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Relations between the Microcanonical and the Canonical Ensembles : Summary of the Microcanonical Ensemble

We defined the ~~microcanonical~~ ^{entropy in the} microcanonical ensemble as

$$S = k \log \Gamma(E)$$

It turns ~~out~~ out that, for very large systems, it is also possible to define the entropy as

$$S = k \log \omega(E)$$

or

$$S = k \log \sum(E)$$

The reason for this is that for a large system these definitions differ by terms that grow more slowly than N (typically like $\log N$)

Once we have a method to compute ~~the~~ the entropy (at fixed total energy E), $S(E, V)$, we compute the thermodynamic quantities using the relations

$$dS = \left(\frac{\partial S}{\partial E}\right)_V dE + \left(\frac{\partial S}{\partial V}\right)_E dV$$

where $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V$ and $P = T \left(\frac{\partial S}{\partial V}\right)_E$

{ Alternatively, we need to invert the relation and

find $E(S, V) \Rightarrow P = - \left(\frac{\partial E}{\partial V}\right)_S$

$$\Rightarrow dS = \frac{1}{T} (dE + PdV) \Leftrightarrow dE = TdS - PdV$$

$$\Rightarrow T = \left(\frac{\partial E}{\partial S}\right)_V$$

Free Energy: $F = E - TS$

Gibbs Free Energy: $G = E + PV - TS$

Specific heat (heat capacity) $C_V = \left(\frac{\partial U}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V$

Equipartition Theorem

Let x_i be either p_i or q_i ($i=1, \dots, 3N$) and

$H = H(q, p)$ be the Hamiltonian. Let us consider the quantity $x_i \frac{\partial H}{\partial x_j}$ and the (microcanonical) ensemble average

$$\langle x_i \frac{\partial H}{\partial x_j} \rangle = \frac{1}{\Gamma(E)} \int_{E < H < E+\Delta} dq \wedge dp \ x_i \frac{\partial H}{\partial x_j}$$

$$= \frac{\Delta}{\Gamma(E)} \frac{\partial}{\partial E} \int_{H < E} dq \wedge dp \ x_i \frac{\partial H}{\partial x_j}$$

Since $\frac{\partial E}{\partial x_i} = 0$ (E is a fixed quantity)

we can integrate by parts

$$\int_{H < E} dq \wedge dp \ x_i \frac{\partial H}{\partial x_j} = \int_{H < E} dq \wedge dp \ x_i \frac{\partial}{\partial x_j} (H - E)$$

$$= \int_{H < E} dq \wedge dp \ \frac{\partial}{\partial x_j} [x_i (H - E)] \quad \left. \right\} = 0 \quad \begin{array}{l} \text{it is a} \\ \text{surface integral} \\ \text{and } H > E \text{ at} \\ \text{the surface} \end{array}$$

$$- \int_{H < E} dq \wedge dp \ \delta_{ij} (H - E)$$

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = -\frac{\Delta}{P(E)} \frac{\partial}{\partial E} \left[\delta_{ij} \int_{H < E} dg \wedge dp (H - E) \right]$$

Since $P(E) = \omega(E)\Delta$ and

$$\int_{H < E} dg \wedge dp = \Sigma(\omega) \quad \left(\frac{\partial \Sigma}{\partial E} = \omega(E) \right)$$

$$\Rightarrow \left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = + \frac{\delta_{ij}}{\omega(E)} \frac{\partial}{\partial E} \int_{H < E} dg \wedge dp (E - H)$$

$$= \frac{\delta_{ij}}{\omega(E)} \int_{H < E} dg \wedge dp = \frac{\delta_{ij}}{\omega(E)} \Sigma(E)$$

$$= \delta_{ij} \frac{\Sigma(E)}{\frac{\partial \Sigma}{\partial E}} = \delta_{ij} \frac{1}{\frac{\partial \log \Sigma}{\partial E}} = k \delta_{ij} / \left(\frac{\partial S}{\partial E} \right)_V$$

$$\Rightarrow \boxed{\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \delta_{ij} k T}$$

Generalized
Equipartition Thm.

