1. Consider a horizontal cylinder of length a, and cross section A, divided into two parts by a piston P of mass m. The piston can slide back and forth inside the cylinder without any friction. The walls of the cylinder as well as the piston are perfect heat insulators. The left side of the piston is filled with N_1 molecules of helium gas, and the right side is filled with N_2 molecules of Helium gas. The total energy of the system is fixed and is given by E. We assume that the piston is heavy and moves slowly so that at any instant of time we can regard the gas on each side to be in equilibrium, obeying ideal gas equation of state.
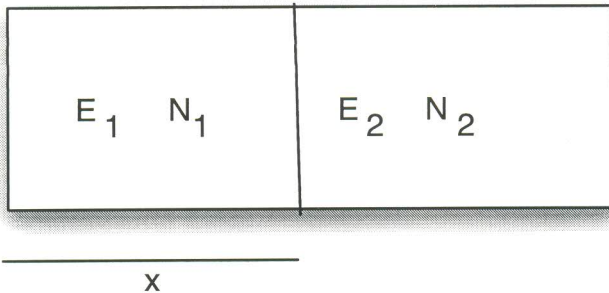
a) Take the distance x of the piston from the left wall, the velocity v of the piston and the energy E_1 of the gas on the left side of the piston as independent variables and write down the equations of motion in the standard form with first order time derivatives only.

b) Express the total entropy of the system in terms of the independent variables E_1, x and v and show, using the equations of motion, that the total entropy does not change with time.

c) Now assume that the system is not in complete thermal equilibrium during the motion of the piston so that the pressure on the piston due to the gas on left compartment differs from the one calculated using the ideal gas equation of state by $c_1 v$ and similarly pressure on the piston due to the gas on right compartment differs from the one calculated using the ideal gas equation of state by $c_2 v$ for some constants c_1, c_2. Find the equations of motion to first order in c_1, c_2.

d) Calculate the rate of change of entropy of the system. Show that for physical choice of the sign of c_1, c_2 the entropy increases with time.

2. Consider a vertical cylinder of cross section A containing helium gas, closed from the top by a piston P of zero mass. The piston can slide up and down without any friction. The walls of the cylinder as well as the piston are perfect heat insulators. The piston is held in place by putting $2n$ equal weights, each of mass m, on top of it. The piston is at a height h above the base of the cylinder.
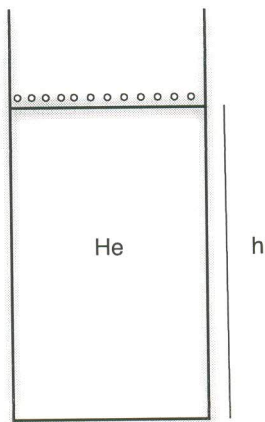
a) Now suppose we suddenly remove n of the weights and wait till the system comes to rest. You can assume that the system is in equilibrium at the beginning and the end of the process but not in the intermediate stage. What will be the final height of the piston? What is the difference between the initial and the final entropy?

b) Next consider the case where we remove n of the weights one by one, and after each removal wait for the system to come to rest before the next one is removed. What will be the height of the system at the end of the process? What is the difference between the initial and the final entropy?

c) Study what happens in the $n \to \infty$ limit.

3. Consider a one dimensional harmonic oscillator with phase space coordinates q, p and Hamiltonian

$$H(q,p) = \frac{p^2}{2m} + \frac{1}{2}Cq^2,$$

where m and C are constants. The system is in thermal contact with a reservoir at temperature T.

a) Calculate the average energy of the oscillator.

b) Calculate the probability that the energy of the oscillator lies between E and $E + \delta E$.

c) Calculate the average value of q^2.

4. Consider a system of N magnetic dipoles, each carrying a dipole moment μ. The dipoles are fixed in space at their centers but are free to rotate about any axis passing through their centers and perpendicular to the axis of the dipole. The moment of inertia of each of the dipoles about any such axis is I. The system is kept in thermal equilibrium with a heat bath of temperature T_R. There is also an external uniform magnetic field B which we take to be in the z direction.

a) Choose appropriate coordinates and momenta for describing this system and write down the Hamiltonian in terms of these coordinates and momenta.

b) Calculate the free energy F, the entropy S, mean energy E and the specific heat at constant magnetic field C_B of the system.

c) Show that the average magnetization of the system is given by $-\partial F/\partial B$. Find an expression for the average magnetization and also the susceptibility, which is defined as the rate of change of the average magnetization with respect to the external magnetic field B.

d) Estimate the total fluctuation in the average energy as well as the average magnetization in the canonical ensemble.

e) Now suppose that the dipoles are not fixed in their positions but are allowed to move freely inside a box of volume V. Determine how the results of a) - d) will change.

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5. Consider a set of N free charged particles moving in a uniform magnetic field inside a box of size V. If $\vec{A}$ is the vector potential so that $\vec{B} = \vec{\nabla} \times \vec{A}$ is the magnetic field, then the hamiltonian of the system is given by

$$H = \frac{1}{2m} \sum_{i=1}^{N} \left(\vec{p}_i - \frac{e}{c}\vec{A}(\vec{x}_i) \right)^2 ,$$

where m and e denote the mass and charge of the particle and c is the velocity of light. As before, the average magnetization is defined to be $-\partial F/\partial B$ where $B = |\vec{B}|$ and F is the free energy.

a) Show that the average magnetization of the system vanishes.

b) Show that the same result holds when we add to the hamiltonian an interaction term of the form:

$$\sum_{\substack{i,j=1 \\ i \neq j}}^{N} V(\vec{r}_i, \vec{r}_j)$$

6. Consider a system of N objects which are free to move inside a box of volume V. Each of these objects, in turn, is made of a pair of point masses, connected by a spring whose length in the absence of any external force is l_0 and whose spring constant is κ. The system is in thermal contact with a heat bath of temperature T_R. (You can ignore the mass of the spring during this calculation.)

a) Write down the expression for the Hamiltonian of the system in terms of appropriate generalized coordinates and momenta.

b) Find an expression for the number of objects in the full system for which the mean separation between pair of particles constituting the object lies between l and $l + dl$.

c) Find an expression for the number of point masses in the full system whose velocity ($|\vec{v}|$) lies between v and $v + dv$.

7. Consider a box containing ideal gas, moving with uniform velocity v_0.

a) Begin with the known velocity distribution function in the rest frame of the box and transform this to the laboratory frame to find the fraction of particles whose velocity ($|\vec{v}|$) lies between v and $v + \delta v$.

