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Entropy (III) - Zero-point entropy and the 3rd law of thermodynamics

The thermodynamic definition of entropy $\Delta S = \int \delta Q/T$ via a reversible process can only determine entropy up to a constant. Does the choice of this constant have a physical meaning? We will see that in order to avoid apparent conceptual difficulties, it is necessary to go beyond the classic physics.

6.1 Sackur-Tetrode formula: entropy of an ideal gas

Since entropy is a function of state, we may calculate the entropy as a function of $S(N, V, T)$. Consider the case for an ideal gas, whose equations of state are

$$PV = Nk_B T = (\gamma - 1)U. \quad (6.1)$$

According to the 1st law of thermodynamics,

$$ds = \frac{\delta Q}{T} = \frac{dU + pdV}{T} = Nk_B \left(\frac{1}{\gamma - 1} \frac{dT}{T} + \frac{dV}{V} \right). \quad (6.2)$$

Hence, the change of entropy is

$$\begin{aligned} S(N, T, V) - S(N, T_0, V_0) &= Nk_B \left(\frac{1}{\gamma - 1} \ln \frac{T}{T_0} + \ln \frac{V}{V_0} \right) \\ &= N \left(c_v \ln \frac{T}{T_0} + k_B \ln \frac{V}{V_0} \right). \end{aligned} \quad (6.3)$$

It can be checked that, along the curve of an adiabatic process satisfying

$$V^{\gamma-1} T = \text{Const}, \quad (6.4)$$

$S(N, T, V)$ is maintained as a constant. For simplicity, we consider the monoatom-

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ic gas for which $c_v = \frac{3}{2}k_B$, then

$$\frac{S(N, T, V)}{Nk_B} = \left(\frac{3}{2} \ln T + \ln V \right) + \frac{C(N)}{Nk_B}, \quad (6.5)$$

where $C(N)$ is a N -dependent constant.

$C(N)$ can be fixed up to an N -independent constant just based on common sense. We assume that entropy is additive, in other words, it is an extensive quantity. Suppose there two ideal gas systems at the same temperature T . One with particle numbers N_1 and volume V_1 , and the other N_2 and V_2 , respectively. They are with the same particle density, i.e., $N_1/V_1 = N_2/V_2$. Naturally, the following condition is expected to hold,

$$\frac{S(N_1, T, V_1)}{N_1} = \frac{S(N_2, T, V_2)}{N_2}, \quad (6.6)$$

which yields

$$\frac{C(N_1)}{N_1k_B} - \frac{C(N_2)}{N_2k_B} = \ln \frac{V_2}{V_1} = -\ln \frac{N_1}{N_2}. \quad (6.7)$$

It can be solved that

$$\frac{C(N_1)}{N_1k_B} = -\ln N + a, \quad (6.8)$$

where a is an N -independent const.

Hence, for a monoatomic ideal gas can be organized as

$$\frac{S(N, T, V)}{Nk_B} = \frac{3}{2} \ln \left(\frac{k_B T}{E_0} \right) + a, \quad (6.9)$$

where $E_0 = \frac{\hbar^2 n^{2/3}}{2m}$ with $n = N/V$ is the energy unit composed by particle density and fundamental quantum mechanical constant, and a is a dimensionless constant.

Eq. 6.9 is the celebrated Sackur-Tetrode equation of the entropy of classic ideal gas. Here the appearance of \hbar is interesting. Basically, we need a quantity carrying the unit of angular momentum here to make the unit correct. The purely classic physics is also unavoidably connect to quantum.

We still have not determine the last constant a yet, which can be done by using the free energy expression for an ideal gas Eq. 5.34 that $F/N = k_B T \left[\ln(\lambda_T^3 n) - 1 \right]$. The entropy S then becomes

$$\frac{S}{Nk_B} = -\frac{\partial F}{\partial T} = -\ln(\lambda_T^3 n) + 1 - 3 \frac{d \ln \lambda_T}{d \ln T} = \ln \left(\frac{1}{\lambda_T^3 n} \right) + \frac{5}{2}. \quad (6.10)$$

Now we have determined even the constant. Please note the different form of

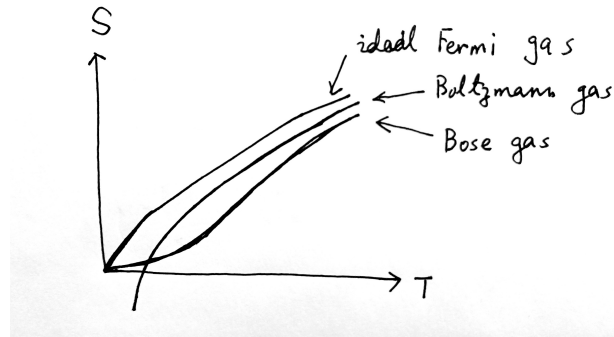


Figure 6.1 Entropy per particle of ideal Fermi gas, ideal Bose gas, and ideal classic (Boltzmann) gas. For quantum systems, the zero temperature entropy is zero, which implies the uniqueness of the quantum ground state. This is also called the 3rd law of thermodynamics, or, Nernst's law.

Eq. 6.10 from that of Eq. 6.9. Actually you may check that they are the same after a few lines of algebra.