In particular $\left\langle p_i \frac{\partial H}{\partial p_i} \right\rangle = kT$, $\left\langle q_i \frac{\partial H}{\partial q_j} \right\rangle = kT$
(no sum)

Since $\frac{\partial H}{\partial P_i} = \dot{q}_i$ $\frac{\partial H}{\partial q_i} = -\dot{p}_i$

$$\Rightarrow \left\langle \sum_{i=1}^{3N} P_i \dot{q}_i \right\rangle = -3NkT$$

Virial Thm

For a Harmonic Oscillator

$$H = \sum_i \cancel{\frac{P_i^2}{2M_i}} + \sum_i \frac{k_i Q_i^2}{2} \quad (\text{Homogeneous function of degree 2})$$

$$\Rightarrow \sum_i \left(P_i \frac{\partial H}{\partial P_i} + Q_i \frac{\partial H}{\partial Q_i} \right) = 2H$$

$$\Rightarrow \underbrace{\langle H \rangle}_{\text{H of oscillators}} = (3N) \left(\frac{1}{2} k_T + \frac{1}{2} k_T \right) = 3NkT$$

↑ KE ↑ PE

average energy in each oscillator

$$\Rightarrow \text{For harmonic systems } E = (3N) \frac{1}{2} k_T$$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = \frac{k}{3} (3N)$$

$$= \frac{3N}{3} k$$

(Bending Redn)



Classical Ideal Gas (Microcanonical Picture)

$$H = \sum_i \frac{p_i^2}{2m}$$

(monoatomic gas with atoms of mass m)

$$\Sigma(E) = \int_{H < E} d^{3N}q \frac{d^{3N}p}{N!(2\pi\hbar)^{3N}}$$

this factor → comes from quantum mechanics and avoids overcounting the states.
(identical particles)

$$\Sigma(E) = \frac{V^N}{N!} \int_{H < E} \frac{d^{3N}p}{(2\pi\hbar)^{3N}} = \frac{1}{N!} \left(\frac{V}{(2\pi\hbar)^3}\right)^{3N} \Omega_{3N}(r)$$

$$\Omega_{3N}(r) = \int_{\sum_{i=1}^n x_i^2 < r^2} dx_1 \dots dx_{3N} \equiv \int_{|\vec{x}| < r} d^n x = (\text{hyper}) \text{volume of a sphere of radius } r \text{ in } n \text{ dimensions}$$

$$r = \sqrt{2mE}$$

$$\Omega_{3N}(r) = C_n r^n$$

$$\text{Consider } \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} d^n x e^{-\sum_{i=1}^n x_i^2} = \left(\int_{-\infty}^{+\infty} dx e^{-x^2} \right)^n = \pi^{n/2}$$

$$\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} d^n x e^{-\sum_{i=1}^n x_i^2} = \int_0^{\infty} dr S_n(r) e^{-r^2}; S_n = \frac{d\Omega_n}{dr}$$

surface area of S_n

$$= n C_n \int_0^\infty dr r^{n-1} e^{-r^2} = \frac{n}{2} C_n \int_0^\infty dt t^{\frac{n}{2}-1} e^{-t}$$

$$= \frac{n}{2} C_n \Gamma\left(\frac{n}{2}\right)$$

Σ Euler R-function

$$\Rightarrow C_n = \frac{\pi^{\frac{n}{2}}}{\Gamma\left(\frac{n}{2} + 1\right)}$$

For $n \rightarrow \infty$ (Stirling formula)

$$\log C_n = \frac{n}{2} \log \pi - \frac{n}{2} \log \frac{n}{2} + \frac{n}{2}$$

$$\Rightarrow \Sigma(E) = \frac{C_{3N}}{N!} \left[\frac{V}{(2\pi h)^3} (2mE)^{3/2} \right]^{3N}$$

$$\Rightarrow \text{Entropy: } S(E, V) = k \log \Sigma(E)$$

$$S(E, V) = k \log C_{3N} - k \log N! + Nk \log \left[\frac{V (2mE)^{3/2}}{(2\pi h)^3} \right]$$

$$\log N! = N \log N - N + \dots \quad (N \rightarrow \infty) \quad (\text{Stirling})$$

$$\log C_{3N} = \frac{3N}{2} \log \pi - \frac{3N}{2} \log \frac{3N}{2} + \frac{3N}{2} + \dots$$

$$\Rightarrow \boxed{S(E, V) = Nk \log \left[\frac{V}{N} \left(\frac{E}{N} \right)^{3/2} \right] + \frac{3}{2} Nk \left(\frac{5}{3} + \log \frac{4\pi m}{3h^2} \right)}$$

$$\Rightarrow E(S, V) = N \left(\frac{N}{V}\right)^{2/3} e^{\frac{2}{3} \left[\frac{S}{Nk} - \frac{5}{2} - \frac{3}{2} \log \frac{4\pi M}{3h^2} \right]}$$

$$T = \left(\frac{\partial E}{\partial S} \right)_V = \frac{2}{3} \frac{E}{Nk} \Rightarrow \boxed{E = \frac{3}{2} NkT}$$

$\Rightarrow \boxed{C_V = \frac{3}{2} Nk}$ Dulong - Petit (equipartition)

$$P = - \left(\frac{\partial E}{\partial V} \right)_S = + \frac{2}{3} \frac{E}{V}$$

$$\Rightarrow PV = \frac{2}{3} E = \frac{2}{3} \frac{3}{2} NkT$$

$$\boxed{PV = NkT}$$

Eqn of state for an ideal classical gas.