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b) Now try to find the velocity distribution of particles in the moving box in the following way. We treat the total momentum as a conserved charge and define the microcanonical ensemble as the one for which

$$\rho = \delta(H(\vec{q}, \vec{p}) - E_0)\, \delta^{(3)}(\vec{P}(\vec{q}, \vec{p}) - \vec{P}_0)$$

where E_0 and $\vec{P}_0$ denote the total energy and momentum of the system and $\vec{P}(q, p)$ is that particular function of the generalized coordinates and momenta of the system which give the total momentum vector. In the same way that we calculated the distribution of energy among the individual molecules of the system at rest, we can now calculate the distribution of energy and momentum among individual molecules of the moving system. Find the velocity distribution function in the moving system this way and compare this to the answer obtained in the previous analysis.

Aliter

We get an exp. involving $\dfrac{\partial S_R}{\partial \vec{P}_R} \cdot \vec{P}$

Now with this evaluate $\langle P_x \rangle, \langle P_y \rangle, \langle P_z \rangle$
& compare with the result expected.

We will find that $\dfrac{\partial S_R}{\partial \vec{P}_R} \cdot \vec{P}$ is related
to $\vec{v_0}$.

Canonical Ensemble

A finite or large system in thermal contact with a much bigger system.

$$\rho(\vec{q},\vec{p}) = \mathcal{N} e^{-\mathcal{H}(\vec{q},\vec{p})/kT_R} \longrightarrow \text{temperature of the reservoir}$$

$$\langle F(\vec{q},\vec{p}) \rangle_{T_R}^{can} = \frac{\int d^N q \, d^N p \; e^{-\beta \mathcal{H}(\vec{q},\vec{p})} F(\vec{q},\vec{p})}{\int d^N q \, d^N p \; e^{-\beta \mathcal{H}(\vec{q},\vec{p})}}$$

where $\beta = \dfrac{1}{kT_R}$

Suppose a system is large.

$\Omega(E)$ increases rapidly with E.

Define $\langle F \rangle_E^{micro} = \dfrac{\int d^N q \, d^N p \; F(\vec{q},\vec{p}) \, \delta(\mathcal{H}(\vec{q},\vec{p})-E)}{\underbrace{\int d^N q \, d^N p \; \delta(\mathcal{H}(\vec{q},\vec{p})-E)}_{\substack{\Omega(E) \\ (\text{upto a normalisation} \\ \text{factor})}}}$

$$\langle F(\vec{q},\vec{p}) \rangle_{T_R}^{can} = \frac{Num}{Den}$$

$$Num = \int dE \int d^N q \, d^N p \; F(\vec{q},\vec{p}) \, e^{-\beta E} \, \delta(\mathcal{H}(\vec{q},\vec{p})-E)$$

$$= \int dE \underbrace{e^{-\beta E}}_{\substack{\downarrow \\ \text{decreases} \\ \text{rapidly} \\ (\text{bcos } E \text{ large})}} \underbrace{\langle F \rangle_E^{micro}}_{\substack{\downarrow \\ \text{smooth} \\ \text{fn. of } E}} \underbrace{\Omega(E)}_{\substack{\text{increases} \\ \text{rapidly} \\ (\text{with } E)}}$$

Integral will be dominated by $E \simeq \bar{E}$.

$$\frac{\partial}{\partial \bar{E}} \left(-\beta \bar{E} + \underbrace{\ln \Omega(\bar{E})}_{\frac{1}{k} S(\bar{E})} \right) = 0$$

$$\Rightarrow -\frac{1}{kT_R} + \frac{1}{k} \frac{1}{T(\bar{E})} = 0$$

$$\Rightarrow T(\bar{E}) = T_R$$

$$Num \simeq \langle F \rangle_{\bar{E}}^{micro} \int dE \, e^{-\beta E} \Omega(E)$$

$\therefore \langle f \rangle$ is a smooth fn. & the other is a sharply peaked fn., we replace f by $\langle f \rangle_{\bar{E}}$ ⊗

$$Den = \int dE \, e^{-\beta E} \Omega(E) \Rightarrow \langle F(\vec{q}, \vec{p}) \rangle_{T_R}^{can}$$
$$= \langle F(\vec{q}, \vec{p}) \rangle_{\bar{E}}^{micro}$$

⊗

$$T(\bar{E}) = T_R$$
↓
$\bar{E}$ is calculated by solving this eqn.

[this relation should be ~~cal~~ found to relate microcan. defined for fixed E, & canonical defined for fixed T

[For large systems, Can. & Microcan. ensemble will give the same ans, for all averages]

Definition

Partition function
$$Z(\beta) = \mathcal{N} \int d^N q \, d^N p \, e^{-\beta \mathcal{H}(\vec{q}, \vec{p})}$$

(analog of Ω, which will appear in Den, but nevertheless it's not the same — as Ω)

$$\Rightarrow Z(\beta) = \mathcal{N} \int d^N q \, d^N p \int dE \, \delta(E - \mathcal{H}(\vec{q}, \vec{p})) e^{-\beta E}$$

$$= \int dE \, e^{-\beta E} \Omega(E)$$

Entropy can always be defined even for a small system, but you can't do thermodyn. with it

$$\Rightarrow Z(\beta) = \int dE \, e^{-\beta E + \frac{1}{k} S(E)}$$

The integrand is sharply peaked bcos $e^{-\beta E}$ is sharply ↓↓ & $e^{S/k}$ is --- ↑

$\downarrow$ has maximum at $\bar{E}$

we $\downarrow$ do Taylor series expansion around $\bar{E}$

$$Z(\beta) = \int dE \, e^{-\beta \bar{E} + \frac{1}{k} S(\bar{E}) + \frac{1}{2} \frac{\partial^2 S(\bar{E})}{\partial \bar{E}^2}(E-\bar{E})^2 + \cdots}$$

negative

The integrand can have more than one local max. — then look at the global max.

$$= e^{-\beta \bar{E} + \frac{1}{k} S(\bar{E})} \int dE \, e^{\frac{1}{2k} \frac{\partial^2 S}{\partial E^2}(E-\bar{E})^2}$$

$\boxed{\beta = \frac{1}{k T_R}}$

$$\Downarrow$$

$$\sqrt{\frac{2\pi}{\left|\frac{\partial^2 S}{\partial E^2}\right|}}$$

Definition

Free energy

$$F(\beta) = -k T_R \ln Z$$

$$= -k T_R \left\{ -\frac{1}{kT_R} \bar{E} + \frac{1}{k} S(\bar{E}) + \frac{1}{2} \ln \frac{2\pi}{\left|\frac{\partial^2 S}{\partial E^2}\right|} \right\}$$

