

- HH0058 -

Entropy

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• definition of entropy

Entropy can be defined for any stochastic systems with random variable X , described by the probability distribution $P(X)$,

$$\sigma \equiv \langle -\log P \rangle = - \sum_x P(x) \log P(x) \quad (1)$$

However, for statistical systems in equilibrium, the expression for entropy is further simplified because of the fundamental assumption that each state is occupied by the same probability. Thus, $P = 1/g$ for all available states. It is straightforward to show that the entropy is $\sigma = -\sum_q (1/g) \log(1/g) = \log g$. This is the celebrated result engraved on Boltzmann's tomb,

$$\sigma = \log g \quad (2)$$

According to the definition of temperature, $1/\tau = (\partial \log g / \partial U)_{V,N}$, the three key quantities U , τ and σ are related,

$$\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U} \right)_{V,N} \iff \tau = \left(\frac{\partial U}{\partial \sigma} \right)_{V,N} \quad (3)$$

More and more thermodynamic identities like the above ones will pop out as we march on. Thus, it is unwise to memorize them. Instead, try to understand the relation first and derive the identity on your own without any external help (like notes, textbook, or a smart classmate).

• trend for entropy

Because of the identity $1/\tau = (\partial \sigma / \partial U)_{V,N}$, the sign of temperature relies on the trend of the entropy. Take N -oscillator model as an example. The

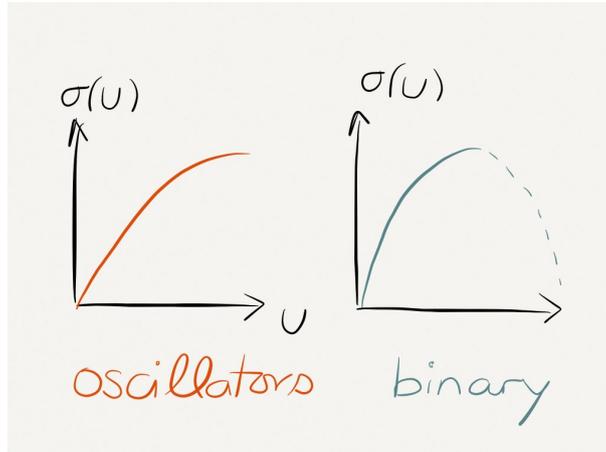


Figure 1: The trends of the entropy $\sigma(U)$ for the N oscillators and for the binary model. The monotonic increasing behavior of the entropy implies the positiveness of the temperature.

multiplicity function is $g = (N + n - 1)!/n!(N - 1)!$. Using the Stirling approximation, $\log n! \approx n \log n - n$, the entropy is approximately

$$\sigma \approx (N + n - 1) \log(N + n - 1) - n \log n - (N - 1) \log(N - 1). \quad (4)$$

Note that $E = n\hbar\omega$ so that the third term is independent of energy. The trend of the entropy is plotted in Figure 1, showing monotonic increasing behavior. It means that $(\partial\sigma/\partial U)_{V,N}$ is *always* positive and thus implies the positiveness of the temperature, $\tau > 0$. **It is important to emphasize that the property of positive temperature τ is a direct consequence of monotonic increasing trend of the entropy σ versus energy.**

For binary model, the situation is more tricky. Within Stirling approximation, the multiplicity function is $g(s) = g(0)e^{-2s^2/N}$. Thus, the corresponding entropy is rather simple,

$$\sigma = \sigma_0 - \frac{2s^2}{N}. \quad (5)$$

Note that $U = -2smB$ and the entropy plotted versus energy is a downward parabola as shown in Figure 1. Before reaching the peak, the slope is positive, meaning the corresponding temperature is positive as well. But! On the other side of the peak, the slope is negative. Amazingly enough, it indeed corresponds to *negative temperature*! Interested students can read Appendix E on pages 460-463 in Kittel's book.

• the second law of thermodynamics

Now we want to understand the evolution of entropy before and after thermal contact. Consider two systems with initial energies E_{10}, E_{20} before thermal contact. The total energy of the system is $U = E_{10} + E_{20}$. The entropy of the whole system is

$$\sigma_{\text{initial}} = \log[g_1(E_{10})g_2(E_{20})] = \log g_1(E_{10}) + \log g_2(E_{20}) = \sigma_{10} + \sigma_{20}. \quad (6)$$

The additive property of entropy for independent systems emerges in above. The equilibrium entropy after thermal contact is

$$\sigma_{\text{final}} = \log\left[\sum_{E_1} g_1(E_1)g_2(U - E_1)\right] \geq \log[g_1(E_{10})g_2(E_{20})] = \sigma_{\text{initial}}. \quad (7)$$

The inequality arises rather trivially: the summation over E_1 is larger because it contains the term with the initial energy E_{10} . In consequence, bringing two independent subsystems into thermal contact, the entropy of the whole system always increases,

$$\boxed{\sigma_{\text{final}} \geq \sigma_{\text{initial}}} \quad (8)$$

The above inequality is the famous second law of thermodynamics.