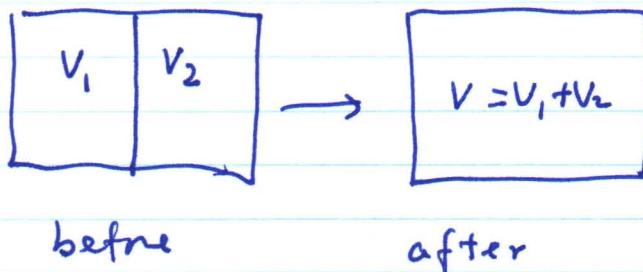
Gibbs Paradox:

Suppose (with Gibbs who did not know better) that there factor of $\frac{1}{N!}$ was not there. \Rightarrow the entropy becomes

$$S = Nk \log \left(V \left(\frac{E}{V} \right)^{3/2} \right) + N \frac{3k}{2} \left(1 + \log \frac{4\pi M}{3h^2} \right)$$

Consider two ideal gases with N_1 and N_2 particles with volumes V_1 and V_2 resp. When

the gases are allowed to mix in a volume $V = V_1 + V_2$



without changing the energy (adiabatic walls) \Rightarrow the

entropy change is

$$\Delta S = N_1 k \log\left(\frac{V}{V_1}\right) + N_2 k \log\left(\frac{V}{V_2}\right) > 0$$

For two different gases this result is correct.

But if the gas was the same on both sides we would also obtain an increase in $S \Rightarrow \Delta S > 0$

\Rightarrow the entropy of a state of a gas would depend not on the equilibrium state but on its history and in fact it would imply that $S \rightarrow \infty$ even for a volume V and # of particles N . This

paradox (Gibbs Paradox) was resolved by Gibbs

who decided to divide $\Sigma(E)$ by $\frac{1}{N!}$ (without real justification). This is required by

quantum mechanics since the state of the

system is invariant under the exchange of identical particles. !

Thermodynamics and the Canonical Ensemble

In the Canonical ensemble the energy is not fixed but the temperature is . The probability to find the system in a state with energy E is

$$P(E) = \frac{1}{Z} e^{-E/kT}$$

where Z is chosen so that $P(E)$ is normalized , i.e.

$$Z = \sum_{\text{States}} e^{-E(\text{state})/kT}$$

partition function.

For a classical system with N particles

$$Z_N(\mathbf{r}, T) = \frac{1}{N!} \int \frac{d^{3N}p d^{3N}q}{(2\pi\hbar)^{3N}} e^{-H(q, p)/kT}$$

no restriction!

Let us show that

$F = -kT \log Z$ behaves like the ~~thermodynamic~~ thermodynamic Free Energy (Helmholtz)

① F is extensive: Take two decoupled systems

$$\Rightarrow H = H_1 + H_2$$

$$\Rightarrow Z = Z_1 Z_2 \quad (\text{factorization})$$

$$\Rightarrow F = -kT \log Z = -kT \log Z_1 - kT \log Z_2 = F_1 + F_2$$

② Let us compute $E = \langle H \rangle$

$$\frac{\partial F}{\partial T} = -k \log Z - \frac{kT}{Z} \frac{\partial Z}{\partial T}$$

$$\frac{1}{Z} \frac{\partial Z}{\partial T} = \frac{1}{Z} \sum_n \left(\frac{E_n}{kT^2} \right) e^{-E_n/kT}$$

$$= \frac{1}{kT^2} \langle H \rangle$$

$$\frac{\partial F}{\partial T} = -k \log Z - kT \frac{1}{kT^2} \langle H \rangle$$

$$\Rightarrow \langle H \rangle = -T \left(\frac{\partial F}{\partial T} \right)_V - kT \log Z$$

$$\Rightarrow \langle H \rangle = -T \left(\frac{\partial F}{\partial T} \right)_V + F$$

$$\Rightarrow F = \langle H \rangle + T \left(\frac{\partial F}{\partial T} \right)_V$$

$\langle H \rangle = E$ (internal energy)

and $\boxed{- \left(\frac{\partial F}{\partial T} \right)_V = S}$ is the entropy

\Rightarrow in the canonical ensemble we first compute the partition function $Z \rightarrow$ we get the free energy $F = -kT \log Z(T, V)$