$\underbrace{}_{\sim N} \quad \underbrace{}_{\sim N} \quad \underbrace{}_{\sim \ln N}$

$\rightarrow$ can be ignored

$$\simeq \bar{E} - T_R \, S(\bar{E})$$

$$\boxed{S(\bar{E}) = \frac{\bar{E} - F}{T_R}}$$

Convention :— $E, S, \cdots$ refer to quantities calculated in canonical ensemble

(this E is indeed $\bar{E}$ bcos a canonical ensemble has T_R as the input parameter & has no $\bar{E}$ otherwise)

can. & microcan. only N agrees in the large N limit $\rightarrow$ thermodynamic limit

There is ~~la limit~~ always finite size corrections bcos here we have neglected $\ln N$

$$F = \bar{E} - TS$$

$$F(T, V) \underset{\longrightarrow}{} \text{for a gas system}$$

Remember T

$t(\bar{E}) = T_R$

so we replace T_R by T.

$$dF = TdS - SdT$$

$$dF = dE - TdS - SdT$$
$$\hookrightarrow TdS - pdV$$

$$\therefore \quad dF = -pdV - SdT$$

$$\Rightarrow \frac{\partial F}{\partial V} = -p, \quad \frac{\partial F}{\partial T} = -S$$

p can be defined for microcan. as S has been defined

$$\boxed{E = F + TS}$$

(Once we calculate F, using Z, everything ~~else~~ else can be calculated using it)

Example : Ideal gas

M mono atomic molecules

$$Z = N \int d^{3M} q \; d^{3M} p \; e^{-\beta \frac{1}{2m} \sum_{i=1}^{3M} p_i^2}$$

$$= N V^M \cdot \left(\sqrt{\frac{2m\pi}{\beta}} \right)^{3M}$$

$$\therefore F = -kT \ln Z = -kT \ln N - MkT \ln V$$
$$- \frac{3MkT}{2} \ln (2m\pi kT)$$

for finite system, the 2 defns

$$\frac{\partial F}{\partial T} = -S$$

& $S = k \ln \Gamma$ won't agree — it depends on your choice which defn you use

won't be of much thermodyn. use — more of an academic exercise

$$\therefore S = -\frac{\partial F}{\partial T} = k \ln N + Mk \ln V$$
$$+ \frac{3Mk}{2} \left\{ \ln(2m\pi kT) + 1 \right\}$$

Upto terms of order $\ln N$ found here & S '' for microcan. ensemble are the same

$$E = F + TS = \frac{3MkT}{2}$$

$$p = -\frac{\partial F}{\partial V} = \frac{MkT}{V} \quad \Rightarrow \boxed{pV = MkT}$$

Example :— Take one molecule of a gas as the finite system & treat the rest of the gas as reservoir.

$\vec{q}_1, \vec{p}_1$: phase space coordinates of this molecule

$$\langle F(\vec{q}_1, \vec{p}_1) \rangle = \frac{\int d^3q_1 \, d^3p_1 \, e^{-\beta H(\vec{q}_1, \vec{p}_1)} \, F(\vec{q}_1, \vec{p}_1)}{\int d^3q_1 \, d^3p_1 \, e^{-\beta H(\vec{q}_1, \vec{p}_1)}}$$

$\beta = \dfrac{1}{kT}$, temperature of the gas.

(bcoz the rest of the gas is acting as the reservoir)

Take
$$F(\vec{q}_1, \vec{p}_1) = \Theta\big(H(\vec{q}_1, \vec{p}_1) - E\big) \, \Theta\big(E + \delta E - H(\vec{q}_1, \vec{p}_1)\big)$$

$\qquad\qquad\longmapsto$ Step function

$$\Theta(x) = \begin{cases} 1 & \text{for } x \geq 0 \\ 0 & \text{for } x < 0 \end{cases}$$

$\qquad\longmapsto F = \begin{cases} 1 & \text{for } E \leq H(\vec{q}, \vec{p}) \leq E + \delta E \\ 0 & \text{otherwise} \end{cases}$

$\langle F \rangle \xrightarrow{\text{will give}}$ probability for the energy of the molecule to ⬭ lie betn. E & $E + \delta E$

$$\langle F(\vec{q}_1, \vec{p}_1) \rangle = \frac{\int d^3q_1 \int d^3p_1 \, e^{-\frac{\beta}{2m}\vec{p}_1^2} \, \Theta\left(\frac{\vec{p}_1^2}{2m} - E\right) \Theta\left(E + \delta E - \frac{\vec{p}_1^2}{2m}\right)}{\int d^3q_1 \int d^3p_1 \, e^{-\frac{\beta}{2m}\vec{p}_1^2}}$$

$p_1 = |\vec{p}_1|$

$$\langle F \rangle = \frac{\int_0^\infty dp_1 \, 4\pi p_1^2 \, e^{-\frac{\beta}{2m}p_1^2} \, \Theta\left(\frac{p_1^2}{2m} - E\right) \Theta\left(E + \delta E - \frac{p_1^2}{2m}\right)}{\int_0^\infty dp_1 \, 4\pi p_1^2 \, e^{-\frac{\beta}{2m}p_1^2}}$$

fraction of phase space vol. when E lies betw. E & $E + \delta E$ is picked up by $\langle F \rangle$

for $\begin{aligned}E &\to \infty \\ \& E + \delta E &\to \infty\end{aligned}$, $\langle F \rangle = 1$

Take $\delta E = $ small

$$p_1^2 \geqslant 2m E \qquad \Rightarrow \qquad p_1 \geqslant \sqrt{2mE}$$

$$p_1^2 \leqslant 2m(E+\delta E) \Rightarrow p_1 \leqslant \sqrt{2m(E+\delta E)}$$

$$\underset{\underset{\displaystyle \sqrt{2mE} + \frac{1}{2}\sqrt{\frac{2m}{E}} \; \delta E \qquad\qquad + O(\delta E^2)}{||}}{}$$

Num : $(2m E) \, e^{-\frac{\beta}{2m} \cdot 2m E} \qquad \frac{1}{2}\sqrt{\frac{2m}{E}} \; \delta E$

Den : $\dfrac{\sqrt{\pi}}{4}\left(\dfrac{2m}{\beta}\right)^{3/2}$

$$\langle F \rangle = \frac{2}{\sqrt{\pi}} \, \beta^{3/2} \, E^{1/2} \, e^{-\beta E} \; \delta E \equiv P(E) \, \delta E$$

$$\underset{\substack{\text{Probability} \\ \text{distribution fn}}}{\overset{\vee}{}}$$