Nevertheless, if we extrapolate the Sackur-Tetrode formula to the zero temperature at a fixed density $n = N/V$, the entropy per particle would go to negative infinity. This is because the assumption that c_V remains a temperature independent constant. In fact, at sufficiently low temperatures, all the degrees of freedom will be frozen, and c_V also drops to zero.

6.2 Zero point entropy

The Sackur-tetrode formula has an unpleasant feature that as temperature goes to zero, the entropy negatively diverge logarithmically as shown in Fig 6.1. This is incompatible with the Boltzmann's statistical interpretation. The reason is that even a single quantum state occupy a finite volume of $(2\pi\hbar)^{3N}$ in the phase space due to the uncertain principle, i.e., coordinate and momentum cannot be simultaneously determined.

In fact, quantum gases behave very differently. According to the statistical feature of particles, they can be classified as bosons and fermions, respectively. Electrons are fermions, and ^4He atoms are bosons. In both cases, their entropies go to zero as $T \rightarrow 0$ as shown in Fig 6.1.

At $T = 0\text{K}$, the system only lies in the lowest energy state called the ground state. If there are multiple ground states, their total numbers g is called the

ground state degeneracy. The zero temperature entropy should be

$$S_0/k_B = \ln g. \quad (6.11)$$

In most systems, the ground state is unique, i.e., $g = 1$. Hence, the zero temperature entropy

$$S_0 = 0, \quad (6.12)$$

which is often called the Nernst law of thermodynamics, or, the 3rd law of thermodynamics.

Nevertheless, the ground states of a quantum system can have degeneracies. In many situations degeneracies are due to symmetries, and thus are not very robust. Nevertheless, in certain situations, the degeneracy are protected by time-reversal symmetry. For example, for electrons with an odd number in the absence of the magnetic field, the ground state is always 2-fold degenerate, which is called Kramers' degeneracy. As another possibility, robust degeneracy can be protected by topology. For example, for the 1/3-fractional quantum Hall state, its ground state degeneracy depends on the genus of the manifold as $g = 3^n$, where n is the genus. Nevertheless, the degeneracy number is often finite, and the zero point entropy per particle still goes to zero.

There do exist cases in which the ground state degeneracies exponentially scales with system's size. This often occurs in frustrated magnetic systems. Nevertheless, this heavy degeneracy is often lifted by quantum fluctuations.

6.3 Zero temperature is unreachable

Here is another frequently used formulation of the 3rd law of thermodynamics: **It is impossible to reach the zero temperature by finite steps of thermodynamic processes.**

Actually, this formulation is closely related to the formulation of the zero temperature entropy to be zero.

Consider a quantum gas, either an ideal Fermi gas, or, an ideal Bose gas. If we plot the curves of entropy $S(N, V, T)$ v.s T by fixing N at different volume. All these curves pass the origin, i.e., $S(N, V, T = 0) = 0$. Looking two curves with two different volumes with $V_2 > V_1$ as shown in Fig 6.2(a). We start from point A with (V_1, T_1) and cool the system. The cooling process can be designed as follows: An adiabatic expansion to V_2 represented by the iso-entropy line followed by an isothermal compression back to the volume V_1 to reduce entropy. Repeating these two processes, the temperature keeps drop but

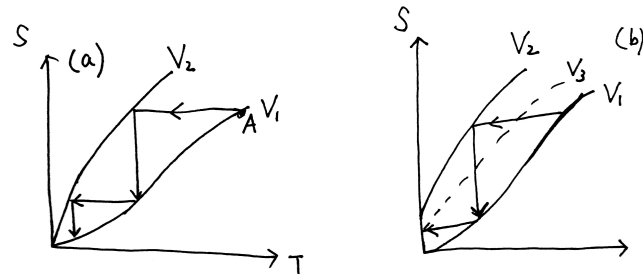


Figure 6.2 Nernst law (The 3rd law of thermodynamics stated that the ground state entropy should be zero. This is consistent with that the zero temperature is unreachable by finite steps. Consider two $S(V, T)$ curves at two different volumes $V_1 > V_2$. The cooling process can be designed as repeated adiabatic compression followed by isothermal expansion. (A) Two curves pass the origin, then zero temperature is unreachable. (B) If two curves would exhibit different interceptions on the vertical axis, then the zero temperature would be reached by finite steps of cooling processes.

the cooling efficiency becomes lower and lower. The origin $S = T = 0$ is a fixed point, but it is unreachable within finite steps of cooling processes.

Nevertheless, imagine the zero temperature entropies exhibit different values at different volumes as shown in Fig. 6.2 (b). Then the zero temperature is clearly reachable.

6.4 Summary of thermodynamic laws

We have seen a few fundamental laws of thermodynamics.

- (i) **The 0th law:** Define the thermal equilibrium. If object A and B are in thermal equilibrium, and so do A and C , then B and C are also in thermal equilibrium. They share the same temperature.
- (ii) **The 1st law:** Energy conservation and transfer, $\Delta U = W + Q$. **The impossibility of the perpetual motion machine of the first kind. No free lunch!**
- (iii) **The 2nd law:** Entropy of an isolated system does not decrease. It is impossible to convert the heat from a single source into work without any other effect. **The impossibility of the perpetual motion machine of the 2nd kind.**
- (iv) **The 3rd law:** **The zero temperature is unreachable via finite steps of thermodynamic processes.**