right) & \dots & 0 \\ \dots & \dots & \dots \\ 0 & \dots & 0 \end{bmatrix}$$

and the relevant quantities for the calculation of the temperature in this case are:

$$\begin{aligned}\frac{\partial}{\partial \Gamma} \cdot \mathbf{B}(\Gamma) &= \sum \frac{\partial}{\partial \mathbf{r}_i} \cdot \mathbf{F}_i \\ \mathbf{B}(\Gamma) \cdot \frac{\partial H}{\partial \Gamma} &= \sum \mathbf{F}_i^2 \\ \mathbf{B}(\Gamma) \cdot \frac{\partial \mathbf{B}(\Gamma)}{\partial \Gamma} \cdot \frac{\partial H}{\partial \Gamma} &= \sum_i \sum_j \mathbf{F}_i \cdot \frac{\partial \mathbf{F}_j}{\partial \mathbf{r}_i} \cdot \mathbf{F}_j \\ \mathbf{B}(\Gamma) \cdot \frac{\partial^2 H}{\partial \Gamma \partial \Gamma} \cdot \mathbf{B}(\Gamma) &= \sum_i \sum_j \mathbf{F}_i \cdot \frac{\partial \mathbf{F}_j}{\partial \mathbf{r}_i} \cdot \mathbf{F}_j\end{aligned}$$

The final expression for the configurational temperature is then

$$\frac{1}{k_B T} = \left\langle \frac{\partial}{\partial \Gamma} \cdot \left[ \frac{\mathbf{B}(\Gamma)}{\mathbf{B}(\Gamma) \cdot \frac{\partial H}{\partial \Gamma}} \right] \right\rangle = - \left( \frac{\sum_i \frac{\partial}{\partial \mathbf{r}_i} \cdot \mathbf{F}_i}{\sum_i \mathbf{F}_i^2} + \frac{\sum_j \sum_i \mathbf{F}_i \cdot \frac{\partial \mathbf{F}_j}{\partial \mathbf{r}_i} \cdot \mathbf{F}_j}{\left( \sum_i \mathbf{F}_i^2 \right)^2} \right)$$

Note that in the second term, the numerator is proportional to  $N$  whereas the denominator is proportional to  $N^2$ , and so this term can be neglected in comparison to the first, in which both the numerator and denominator are of order  $N$ .

### Canonical ensemble

To obtain an expression for temperature in the canonical ensemble, it is convenient to consider the phase space integral of the divergence of a phase vector multiplied by the canonical weight i.e.

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

The left hand side is the phase space volume integral of a divergence, which can be recast as a surface integral using Gauss's theorem,

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

For most reasonable Hamiltonians, the probability goes to zero as the momenta go to infinity, so this integral is zero. Then we obtain the result

$$\frac{1}{Z} \int \frac{\partial}{\partial \Gamma} \cdot \mathbf{B}(\Gamma) e^{-\beta H} d\Gamma = \frac{\beta}{Z} \int \mathbf{B}(\Gamma) \cdot \frac{\partial H}{\partial \Gamma} e^{-\beta H} d\Gamma$$

or,

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