(encircled note)

Instead of thinking many systems in an ensemble you can equivalently think many single molecules in the same gas → so it gives prob. dist. of energy in the gas

Nothing tells u that this particle has to be a molecule of the gas — it may be any other suspended particle

---

Velocity distribution

$\widetilde{P}(v) \, \delta v = $ prob. of a molecule having velocity betn v & $v + \delta v$

$$\widetilde{P}(v) \, dv = P(E) \, \delta E$$

$$E = \frac{1}{2} m v^2 \Rightarrow \delta E = m v \, \delta v$$

$$\widetilde{P}(v) = m v \, P(E)$$

$$= m v \cdot \frac{2}{\sqrt{\pi}} \, \beta^{3/2} \left(\frac{1}{2} m v^2\right)^{1/2}$$

$$\times \, e^{-\frac{1}{2}\beta m v^2}$$

Microcanonical ensemble

$$\rho(\vec{q}, \vec{p}) = \mathcal{N}\, \delta(\mathcal{H}(\vec{q}, \vec{p}) - E)$$

Canonical ensemble

$$\rho(\vec{q}, \vec{p}) = \mathcal{N}\, e^{-\beta \mathcal{H}(\vec{q}, \vec{p})}$$

> Norm. factors cancel out --- so not imp.

What can we say about $\mathcal{N}$?

→ focus on the canonical ensemble.

for ideal gas :

$$S = k\, M \ln V + \frac{3Mk}{2}(\ln T + 1)$$
$$+ \frac{3Mk}{2} \ln(2\pi mk) + k \ln \mathcal{N}(M)$$
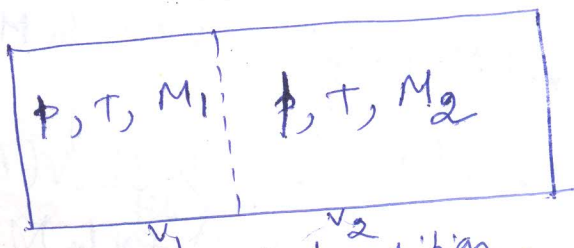
M : Total no. of molecules

~~Consider the following experiment~~

$$pV = MkT$$
$$S = k\, M \ln\left(\frac{MkT}{p}\right) + \frac{3Mk}{2}(\ln T + 1)$$
$$+ \frac{3Mk}{2} \ln(2\pi mk) + k \ln \mathcal{N}(M).$$

mass of the particle

Consider the following experiment! —

$$\boxed{\begin{array}{c|c} p, T, M_1 & p, T, M_2 \\ V_1 & V_2 \end{array}}$$

Now remove the partition.

Q. Should the entropy change?

Ans. → If S is extensive then it should not change.

(We'll get back the original situation if we put back the partition).

$$M_1 \, s(p,T) + M_2 \, s(p,T) = (M_1 + M_2) \, s(p,T)$$

$$\boxed{\text{Entropy shouldn't change}}$$

$$V_1^{M_1} V_2^{M_2} \longrightarrow \text{initially (coord. had small vol.)}$$

$$(V_1 + V_2)^{M_1 + M_2} \longrightarrow \text{finally}$$

(The way we have defined phase space vol. & as a result entropy, they change).

(Adjust N's so that the change due to vol. is adjusted by the change in N:)

$$V_1^{M_1} V_2^{M_2} N(M_1) N(M_2) \longrightarrow \text{initially}$$

$$(V_1 + V_2)^{M_1 + M_2} N(M + M_2) \longrightarrow \text{finally}$$

[The source of the non-extensive prop. of formula for the entropy is the term

$$k\, M \ln\left(\frac{M k T}{p}\right) = k \ln\left(\frac{M^M k^M T^M}{p}\right).$$

S should grow $\sim M$]

$$S(p, T, M_1 + M_2) - S(p, T, M_1) - S(p, T, M_2) \overset{?}{=} 0$$

$$\downarrow$$

desired

$$k(M_1 + M_2) \ln(M_1 + M_2) - k M_1 \ln M_1 - k M_2 \ln M_2$$

$$+ k \ln N(M_1 + M_2) - k \ln N(M_1) - k \ln N(M_2) = 0$$

Define $f(M) = \ln N(M) + k \ln M$

$$f(M_1 + M_2) = f(M_1) + f(M_2)$$

At the macroscopic level, classically also it is rev.

Process looks indistinguishable microscopically if you treat the particles as dist. — classically particles should be treated as distinguishable

for $M_1 = M$, $M_2 = \epsilon$

$$f(M+\epsilon) - f(M) = f(\epsilon) = f'(0)\epsilon$$

$$\Rightarrow \epsilon \, \frac{df}{dm} = f'(0) \epsilon$$

$$f = f'(0)M + K'' \, 0$$

$$\boxed{\begin{array}{l} c(M_1 + M_2) + K \\ = cM_1 + K + cM_2 + K \\ \Rightarrow K = 0 \end{array}}$$

Solution :—

$$f(M) = CM$$
$$\quad \hookrightarrow \text{ constant}$$

$$\ln \mathcal{N}(M) = CM - M \ln M$$
$$= CM - (\ln M! + M)$$
$$\qquad \text{for large } M$$

$$\boxed{\begin{array}{l} \ln x! \\ = x \ln x - x \\ \Rightarrow x \ln x \\ = \ln x! + x \end{array}}$$

$$= \tilde{c} M - \ln M! \qquad \left(\text{where} \atop \tilde{c} = c - 1\right)$$

$$\Rightarrow \mathcal{N}(M) = \frac{e^{\tilde{c}M}}{M!} \qquad \text{set } \tilde{c} = 0$$

$$= \frac{1}{M!}$$

We can as well set $\tilde{c} = 0$ bcos that is not going to change the initial & final total entropy. Any $\tilde{c}$ will do the job – so for convenience set $\tilde{c} = 0$

Consider 2-particle phase space

$$\int d^3p_1 \, d^3q_1 \, d^3p_2 \, d^3q_2$$

For indistinguishable particles:—

$$\left(\vec{p}_1 = \vec{p}_1^{\,(0)}, \; \vec{q}_1 = \vec{q}_1^{\,(0)}, \; \vec{p}_2 = \vec{p}_2^{\,(0)}, \; \vec{q}_2 = \vec{q}_2^{\,(0)}\right)$$

is the same phase space point as

$$\left(\vec{p}_1 = \vec{p}_2^{\,(0)}, \; \vec{q}_1 = \vec{q}_2^{\,(0)}, \; \vec{p}_2 = \vec{p}_1, \; \vec{q}_2 = \vec{q}_1^{\,(0)}\right)$$

they rep. the same phys. configuration

not allowed to say which particle is what

for M particles we have $\dfrac{1}{M!}$

$\dfrac{1}{2!}$

(We'll use this as an ad hoc rule in class. stat. mech. ∅ that $N = \frac{1}{M!}$)

[In order to treat S as an extensive prop., particles should be indistinguishable]

(Don't have to mix up with $\frac{1}{M!}$ with distinguishability of particles — Don't have to absorb $\frac{1}{M!}$ into the phase space integral — take it as the norm. factor — so no conflict with class. stat. mech.)