\Rightarrow we get thermodynamics.

$$P = - \left(\frac{\partial F}{\partial V} \right)_T$$

$$S = - \left(\frac{\partial F}{\partial T} \right)_V$$

$$G = F + PV \quad (\text{Gibbs potential})$$

~~$E = \langle H \rangle = F + TS$~~ (internal energy)

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V$$

The Entropy and the Density Matrix

In the canonical ensemble the Density Matrix is

$$\hat{\rho} = \frac{e^{-\beta \hat{H}}}{Z}, \quad Z = \text{tr } e^{-\beta \hat{H}} = \sum_{\text{states}} e^{-\beta E_n}$$

We also found that the entropy S can be computed from the Free energy F

$$S = - \left(\frac{\partial F}{\partial T} \right)_V$$

$$\text{since } F = -kT \log Z \Rightarrow S = k \frac{\partial}{\partial T} (T \log Z)$$

$$\Rightarrow F = k \log Z + \frac{kT}{Z} \frac{\partial Z}{\partial T} = k \log Z + \frac{U}{T}$$

$$U = \langle E \rangle = \langle \hat{H} \rangle = \frac{1}{Z} \text{tr}(\hat{H} e^{-\beta \hat{H}}) = \text{tr}(\hat{\rho} \hat{H})$$

On the other hand the expression

$$-\log(\hat{\rho} \log \hat{\rho}) = \frac{U}{T} + k \log Z$$

$$\Rightarrow S = -k \text{tr}[\hat{\rho}(\log \hat{\rho})] = -k \sum_n [p_n \log p_n]$$

(von Neumann)

↑
probability of
the state.

This is a commonly used formula for S .

Comment
on quantum
entanglement

Energy Fluctuations: Connection between the microcanonical and the canonical ensembles

In the microcanonical ensemble E is fixed, in the canonical ensemble T is fixed. Are they equivalent?

Let us compute the mean square fluctuations (variance) of the energy in the canonical ensemble. Let $\bar{U} = \langle H \rangle$ be the internal energy

$$\bar{U} = \bar{E}$$

$$\bar{U} = \frac{\sum_n E_n e^{-E_n/kT}}{\sum_n e^{-E_n/kT}} = \frac{\int d\mathbf{q} d\mathbf{p} H(\mathbf{q}, \mathbf{p}) e^{-H(\mathbf{q}, \mathbf{p})/kT}}{\int d\mathbf{q} d\mathbf{p} e^{-H(\mathbf{q}, \mathbf{p})/kT}}$$

$$\begin{aligned} \text{Variance: } \langle (H - \bar{U})^2 \rangle &= \langle H^2 \rangle + \bar{U}^2 - 2\bar{U}^2 \\ &= \langle H^2 \rangle - \bar{U}^2 = \langle H^2 \rangle - \langle H \rangle^2 \end{aligned}$$

$$\bar{U} = \frac{\text{tr}(H e^{-\beta H})}{\text{tr } e^{-\beta H}} \quad (\text{tr} = \sum_n \text{states})$$

$$\Rightarrow \text{tr}(H e^{-\beta H}) = \bar{U} Z = \bar{U} e^{-\beta F}$$

$$\langle H^2 \rangle = \frac{\text{tr} (\hat{H}^2 e^{-\beta \hat{H}})}{\text{tr} e^{-\beta \hat{H}}}$$

$$F = -kT \log Z$$

$$\begin{aligned} \frac{\partial \log Z}{\partial \beta} &= \frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{1}{Z} \frac{\partial}{\partial \beta} \text{tr} e^{-\beta H} \\ &= -\frac{1}{Z} \text{tr} (H e^{-\beta H}) = -\langle H \rangle \end{aligned}$$

$$\frac{\partial^2 \log Z}{\partial \beta^2} = -\frac{1}{Z^2} \left(\frac{\partial Z}{\partial \beta} \right)^2 + \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}$$

$$\begin{aligned} \frac{\partial^2 Z}{\partial \beta^2} &= \frac{\partial}{\partial \beta} \left[-\text{tr} (H e^{-\beta H}) \right] \\ &= +\text{tr} (\hat{H}^2 e^{-\beta H}) \end{aligned}$$

$$\frac{\partial^2 \log Z}{\partial \beta^2} = \langle H^2 \rangle - \langle H \rangle^2 = \langle (H - U)^2 \rangle \geq 0$$

$$\text{But } U = \langle H \rangle \text{ and } \frac{\partial U}{\partial \beta} = \frac{\partial}{\partial \beta} \left[\frac{1}{Z} \text{tr} (H e^{-\beta H}) \right]$$

