

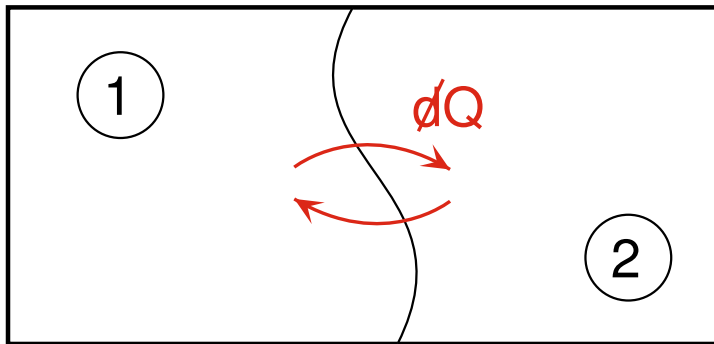
$\Omega = \Omega(E, V, N \dots) \equiv$ Volume of the accessible region of phase space.

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 $^{\circ}K$.

5. Statistical Mechanical Definition of Temperature



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

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

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

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

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

$$\frac{\partial}{\partial E_1} \ln p(E_1) = \frac{1}{k} \left(\left(\frac{\partial S_1}{\partial E_1} \right)_{\not{d}W_1=0} - \left(\frac{\partial S_2}{\partial E_2} \right)_{\not{d}W_2=0} \right) = 0$$

The condition for determining E_1^* is

$$\underbrace{\left(\frac{\partial S_1}{\partial E_1}\right)_{\not{d}W_1=0}}_{f \text{ of } \textcircled{1}} = \underbrace{\left(\frac{\partial S_2}{\partial E_2}\right)_{\not{d}W_2=0}}_{f \text{ of } \textcircled{2}}$$

But this also specifies the equilibrium condition.

Thus

$$\left(\frac{\partial S}{\partial E}\right)_{\not{d}W=0} = f(T) \equiv \frac{1}{T} \quad (\text{in equilibrium})$$

6. Two Fundamental Inequalities

What if $E_1 \neq E_1^*$?

① \rightarrow ①* as equilibrium is established.

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

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

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

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

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

$$\Delta S \geq 0$$

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

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

$$dS_2 = \frac{dE_2}{T_2} = \frac{\delta Q_2}{T_2} = -\frac{\delta Q_1}{T_{\text{bath}}}$$

$$dS = dS_1 + dS_2 = dS_1 - \frac{\delta Q_1}{T_{\text{bath}}} \geq 0$$

$$\Rightarrow \bullet \quad dS_1 \geq \frac{\delta Q_1}{T_{\text{bath}}}$$

In particular, for systems in equilibrium with a bath

$$dS = \delta Q/T.$$

Example Ideal Monatomic Gas

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

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

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

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

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 .

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

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

Microcanonical: E fixed + equal a priori probabilities

⇒ microscopic probability densities [S.M.]

Together with the definition of entropy

⇒ temperature scale and 2^{ND} law inequalities [Thermodynamics]

$$\left. \begin{aligned} \Delta S &\geq 0 \\ dS_1 &\geq \frac{dQ_1}{T} \end{aligned} \right\} 2^{ND} \text{ Law}$$

Quasi-static means arbitrarily close to equilibrium.

- Necessary for work differentials to apply
- Required for = in above 2^{ND} law relations

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