If the gas contains a mixture of M_1 particles of type 1, M_2 particles of type 2, etc. then we can choose

$$N = \frac{1}{M_1! \, M_2! \, \cdots \, M_k!}$$

Consider

A big system R (reservoir) in contact with a finite system S such that they can exchange energy as well as particles.

$$E_0 = E_R + E \rightarrow \text{energy of } S$$

$\downarrow$ total energy

$\searrow$ energy of R

$$M_0 = M_R + M \rightarrow \text{\# of molecules in } S$$

$\downarrow$ total no. of molecules

$\downarrow$ \# of molecules in R

$K(\vec{q}, \vec{p}, M)$: Some fn. of the phase space coordinates $(\vec{q}, \vec{p})$ of M.

$$\langle K(\vec{q}, \vec{p}, M)\rangle^{micro}_{E_0} = \langle K(\vec{q}, \vec{p}, M)\rangle^{can}_{\beta_0 = \frac{1}{k T_0}}$$

$$= \frac{\frac{1}{M_0!}\int d^{3M_0}q_0 \, d^{3M_0}p_0 \, K(\vec{q},\vec{p},M) e^{-\beta \mathcal{H}(\vec{q},\vec{p},M) - \beta_0 \mathcal{H}_R(\vec{q}_R, \vec{p}_R, M_R)}}{\frac{1}{M_0!}\int d^{3M_0}q_0 \, d^{3M_0}p_0 \, e^{-\beta\mathcal{H}(\vec{q},\vec{p}) - \beta_0 \mathcal{H}_R(\vec{q}_R,\vec{p})}}$$

$$= \frac{\frac{1}{M_0!}\int d^{3M_0}q_0 \, d^{3M_0}p_0 \, K(\vec{q},\vec{p},M)\, e^{-\beta_0 \mathcal{H}_0(\vec{q}_0,\vec{p}_0, M_0)}}{\frac{1}{M_0!}\int d^{3M_0}q_0 \, d^{3M_0}p_0 \, e^{-\beta_0 \mathcal{H}_0(\vec{q}_0, \vec{p}_0, M_0)}}$$

Numerator

$$= \frac{1}{M_0!}\sum_{M=0}^{M_0} \frac{M_0!}{M!(M_0-M)!}\int d^{3M}q \, d^{3M}p \, d^{3(M_0-M)}q_R \, d^{3(M_0-M)}p_R$$
$$K(\vec{q},\vec{p},M)\, e^{-\beta_0 \mathcal{H}(\vec{q},\vec{p},M) - \beta_0 \mathcal{H}(\vec{q}_R, \vec{p}_R, M_0-M)}$$

$$\binom{M_0}{M} = {}^{M_0}C_M$$

First-int. q_0 & p_0
over R & then
over S

$$\int_V d^3 q_0 = \int_{V_R} d^3 q_1 + \int_{V_S} d^3 q_M$$

$$= \sum_{M=0}^{M_0}\frac{1}{M!}\int d^{3M}q \, d^{3M}p \, K(\vec{q},\vec{p},M)\, e^{-\beta_0 \mathcal{H}(\vec{q},\vec{p},M)} \underbrace{Z_R(\beta_0, M_0-M)}_{}$$

$$\parallel$$

$$e^{-\beta_0 F_R(\beta_0, M_0-M)}$$

$F_R \to$ free energy
of R

$$\int_V d^3 q_1 \cdots \int_V d^3 q_{M_0}$$
$$= \left(\int_{V_R} d^3 q_1 + \int_{V_S} d^3 q_1\right)\left(\int_{V_R} d^3 q_2 + \int_{V_S} d^3 q_2\right)\cdots \left(\int_{V_R} d^3 q_{M_0} + \int_{V_S} d^3 q_{M_0}\right)$$
$$= \sum_{M=0}^{M_0}\left(\int_{V_S} d^3 q_1 \cdots d^3 q_M\right)\left(\int_{V_R} \cdots d^3 q_{M_0}\right)\binom{M_0}{M}$$

Now, $e^{-\beta_0 F_R(M_0 - M)}$

$$= e^{-\beta_0 \left\{ F_R(\beta_0, M_0) - M \frac{\partial F_R(\beta_0, M_0)}{\partial M_0} + \frac{1}{2} M^2 \frac{\partial^2 F_R(\beta_0, M_0)}{\partial M_0^2} + \cdots \right\}}$$

negligible for $M \ll M_0$

$M \to$ finite bcos we are dealing with a finite system

$$= e^{-\beta_0 F_R(\beta_0, M_0) + \mu_R M}$$

when $\mu_R \equiv \beta_0 \frac{\partial F_R(\beta_0, M_0)}{\partial M_0}$

(There won't be appreciable contribution to the sum when M is close to or equal to M_0 — prob. that all particles will be in S is very small as S is small compared to $R + S$

$$\therefore \quad \langle K(\vec{q}, \vec{p}, M) \rangle_{\beta_0}^{can}$$

$$= \frac{\sum_M \frac{1}{M!} \int d^{3M} q \; d^{3M} p \; e^{-\beta_0 H(\vec{q}, \vec{p}, M) + \mu_R M} K(\vec{q}, \vec{p}, M)}{\sum_M \frac{1}{M!} \int d^{3M} q \; d^{3M} p \; e^{-\beta_0 H(\vec{q}, \vec{p}, M) + \mu_R M}}$$

$$\times \frac{e^{-\beta_0 F_R(\beta_0, M_0)}}{e^{-\beta_0 F_R(\beta_0, M_0)}}$$

as $\Longleftrightarrow$ averaging over an ensemble if with varying energy & varying no. of particles with

this fact has come only as a consequence of counting/treating the particles as distinguishable

$$\mathcal{P}(\vec{q}, \vec{p}, M) = \frac{1}{M!} e^{-\beta_0 H(\vec{q}, \vec{p}) + \mu_R M}$$