$$= -\frac{1}{Z^2} \frac{\partial Z}{\partial \beta} \left(-\frac{\partial Z}{\partial \beta} \right) = \frac{1}{Z} \text{tr} (H^2 e^{-\beta H})$$

$$= \langle H \rangle^2 - \langle H^2 \rangle = -\langle (H - U)^2 \rangle$$

$$\left(\frac{\partial U}{\partial \beta}\right)_V = -\langle (H-U)^2 \rangle$$

but $\left(\frac{\partial U}{\partial \beta}\right)_V = \frac{\partial U}{\partial \frac{1}{kT}} \Big|_V = -kT^2 \left(\frac{\partial U}{\partial T}\right)_V$

$$\Rightarrow kT^2 \left(\frac{\partial U}{\partial T}\right)_V = \langle (H-U)^2 \rangle = \langle H^2 \rangle - \langle H \rangle^2$$

$$\Rightarrow \text{Fluctuation of the energy } (\Delta H)^2 = \langle H^2 \rangle - \langle H \rangle^2$$

is related to the specific heat (heat capacity)

$$(\Delta H)^2 = kT^2 C_V \geq 0 \Rightarrow C_V \geq 0$$

But $C_V \propto N$ (extensivity)

$$\Rightarrow (\Delta H)^2 \propto N$$

$$\Rightarrow \Delta H \propto \sqrt{N}$$

$$\Rightarrow \frac{\Delta H}{U} = \frac{\Delta H}{\langle H \rangle} \propto \frac{\sqrt{N}}{N} = N^{-1/2} \xrightarrow[N \rightarrow \infty]{} 0$$

In the thermodynamic limit U is a sharply defined quantity! ($\Delta H \rightarrow 0$). Notice that this ^{result} requires that $C_V < \infty$. This condition is violated at a continuous phase transition.

Another picture:

$$Z = \sum_n e^{-E_n/kT} = \int_0^\infty dE \omega(E) e^{-\beta E}$$

↑
 sum
over
states

↑
 density of
states

$$\omega(E) = \sum_{\text{states}} \delta(E - E_n)$$

$$Z = \int_0^\infty dE e^{\beta(TS(E) - E)}$$

Both $E \propto N$ and $S \propto N$. For $N \rightarrow \infty$

the quantity $TS(E) - E \propto N \rightarrow \infty \Rightarrow$

the maximum of $TS(E) - E$ becomes sharply defined. Let us evaluate it by saddle point methods (or steepest descent)

$$\int_{-\infty}^{+\infty} dx e^{Nf(x)} \approx \int_{-\infty}^{+\infty} dx e^{Nf(x_0) + \frac{N}{2!} f''(x_0) (x-x_0)^2}$$

where $x_0 / f'(x_0) = 0$ (saddle point)

If $f''(x_0) < 0$ (maximum)

$$f''(x_0) = -|f''(x_0)|$$

$$\int_{-\infty}^{+\infty} dx e^{Nf(x)} \approx e^{Nf(x_0)} \frac{\sqrt{2\pi}}{\sqrt{|f''(x_0)| N}}$$

$\left\{ 1 + O(\frac{1}{N}) \right\}$

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$$\int_{-\infty}^{+\infty} dx e^{Nf(x)} \approx e^{Nf(x_0) - \frac{1}{2}\log N + \frac{1}{2}\log \frac{2\pi}{|f'(x_0)|}} \times (1+O(\frac{1}{N}))$$

$$\Rightarrow \log \int_{-\infty}^{+\infty} dx e^{Nf(x)} = Nf(x_0) - \frac{1}{2}\log N + \frac{1}{2}\log \left(\frac{2\pi}{|f'(x_0)|} \right) + O(\frac{1}{N})$$

$$f = \frac{1}{N} \sum_i (TS(E_i) - E_i)$$

~~∂E ∂S ∂T ∂V ∂E ∂S ∂T ∂V~~

$$\frac{\partial f}{\partial E} \Big|_V = 0 = \frac{1}{N} \left(T \left(\frac{\partial S}{\partial E} \right)_V - 1 \right)$$

$$\Rightarrow \left(\frac{\partial S}{\partial E} \right)_V = \frac{1}{T} \Rightarrow E = V = \langle H \rangle$$

$$\frac{\partial^2 f}{\partial E^2} \Big|_V = \frac{1}{N} T \left(\frac{\partial^2 S}{\partial E^2} \right)_V = \frac{1}{Nk} \left(\frac{\partial^2 S}{\partial E^2} \right)_{E=V}$$