The second law dictates the direction of energy flow from the higher temperature to the lower. To illustrate this property, it is convenient to consider two spin systems in thermal contact again. For simplicity, we assume that the initial energies E_{10}, E_{20} are quite close to the equilibrium ones $U_1 = E_{10} + \Delta U, U_2 = E_{20} - \Delta U$. The multiplicity function in equilibrium is

$$(g_1g_2)_{\text{final}} = \sum_{E_1} g_1(E_1)g_2(U - E_1) \approx g_1(U_1)g_2(U_2). \quad (9)$$

Recall that temperature sets the energy scale for the multiplicity growth,

$$g_1(U_1) \approx g_1(E_{10})e^{\Delta U/\tau_1}, \quad g_2(U_2) \approx g_2(E_{20})e^{-\Delta U/\tau_1}. \quad (10)$$

Combine the above results together, the multiplicity is approximately

$$(g_1g_2)_{\text{final}} \approx (g_1g_2)_{\text{initial}} \times \exp\left[\Delta U \left(\frac{1}{\tau_1} - \frac{1}{\tau_2}\right)\right]. \quad (11)$$

Taking logarithm on both sides, the second laws, $\sigma_{\text{final}} \geq \sigma_{\text{initial}}$, gives rise to another inequality,

$$\sigma_{\text{final}} \approx \sigma_{\text{initial}} + \Delta U \left(\frac{\tau_2 - \tau_1}{\tau_1\tau_2}\right) \Rightarrow \Delta U \left(\frac{\tau_2 - \tau_1}{\tau_1\tau_2}\right) \geq 0. \quad (12)$$

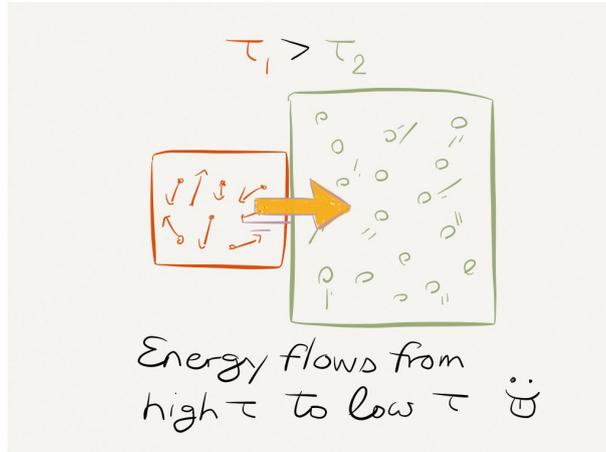


Figure 2: When two systems are in thermal contact, energy flows from the high temperature to the lower temperature.

For $\tau_2 > \tau_1$, $\Delta U > 0$ and the energy flows from subsystem 2 (higher temperature) to subsystem 1 (lower temperature). On the other hand, for $\tau_1 > \tau_2$, $\Delta U < 0$ and the energy flows from subsystem 1 (higher temperature) to subsystem 2 (lower temperature). Therefore, for two subsystems in thermal contact, the energy always flows from the higher temperature to the lower, reflecting the underlying second law of thermodynamics.

• the first and the third laws

For completeness, it shall be fun to learn the first and the third laws of thermodynamics. According to the definition, $\sigma = \log g$ depends on the variables U, V, N . Thus, one can convert the relation between σ and U , viewing the average energy $U = U(\sigma, V, N)$ as a function of variables σ, V, N ,

$$dU = \left(\frac{\partial U}{\partial \sigma} \right)_{V,N} d\sigma + \left(\frac{\partial U}{\partial V} \right)_{\sigma,N} dV + \left(\frac{\partial U}{\partial N} \right)_{\sigma,V} dN = \tau d\sigma - PdV + \mu dN, \quad (13)$$

where the definitions for pressure $P = -(\partial U / \partial V)_{\sigma,N}$ and chemical potential $\mu = (\partial U / \partial N)_{\sigma,V}$ are used. Moving the terms around the equal sign, it leads to the differential form of the first law,

$$\tau d\sigma = dU + PdV - \mu dN. \quad (14)$$

The third law is not as famous as the first and the second laws. It states that the entropy for a statistical system reaches a constant when approaching zero temperature. In modern statistical language, the third law is pretty

trivial. Suppose the multiplicity of the ground state is $g(0)$. When approaching zero temperature, the entropy approaches the constant, $\sigma(0) = \log g(0)$. This is the third law, done.



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