$\Longrightarrow$ grand canonical ensemble

20/1/06

R

S

$$\langle K(\vec{q}, \vec{p}, M) \rangle^{can}_{\beta_0}$$

$$= \frac{\sum_{M=0}^{M_0} \frac{1}{M!} \int K(\vec{q}, \vec{p}, M) d^{3M}q \, d^{3M}p \times e^{-\beta H(\vec{p}, \vec{q}, M) + \mu_R M}}{\sum_{M=0}^{M_0} \frac{1}{M!} \int d^{3M}q \, d^{3M}p \, e^{-\beta_0 H(\vec{q}, \vec{p}, M) + \mu_R M}}$$
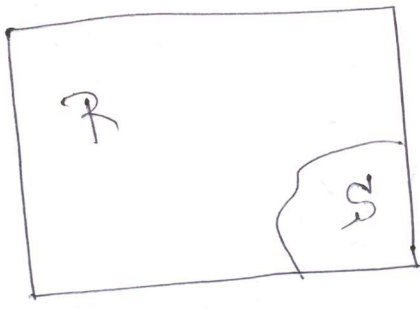
LHS isn't
a fn. of $\vec{q}, \vec{p}$ or M
→ it just specifies
the variables
on which we are
summing over

$$\langle K(\vec{q}, \vec{p}, M) \rangle^{can}_{\beta_0}$$

$$= \frac{\sum_{M=0}^{M_0} \frac{1}{M!} \int K(\vec{q}, \vec{p}, M) \, d^{3M}q \, d^{3M}p \, e^{-\beta_0 H(\vec{p}, \vec{q}, M) + \mu_R M}}{\sum_{M=0}^{M_0} \frac{1}{M!} \int d^{3M}q \, d^{3M}p \, e^{-\beta_0 H(\vec{q}, \vec{p}, M) + \mu_R M}}$$

$$\mu_R = \beta_0 \frac{\partial F(\beta_0, M_0)}{\partial M_0}$$

Change convention

$$\mu_R = \frac{\partial F(\beta_0, M_0)}{\partial M_0}$$

$$\langle K(\vec{q}, \vec{p}, M) \rangle_{\beta_0, M_0}$$

$$= \frac{\sum_{M=0}^{M_0 \to \infty} \frac{1}{M!} \int K(\vec{q}, \vec{p}, M) \, d^{3M}q \, d^{3M}p \, e^{-\beta_0 H(\vec{q}, \vec{p}, M) + \beta_0 \mu_R M}}{\sum_{M=0}^{M_0 \to \infty} \frac{1}{M!} \int e^{-\beta_0 H(\vec{q}, \vec{p}, M) + \mu_R \beta_0 M} \, d^{3M}q \, d^{3M}p}$$

$\longrightarrow$ Grand canonical ensemble

$M_0 \to \infty$ limit

bcos by defn.
reservoir has
infinite energy
or particles

In canonical, E was
let to run for all
possible values upto ∞
by assuming the reservoir
has infinite
energy

$$\Rightarrow \langle K(\vec{q}, \vec{p}, M) \rangle_{\beta_0, M_0}$$

$$= \frac{\sum_{M=0}^{\infty} e^{\beta_0 \mu_R M} \langle K \rangle_{\beta_0, M}^{can} Z(\beta_0, M)}{\sum_{M=0}^{\infty} e^{\beta_0 \mu_R M} Z(\beta_0, M)}$$

Now $\oplus$ $\langle K \rangle_{\beta_0, M}^{can} = \frac{\frac{1}{M!} \int d^{3M}q \, d^{3M}p \, K(\vec{q}, \vec{p}, M) e^{-\beta_0 \mathcal{H}(\vec{q}, \vec{p}, M)}}{Z(\beta_0, M)}$

$\boxed{\frac{1}{M!} \text{ has been} \atop \text{absorbed into} \atop \text{the defn of } Z(\beta_0, M)}$

Suppose S is large.

Expect $e^{\beta_0 \mu_R M} \, Z(\beta_0, M)$ is sharply peaked

$$\Downarrow$$

$$e^{\beta_0 \mu_R M - \beta_0 F(\beta_0, M)}$$

$\boxed{\begin{array}{l} F = -kT \ln Z \\ \Rightarrow Z = e^{-F/kT} = e^{-\beta F} \end{array}}$

$\underset{maximum}{\overset{find}{\Longrightarrow}} \quad \beta_0 \mu_R - \beta_0 \dfrac{\partial F(\beta_0, M)}{\partial M} = 0$

$$\Downarrow \mu(\beta_0, M) \left\{ {\mu \text{ of the} \atop \text{sub-system}} \right.$$

$$\Rightarrow \mu(\beta_0, \bar{M}) = \mu_R$$

$$\underset{determines \ \bar{M}}{\Downarrow}$$

$\boxed{\begin{array}{l} \text{No. of particles in} \\ \text{the subsystem} \\ \text{will fluctuate} \\ \text{but dominant} \\ \text{contribution will} \\ \text{come from } \bar{M} \end{array}}$

$$\langle K \rangle = \frac{\langle K \rangle_{\beta_0, \bar{M}}^{can} \sum_{M=0}^{\infty} e^{\beta_0 \mu_R M} Z(\beta_0, M)}{\sum_{M=0}^{\infty} e^{\beta_0 \mu_R M} Z(\beta_0, M)}$$

$$= \langle K \rangle_{\beta_0, \bar{M}}^{can}$$

$$\Rightarrow \langle K \rangle^{grand}_{\beta_0, \mu_R} = \langle K \rangle^{can}_{\beta_0, \overline{M}}$$

$$\hookrightarrow \text{determined from}$$
$$\mu(\beta_0, \overline{M}) = \mu_R$$

Grand Canonical partition function

$$Q = \sum_{M=0}^{\infty} e^{\beta_0 \mu_R M} Z(\beta_0, M)$$

$$\xrightarrow[\text{large size}]{} e^{\beta_0 \mu_R \overline{M}} Z(\beta_0, \overline{M})$$

> assuming it is sharply peaked around $\overline{M}$

$$\ln Q \simeq \beta_0 \mu_R \overline{M} + \ln Z(\beta_0, \overline{M})$$
$$= \beta_0 \mu_R \overline{M} - \beta_0 F(\beta_0, \overline{M})$$

knowing Q, u can in principle use to derive all other thermodyn. quantities

large system so we don't care which ensemble we are using — all average are the same