$$\begin{aligned} \left(\frac{\partial^2 S}{\partial E^2} \right)_{E=V} &= \frac{\partial}{\partial E} \left(\frac{\partial S}{\partial E} \right) = \frac{\partial}{\partial E} \left(\frac{1}{T} \right) = -\frac{1}{T^2} \left(\frac{\partial T}{\partial E} \right) \\ &= -\frac{1}{T^2} \left(\frac{1}{\left(\frac{\partial E}{\partial T} \right)_V} \right) \end{aligned}$$

$$\Rightarrow \frac{\partial^2 S}{\partial E^2} = -\frac{1}{T^2 C_V} < 0$$

$$\begin{aligned} \Rightarrow TS(E) - E &= [TS(V) - V] + \frac{1}{2}(E-V)^2 T \left(\frac{\partial^2 S}{\partial E^2} \right)_{E=V} + \dots \\ &= (TS(V) - V) + \frac{1}{2T C_V} (E-V)^2 + \dots \end{aligned}$$

$$Z \approx e^{\beta(TS(U) - U)} \int dE e^{-\frac{\beta}{2TC_V}(E-U)^2} [1 + \dots]$$

$$\approx e^{\beta(TS(U) - U)} \sqrt{2\pi kT^2 C_V} \left[1 + O(\frac{1}{N}) \right]$$

$$\Rightarrow Z = e^{-\beta F}$$

$$F = -kT \log Z = U - TS(U) - \frac{kT}{2} \log(2\pi kT^2 C_V) + \dots$$

$$\frac{F}{N} = \frac{U}{N} + TS(U) - \frac{kT}{2N} \log(2\pi kT^2 C_V) + \dots$$

the last term $\sim \frac{\log N}{N} \rightarrow 0$ as $N \rightarrow \infty$

\Rightarrow the key to the equivalence of both ensembles is the sharpness of the distribution of the energy. This follows from the estimate of the growth of the density of states $\omega(E) \sim e^E$ for $E \sim N \rightarrow \infty$

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Systems with a variable number of particles :

The Grand Canonical Ensemble

We have discussed so far two types of statistical descriptions (or Ensembles) : (a) the Microcanonical Ensemble , in which the energy is fixed and the temperature is ^a derived concept , and (b) the canonical ensemble in which the temperature is fixed but the energy fluctuates . We also saw that in the thermodynamic limit both ensembles are equivalent . In both cases we kept the number of particles N fixed.

We will consider now the case in which we have a subsystem with N_1 particles in contact with a much larger system with N_2 particles , $N_2 \gg N_1$. The large system has volume $V_2 \gg V_1$, the volume of the small system . The total Hamiltonian is

$$H(q, p, \lambda) = H_1(q_1, p_1, N_1) + \lambda H_2(q_2, p_2, N_2)$$

$$\text{Let } N = N_1 + N_2, \quad v = v_1 + v_2$$

$$Z_N(v, T) = \sum_{N_1=0}^N Z_{N_1}(v_1, T) Z_{N_2}(v_2, T)$$

The probability that there are N_1 particles in the small system, with coordinates q_1, p_1 is

$$P(q_1, p_1, N_1) = \frac{1}{N_1! Z_N(v, T)} e^{-\beta H(q_1, p_1, N_1)} Z_{N_2}(v_2, T)$$

Notice that

$$\sum_{N_1=0}^N \int \frac{dq_1^{3N_1} dp_1^{3N_2}}{(2\pi\hbar)^{3N_1}} P(q_1, p_1, N_1) = 1$$

$$\text{But } \frac{Z_{N_2}(v_2, T)}{Z_N(v, T)} = e^{-\beta [F(N-N_1, v-v_1, T) - F(N, v, T)]}$$

$$\text{and } F(N-N_1, v-v_1, T) - F(N, v, T) = -N_1 \mu + V_1 P + \dots$$

(since $N \gg N_1$, $V \gg V_1$)

where μ is called the chemical potential:

$\mu = \left. \frac{\partial F(N_1, v, T)}{\partial N_1} \right|_{N_1=N}$, i.e. the ^{free} energy cost of adding a particle.

$$\text{and } P = - \left. \frac{\partial F}{\partial v} \right|_{v=v_1}$$

$$\text{Fugacity: } z = e^{\beta \mu} \Rightarrow \log z = \beta \mu$$

$$\Rightarrow \rho(\beta, p, N) = \frac{z^N}{N!} e^{-\beta PV - \beta H(\beta, p)}$$

Grand Partition Function

$$Z(z, V, T) = \sum_{N=0}^{\infty} z^N Z_N(V, T)$$

$$\Rightarrow \log Z(z, V, T) = \frac{PV}{kT}$$

What is the average # of particles?

