8.044 Statistical Physics I
Spring 2008

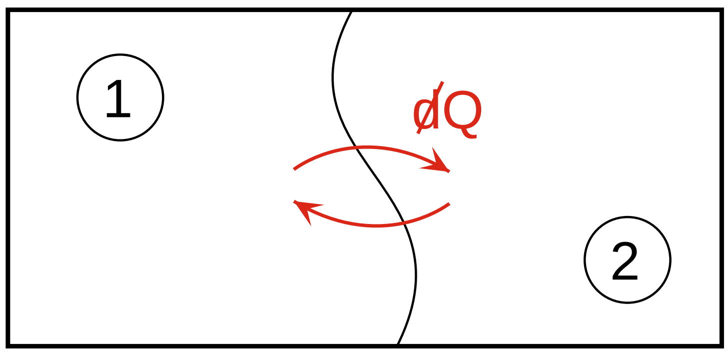
$\Omega = \Omega(E, V, N \ldots) \equiv$ Volume of the accessible region of phase space.

4. Entropy

$$\left.\begin{aligned} S(E,V,N) &\equiv k \ln \Omega(E,V,N) \\ &\approx k \ln \Phi(E,V,N) \\ &\approx k \ln \omega(E,V,N) \end{aligned}\right\} \text{ Differ only by } \ln N$$

- It is a state function.
- It is extensive.
- It is a logarithmic measure of the microscopic degeneracy associated with a macroscopic (that is, thermodynamic) state of the system.
- k is Boltzmann's constant, units of energy per ^0K.

5. Statistical Mechanical Definition of Temperature



Find the most probable E_1 $\equiv E_1^*$

- Total is microcanonical
- $đW_{1\to 2} = 0$
- interaction between 1 & 2 is so small that Ω can be separated

$$p(E_1) = \frac{\Omega'}{\Omega} = \frac{\Omega_1(E_1)\,\Omega_2(E-E_1)}{\Omega(E)}$$

$$\ln p(E_1) = \ln \Omega_1(E_1) + \ln \Omega_2(E-E_1) - \ln \Omega(E)$$

$$= \frac{1}{k}\left(S_1(E_1) + S_2(E-E_1) - S(E) \right)$$

$$\frac{\partial}{\partial E_1} \ln p(E_1) = \frac{1}{k}\left(\left(\frac{\partial S_1}{\partial E_1}\right)_{đW_1=0} - \left(\frac{\partial S_2}{\partial E_2}\right)_{đW_2=0} \right) = 0$$

The condition for determining E_1^* is

$$\underbrace{\left(\frac{\partial S_1}{\partial E_1}\right)_{đW_1=0}}_{f \text{ of } ①} = \underbrace{\left(\frac{\partial S_2}{\partial E_2}\right)_{đW_2=0}}_{f \text{ of } ②}$$

But this also specifies the equilibrium condition. Thus

$$\left(\frac{\partial S}{\partial E}\right)_{đW=0} = f(T) \equiv \frac{1}{T} \quad \text{(in equilibrium)}$$

6. Two Fundamental Inequalities What if $E_1 \neq E_1^*$?

① → ①* as equilibrium is established.

$$p(E_1) \;\leq\; p(E_1^*)$$

$$\Omega_1(E_1)\Omega_2(E - E_1) \;\leq\; \Omega_1(E_1^*)\Omega_2(E - E_1^*)$$

$$1 \;\leq\; \frac{\Omega_1(E_1^*)}{\Omega_1(E_1)}\;\frac{\Omega_2(E - E_1^*)}{\Omega_2(E - E_1)}$$

$$0 \leq \underbrace{S_1(E_1^*) - S_1(E_1)}_{\Delta S_1} + \underbrace{S_2(E - E_1^*) - S_2(E - E_1)}_{\Delta S_2}$$

$$\Rightarrow \bullet \qquad \Delta S \;=\; \Delta S_1 + \Delta S_2 \;\; \text{increases}$$

$$\Delta S \;\geq 0$$

The total entropy of an isolated system always increases or, at equilibrium, remains constant.

Now assume ② ≫ ①* $\Rightarrow T_2 \equiv T_{\text{bath}}$ does not change.

$$dS_2 = \frac{dE_2}{T_2} = \frac{đQ_2}{T_2} = -\frac{đQ_1}{T_{\text{bath}}}$$

$$dS = dS_1 + dS_2 = dS_1 - \frac{đQ_1}{T_{\text{bath}}} \geq 0$$

$$\Rightarrow \bullet \qquad dS_1 \geq \frac{đQ_1}{T_{\text{bath}}}$$

In particular, for systems in equilibrium with a bath $dS = đQ/T$.

Example Ideal Monatomic Gas

$$\Phi \approx V^N \left(\frac{4\pi emE}{3N}\right)^{3N/2} = \left\{V \left(\frac{4\pi emE}{3N}\right)^{3/2}\right\}^N$$

$$\rightarrow S(E,N,V) = kN \ln\left\{V \left(\frac{4\pi emE}{3N}\right)^{3/2}\right\}$$

$$\Omega \approx \left(\frac{3N}{2}\frac{\Delta}{E}\right) V^N \left(\frac{4\pi emE}{3N}\right)^{3N/2}$$

$$\rightarrow S(E,N,V) = kN \ln\left\{V \left(\frac{4\pi emE}{3N}\right)^{3/2}\right\} - \ln\left(\frac{2}{3}\,\frac{1}{\Delta}\,\frac{E}{N}\right)$$

The Energy Relation

$$\frac{1}{T} \;\equiv\; \left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{Nk}{\{\}}\,\frac{3}{2}\,\frac{1}{E}\,\{\} = \frac{(3/2)Nk}{E}$$

$$\Rightarrow\;\; E = (3/2)NkT$$

Here $U = E$ so $C_V = \left(\frac{\partial U}{\partial T}\right)_V = (3/2)Nk$.

The Adiabatic Condition

$\Delta Q = 0 \Rightarrow \Delta S = 0$ for a quasistatic process.

$$S(E,N,V) = kN \ln \left\{ V \left(\frac{4\pi emE}{3N} \right)^{3/2} \right\}$$

Use the energy relation to eliminate E.

$$S(E,N,V) = kN \ln \left\{ V \left(\frac{4\pi em((3/2)\not{N}kT}{3\not{N}} \right)^{3/2} \right\}$$

$$\Delta S|_{\Delta N=0} \Rightarrow \underline{VT^{3/2} = \text{constant}}$$