All distributions are infinitely sharply peaked

Consider a large system with temp. T, pressure p, chemical potential μ, volume V, energy E, # of molecules M etc.

$$\boxed{\ln Q = \frac{1}{kT}\{\mu M - F\}}$$

$$dF = -SdT - pdV \longrightarrow \text{doesn't capture what happens when # of molecules change}$$

$$\therefore \boxed{dF = -SdT - pdV + \mu dM}$$

$$\therefore \left(\frac{\partial F}{\partial M}\right)_{T,V} = \mu$$

$$d(\ln Q) = -\frac{dT}{kT^2}\{\mu f - F\}$$
$$+ \frac{1}{kT}\{+\mu dM + M d\mu + SdT$$
$$+ pdV - \mu dM\}$$

$$\Rightarrow d(\ln \mathcal{Q}) = + \frac{dT}{kT^2} \left\{ -\mu M + F + TS \right\}$$
$$+ \frac{M}{kT} d\mu + \frac{p}{kT} dV$$

$$\Rightarrow \left(\frac{\partial}{\partial T} \ln \mathcal{Q} \right)_{\mu, V} = \frac{1}{kT^2} (-\mu M + \overbrace{F + TS}^{E})$$
$$= \frac{1}{kT^2} (E - \mu M)$$

$$\left(\frac{\partial}{\partial \mu} \ln \mathcal{Q} \right)_{T, V} = M/kT \left. \vphantom{\frac{\partial}{\partial}} \right\} \Rightarrow$$

$$\left(\frac{\partial}{\partial V} \ln \mathcal{Q} \right)_{T, \mu} = p/kT \left. \vphantom{\frac{\partial}{\partial}} \right\}$$

E as fn. of μ, V, T

M as fn. of μ, V, T

p as fn. of μ, V, T

M, V, E are input parameters in microcanonical

what variables we treat as indep. variables depends on the choice of ensemble

Example: Ideal gas

$$Z(\beta, V, M) = N_{(M)} V^M \left(\sqrt{\frac{2m\pi}{\beta}} \right)^{3M}$$
$$\Downarrow$$
$$\frac{1}{M!}$$

$$\mathcal{Q}(\beta, \mu, V)$$
$$= \sum_{M=0}^{\infty} e^{\beta \mu M} Z(\beta, V, M)$$
$$= \sum_{M=0}^{\infty} \frac{1}{M!} e^{\beta \mu M} V^M \left(\sqrt{\frac{2m\pi}{\beta}} \right)^{3M}$$
$$= \exp \left\{ e^{\beta \mu} V \left(\frac{2m\pi}{\beta} \right)^{3/2} \right\}$$

$$\Rightarrow \ln \mathcal{Q} = e^{\beta \mu} V \left(\frac{2m\pi}{\beta} \right)^{3/2}$$
$$= e^{\beta \mu} V (2m\pi kT)^{3/2}$$

Now, $\frac{M}{kT} = \frac{\partial}{\partial \mu} \ln \mathcal{Q} = \beta e^{\beta \mu} V (2m\pi kT)^{3/2}$

$$\Rightarrow M = e^{\beta \mu} V (2m\pi kT)^{3/2}$$

$$E - \mu M = kT^2 \frac{\partial}{\partial T}(\ln \mathcal{Q})$$

$$= kT^2 \left\{ -\frac{\mu}{kT^2} e^{\beta \mu} V (2m \pi kT)^{3/2} + \frac{3}{2} e^{\beta \mu} V (2m \pi k)^{3/2} T^{1/2} \right\}$$

$$\Rightarrow E - \mu M = -\mu M + kT^2 \times \frac{3}{2} e^{\beta \mu} V (2m \pi k)^{3/2} T^{1/2}$$

$$\Rightarrow E = \frac{3}{2} kT V (2m \pi kT)^{3/2} e^{\beta \mu}$$

$$\Rightarrow \boxed{E = \frac{3}{2} M kT}$$

$$p = kT \frac{\partial}{\partial V} \ln \mathcal{Q}$$

$$= kT e^{\beta \mu} (2m \pi kT)^{3/2}$$

$$= kT \cdot M/V$$

$$\Rightarrow \boxed{p V = M kT}$$

provided we make the right identification
μ & M
&
let T & E be
all ensembles
will give the same
ans. for large
system

for finite systems there
are finite size
corrections

there are certainly
quantities which'll differ.
e.g. → RMS of energy

zero
in microcan.
E fixed

$\neq 0$
in can.
weighted
avg.

$$\mathcal{Q} = \sum_M \frac{1}{M!} \int d^{3M}q \, d^{3M}p \, e^{-\beta H(\vec{q}, \vec{p}, M) + \beta \mu M}$$

$$\frac{\partial}{\partial \mu}(\ln \mathcal{Q})$$

$$= \frac{1}{\mathcal{Q}} \sum_M \frac{1}{M!} \int d^{3M}q \, d^{3M}p \, e^{-\beta H(\vec{q}, \vec{p}) + \beta \mu M} \cdot \beta M$$

$$= \beta \overline{M}$$

$$\left[\text{compare with} \left(\frac{\partial}{\partial \mu} \ln \mathcal{Q}\right)_{T,V} = M/kT \right]$$

Even if a physical situation dictates a particular ensemble, you can use any ensemble acc. to ease of calculation

Grand can: will come handy when you have to do some counting — then no constraint on # of particles will make calculation of part-fn. easier

less constraint means easier calculation

$$\frac{\partial}{\partial \beta} \ln \mathcal{Q} = \frac{1}{\mathcal{Q}} \frac{\partial \mathcal{Q}}{\partial \beta} = \left(-\overline{E} + \mu \overline{M} \right)$$

p isn't an ~~extensive~~ quantity

p is the response to volume

T & μ were direct parameters in expression for $\mathcal{Q}$

V is on the other hand implicit

↳ it's a bit tricky

→ so p is not an arg.