$$\bar{N} = \langle N \rangle = \frac{\sum_{N=0}^{\infty} N z^N Z_N(V, T)}{\sum_{N=0}^{\infty} z^N Z_N(V, T)} = z \frac{\partial \log Z}{\partial z}$$

$$\Rightarrow \langle N \rangle = z \frac{\partial \log Z}{\partial z} = \frac{\partial \log Z}{\partial \log z} = \frac{1}{\beta} \frac{\partial \log Z}{\partial \mu}$$

Likewise the internal energy ~~this~~ E is

$$E = - \frac{\partial \log Z}{\partial \beta}$$

Clearly we get

$$dE = T dS - P dV + \mu dN$$

Grand
General Potential: $\Omega = F - \mu N$

$$d\Omega = -S dT - N d\mu - P dV$$

The Gibbs potential (free energy) for N fixed
obeys $dG = -SdT + VdP$

and $G = Ng(p, V)$ since it's extensive

For a system with N variable

$$dG = -SdT + VdP + \mu dN$$

$$\Rightarrow \left(\frac{\partial G}{\partial N} \right)_{T, P} = \mu = g(p, V)$$

$$\Rightarrow G(p, V, N) = \mu N$$

$$\Rightarrow \Omega = F - \mu N = F - G \Rightarrow \boxed{-PV = \Omega}$$

$\Rightarrow \Omega$ determines the equation of state

For a quantum system the Grand Partition function

Z is

$$Z = \sum_{N, n} z^{N\beta} e^{-\beta E_n} = \sum_{N=0}^{\infty} \sum_n e^{-\beta(E_n - \mu)}$$

$$\text{and } \Omega = -kT \log Z$$

$$\Rightarrow \frac{PV}{kT} = \log Z(z, V, T)$$

$$z = e^{\mu/kT}$$

where ~~$\langle N \rangle = \bar{N}$~~ $\langle N \rangle = \bar{N} = kT \frac{\partial \log Z}{\partial \mu}$ \Rightarrow this eqn.
determines $\mu = \mu(\bar{N}, V, T)$

$$\Rightarrow \overline{\Delta N} = \sqrt{\langle (\Delta N)^2 \rangle} = \sqrt{\langle N \rangle} \sqrt{kT \frac{K_T}{v}}$$

$$\Rightarrow \frac{\overline{\Delta N}}{\overline{N}} = \frac{1}{\sqrt{N}} \sqrt{kT \frac{K_T}{v}} \xrightarrow[N \rightarrow \infty]{ } 0$$

(if $K_T < \infty$)

$$(\bar{N} = \langle N \rangle)$$

\Rightarrow in the thermodynamic limit the fluctuations are suppressed.

Notice the analogy

$$\begin{aligned} \overrightarrow{\langle (\Delta E)^2 \rangle} &= kT^2 C_V && \text{"susceptibility"} \\ \text{fluctuation} & & & \\ \overrightarrow{\langle (\Delta N)^2 \rangle} &= kT \frac{K_T}{v} && \end{aligned}$$

At critical points $\frac{\partial P}{\partial v} = 0 \Rightarrow \langle (\Delta N)^2 \rangle \rightarrow \infty$

$(K_T \rightarrow \infty)$

Likewise $C_V \rightarrow \infty$ at $T_c \Leftrightarrow \langle (\Delta E)^2 \rangle \rightarrow \infty$

Partition Function for an Ideal Classical Gas

$$Z_N(v, T) = \frac{1}{N!} \int \frac{d^{3N}p d^{3N}q}{(2\pi\hbar)^{3N}} e^{-\beta H(p, q)}$$

$$H(p, q) = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m}$$

$$\int d^{3N}q = V^N$$

$$Z_N(v, T) = \frac{V^N}{N!} \int \frac{d^{3N}p}{(2\pi\hbar)^{3N}} e^{-\sum_{i=1}^N \frac{\vec{p}_i^2}{2mkT}}$$

$$= \frac{V^N}{N!} \left[\int_{-\infty}^{+\infty} \frac{dp}{2\pi\hbar} e^{-p^2/2mkT} \right]^{3N}$$

$$= \frac{V^N}{N!} \left[\frac{\sqrt{2\pi}}{2\pi\hbar} \frac{\sqrt{mkT}}{\sqrt{\cancel{mkT}}} \right]^{3N}$$

$$\Rightarrow Z_N = \frac{V^N}{N!} \frac{1}{(2\pi\hbar^2/mkT)^{3N/2}} = \frac{V^N}{N!} \left(\frac{mkT}{2\pi\hbar^2} \right)^{\frac{3N}{2}}$$

$$\Rightarrow F_N(v, T) = -kT \log Z_N$$

$$F_N(v, T) = -kT N \left[\log V + \frac{3}{2} \log \frac{mkT}{2\pi\hbar^2} \right] + kT N \left[\log N - 1 \right]$$