Relation of μ to $\left(\dfrac{\partial S\,(E,V,M)}{\partial M} \right)_{E,V}$

$$dF = -S\,dT - p\,dV + \mu\,dM$$
$$\shortparallel$$
$$d(E - TS)$$

$$\Rightarrow dE - T\,dS - S\,dT$$
$$= -S\,dT - p\,dV + \mu\,dM$$

$$\Rightarrow T\,dS = dE + p\,dV - \mu\,dM$$

$$\Rightarrow dS = \frac{1}{T}\,dE + \frac{p}{T}\,dV - \frac{\mu}{T}\,dM$$

$$\Rightarrow \left(\frac{\partial S}{\partial M} \right)_{E,V} = -\frac{\mu}{T}$$

$\left(\dfrac{\partial S}{\partial M} \right)_1 = \left(\dfrac{\partial S}{\partial M} \right)_2$

$\Rightarrow \dfrac{\mu_1}{T_1} = \dfrac{\mu_2}{T_2}$

But, also
$\left(\dfrac{\partial S}{\partial E} \right)_1 = \left(\dfrac{\partial S}{\partial E} \right)_2$

$\Rightarrow T_1 = T_2$

so $\mu_1 = \mu_2$

μ is the same upto the factor of T

But T has to match on 2 sides for 2 systems in equm → so μ has to match on 2 sides

(Not writing volume factor V)

Fluctuation in M for grand canonical ensemble

$$\langle K(\vec{E}, \vec{B}, M) \rangle^{\text{grand}}_{\beta, \mu}$$

$$= \frac{\displaystyle\sum_M \langle K \rangle^{\text{can}}_{\beta, \mu}\, e^{\beta \mu M}\, Z(\beta, M)}{\displaystyle\sum_M e^{\beta \mu M}\, Z(\beta, M)}$$

$$= \frac{\displaystyle\sum_M \langle K \rangle^{\text{can}}_{\beta, M}\, e^{\beta \mu M - \beta F(\beta, M)}}{\displaystyle\sum_M e^{\beta \mu M - \beta F(\beta, M)}}$$

systems finite but large

$$\beta \mu M - \beta F(\beta, M)$$
$$= \beta \mu \bar{M} - \beta F(\beta, \bar{M})$$
$$- \beta \frac{1}{2} \frac{\partial^2 F(\beta, \bar{M})}{\partial \bar{M}^2} (M - \bar{M})^2 + \cdots$$

$$\Delta M \sim \sqrt{\frac{2}{\beta} \frac{1}{\left| \frac{\partial^2 F}{\partial M^2} \right|}}$$

→ quantity controlling the peak
if zero — ~~no peak~~ peak broad, consider next term
if large — peak is sharp

Calculation of $\frac{\partial^2 F}{\partial M^2}$

F is extensive
$$F(\beta, M, V) = M \, f\left(\beta, \frac{V}{M}\right)$$

$$\frac{\partial F}{\partial M} = f(\beta, V/M) + M \frac{\partial}{\partial M} f(\beta, V/M)$$

$$= f(\beta, V/M) - V \frac{\partial}{\partial V} f(\beta, V/M)$$

$$= f(\beta, V/M) - \frac{V}{M} \frac{\partial}{\partial V} F(\beta, M, V)$$

$$= f(\beta, V) + \frac{V}{M} p(\beta, V/M)$$

f is a homogeneous fn of M & V of degree zero

$p \rightarrow$ homogeneous fn of degree zero in M/V → intensive quantity

$$\frac{\partial^2 F}{\partial M^2} = \frac{\partial}{\partial M} f(\beta, V/M)$$
$$- \frac{V}{M^2} p(\beta, V/M)$$
$$+ \frac{V}{M} \frac{\partial}{\partial M} p(\beta, V/M)$$

$$= \frac{V}{M^2} p(\beta, V/M) - \frac{V}{M^2} p(\beta, V/M)$$
$$+ \frac{V}{M^2} \left(-V \frac{\partial}{\partial V} p(\beta, V/M) \right)$$

Define: $\rho = \frac{M}{V}$, $v = \frac{1}{\rho} = V/M$

$\underset{\text{volume/particle}}{\Downarrow}$

$\therefore \frac{\partial^2 f}{\partial M^2} = -\frac{V^2}{M^2} \cdot \frac{1}{M} \frac{\partial}{\partial v} p(\beta, v)$

$= -v^2 \frac{\partial p}{\partial v} \cdot \frac{1}{M}$

$= \frac{\partial p}{\partial \rho} \cdot \frac{1}{M}$

$\therefore \Delta M \sim \sqrt{\frac{2}{\beta} \cdot \frac{1}{\left|\frac{\partial^2 f}{\partial M^2}\right|}} \sim \sqrt{kT} \frac{\sqrt{M}}{\sqrt{\left|\frac{\partial p}{\partial \rho}\right|}}$

$\therefore \frac{\Delta M}{M} = \sqrt{kT} \frac{1}{\sqrt{\left|\partial p / \partial \rho\right|}} \frac{1}{\sqrt{M}}$

small for large M
provided $\left|\partial p / \partial \rho\right| \neq 0$

We are to make sure $\frac{\partial^2 f}{\partial M^2}$ is +ve $\longrightarrow$ so $\partial p / \partial \rho$ must be +ve

in those cases grand canonical ens. will be a valid one

$\frac{\partial p}{\partial \rho}$ may vanish at phase transition — e.g. ρ at fixed pressure, density changes for condensation of vapour into water

Density fluctuation leads to opacity of the — if you look at smaller & smaller system, the fluctuations becomes larger

at a critical pt. system becomes

$$\int d^3q_1 \quad \text{---} \quad \int_V d^3q_{M_0}$$
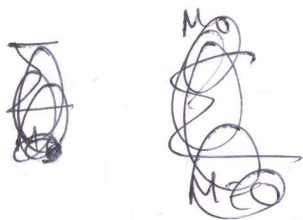
$$= \left(\int_{V_R} d^3q_1 + \int_{V_S} d^3q_1 \right)$$

$$\left(\int_{V_R} d^3q_2 + \int_{V_S} d^3q_2 \right) \text{----}$$

$$= \sum_{M=0}^{M_0} \binom{M_0}{M} \left(\int_{V_S} d^3q_1 \quad \text{---} \quad d^3q_M \right)$$

$$\left(\int_{V_R} d^3q_{M+1} \text{---} d^3q_{M_0} \right) \binom{M_0}{M}$$

$$= \sum_{M=0}^{M_0} \binom{M_0}{M} \int d^{3M}q \; d^{3M}p \int d^{3(N_0-M)}q \; d^{3(N_0-M)}p$$

H.W.

$$f = f(M/v)$$

$$M \, \partial f / \partial M = M \, \frac{df(z)}{dz} \frac{\partial}{\partial M}(M/v) = M/v \; f'(z)\big|_{z=M/v}$$

$$v \, \partial f / \partial v = - M/v \; f'(z)\big|_{z=M/v}$$