(L11)

Density Fluctuations

$$\Delta N = \sqrt{(N - \langle N \rangle)^2}$$

$$\langle N^2 \rangle - \langle N \rangle^2 = \langle (\Delta N)^2 \rangle =$$

$$\Rightarrow \langle (\Delta N)^2 \rangle \approx \frac{\partial}{\partial z} \left[z \frac{\partial}{\partial z} \log Z \right] = kT V \frac{\partial^2 P}{\partial \mu^2}$$

$$F(N, V, T) = N f(v, T)$$

$$v = \frac{V}{N} \text{ specific volume}$$

$$\Rightarrow \mu = f(v, T) - v \frac{\partial f(v, T)}{\partial v}$$

$$P = - \frac{\partial f(v, T)}{\partial v}$$

$$\mu = \mu(v, T)$$

$$P = P(v, T)$$

$$\Rightarrow \frac{\partial \mu}{\partial v} = -v \frac{\partial^2 f}{\partial v^2}$$

$$\frac{\partial P}{\partial \mu} = \frac{\frac{\partial P}{\partial v}}{\frac{\partial \mu}{\partial v}} = \frac{1}{v}$$

$$\Rightarrow \frac{\partial^2 P}{\partial \mu^2} = -\frac{1}{v^2} \frac{\partial v}{\partial \mu} = \frac{1}{v^3} \frac{\partial^2 f}{\partial v^2} = -\frac{1}{v^3} \frac{\partial P}{\partial v}$$

$$\Rightarrow \langle (\Delta N)^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2 = \langle N \rangle kT \frac{\kappa_T}{v}$$

$$\kappa_T = \frac{1}{v(-\frac{\partial P}{\partial v})_T} : \text{isothermal compressibility.}$$

$$F_N(v, T) = -NkT \left[\log v + \frac{3}{2} \log \left(\frac{mkT}{2\pi\hbar^2} \right) + 1 \right]$$

$$v = \frac{V}{N}$$

$$F_N(v, T) = N f(v, T)$$

$$f(v, T) = -kT \left[\log v + \frac{3}{2} \log \left(\frac{mkT}{2\pi\hbar^2} \right) + 1 \right]$$

is the free energy density.

Chemical potential: $\mu = \left(\frac{\partial F}{\partial N} \right)_{V, T} = \left(\frac{\partial G}{\partial N} \right)_{P, T}$

$$\mu = f(v, T) + N \left[+ \frac{kT}{\Delta S} \right]$$

$$\mu = kT + f(v, T)$$

$$\mu = -kT \left[\log v + \frac{3}{2} \log \left(\frac{mkT}{2\pi\hbar^2} \right) \right]$$

$$n = \frac{N}{V}$$

$$\mu = kT \left[\log n + \frac{3}{2} \log \left(\frac{2\pi\hbar^2}{mkT} \right) \right]$$

$$\lambda = \left(\frac{2\pi\hbar^2}{mkT} \right)^{1/2} \Rightarrow \mu = kT \log(n \lambda^3)$$

↑
dimensionless

it has units of length: "thermal wavelength"

Classical

Grand-Partition Function: Ideal Gas.

$$Z = \sum_{N=0}^{\infty} z^N Z_N(V, T)$$

$$= \sum_{N=0}^{\infty} \frac{z^N}{N!} \left[V \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \right]^N$$

$$= e^{-V \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2}}$$

$$\Rightarrow \log Z = -V \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2}$$

$$\Omega = -kT \log Z = -kT - V \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2}$$

$$\text{Since } \Omega = -PV$$

$$\Rightarrow PV = kT - V \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2}$$

$$\langle N \rangle = \bar{N} = z \frac{\partial}{\partial z} \log Z$$

$$\Rightarrow \bar{N} = z \left[V \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \right] \Rightarrow \text{determines } \mu$$

$$\Rightarrow PV = \bar{N}kT \quad \text{which is the eqn of state}$$

$$z = e^{\frac{\mu}{kT}}$$

$$\Rightarrow \frac{\mu}{kT} = \log \left[\frac{\bar{N}}{V} \left(\frac{2\pi\hbar^2}{mkT} \right)^{3/2} \right] = \log(n\lambda^3) \quad \checkmark$$