

## A note about coordinates

We can write the partition function as

microcanonical  $\Omega(E, V, N) = \int_{\text{all degrees of freedom}} \delta(E - H)$

canonical

$$Q_N(T, V) = \int_{\text{all degrees of freedom}} e^{-\beta H}$$

where by  $\int_{\text{all degrees of freedom}}$  I mean a sum or integral over

all the degrees of freedom that characterize the system. If degrees of freedom are continuous then the integration should include an appropriate factor (like  $\frac{1}{h^{3N}}$  for the gas of  $N$  classical particles) so that the partition function is dimensionless.

For classical systems with continuous degrees of freedom, it is ESSENTIAL that the degrees of freedom one integrates over be a set of Hamiltonian canonically conjugate coordinate-momentum pairs  $(q_i, p_i)$ .

The reason for this has to do with Liouville's Theorem. To describe equilibrium we needed that the probability density for the system to be at a particular point in phase space should NOT change in time, i.e.  $\frac{\partial \rho}{\partial t} = 0$ . Liouville's Theorem told us that this will be the case whenever all states of a given total energy  $E$  are equally likely. But Liouville's Theorem only applies if we are labeling our states by a set of Hamiltonian canonically conjugate coordinate-momentum pairs. - recall we had to use Hamilton's equations of motion in deriving Liouville's Theorem.

If  $(q_i, p_i)$  are such a set of canonically conjugate degrees of freedom, then we can write the canonical partition function, for example, as

$$Q_N(T, V) = \int dq_1, \dots, dq_N \int dp_1, \dots, dp_N e^{-\beta H(q_1, \dots, q_N, p_1, \dots, p_N)}$$

add  $\frac{1}{N!}$  if indistinguishable particles

Now sometimes it might be convenient to label states by some other set of coordinates, for example  $(q_i, \dot{q}_i)$  instead of  $(q_i, p_i)$ . In that case one can compute the partition function in terms of the convenient coordinates, provided one makes the correct transformation of the variables of integration.

$$Q_N(T, V) = \int dq_i dp_i e^{-\beta H(q_i, p_i)}$$

$$= \int dq_i d\dot{q}_i J e^{-\beta H(q_i, \dot{q}_i)}$$

where  $J$  is the Jacobian of the transformation from  $(q_i, p_i)$  to  $(q_i, \dot{q}_i)$ . It is crucial to include this Jacobian factor to get the correct result for the partition function.

If one goes from a set of variables  $y_1, y_2, \dots, y_M$  to a new set  $x_1, x_2, \dots, x_M$ , then the Jacobian is

$$\prod_i \int dy_i = \prod_i \int dx_i J$$

$$J = \det \begin{bmatrix} \frac{\partial y_1}{\partial x_1} & \frac{\partial y_1}{\partial x_2} & \dots \\ \frac{\partial y_2}{\partial x_1} & \frac{\partial y_2}{\partial x_2} & \dots \\ \vdots & \vdots & \ddots \end{bmatrix}$$

det is  
determinant  
of the matrix

Example. A classical gas of particles in an external magnetic field.

$$H = \sum_{i=1}^N \frac{1}{2m} |\vec{P}_i - \frac{e}{c} \vec{A}(\vec{r}_i)|^2$$

$\vec{A}(\vec{r})$  is the magnetic vector potential.

The particles velocity, in terms of the canonical momentum  $\vec{P}_i$  is

$$\vec{v}_i = \frac{\vec{P}_i - \frac{e}{c} \vec{A}(\vec{r}_i)}{m}$$

At first glance ~~we could~~ it seems that we could not compute the average total energy  $E = \langle H \rangle$  using the equipartition theorem, since  $H$  couples  $\vec{P}_i$  to  $\vec{r}_i$  via  $\vec{A}(\vec{r}_i)$ .

However, if we directly compute  $Q_1$

$$Q_1 = \int d^3r \frac{\int d^3p}{h^3} e^{-\beta \frac{|\vec{p} - \frac{e}{c} \vec{A}(\vec{r})|^2}{2m}}$$

we can do the following trick. Since  $\vec{r}$  is fixed when we do the  $\vec{p}$  integration, then as far as the  $\vec{p}$  integration is concerned

$\frac{e}{c} \vec{A}(\vec{r})$  is just some constant  $\vec{p}_0$ .

We can then make a transformation of variables in the integration  $\vec{p}' = \vec{p} - \frac{e}{c} \vec{A}(\vec{r})$  to write

$$Q_1 = \int d^3r \frac{\int d^3p'}{h^3} e^{-\beta |\vec{p}'|^2 / 2m}$$

which gives exactly the same  $Q_1$  as for a gas that is NOT in a magnetic field!

Hence we conclude that the total energy of the gas in the magnetic field is the same as in zero field, and so  $E = \frac{3}{2} N k_B T$ .

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We can view this result in terms of coordinates. Instead of writing the partition function down in terms of the canonical coordinates  $\vec{r}_i, \vec{p}_i$ , we could use instead the coordinates  $\vec{r}_i, \vec{v}_i$ . We then have  $\vec{v} = \frac{\vec{p} - \frac{e}{c} \vec{A}(\vec{r})}{m}$

$$Q_1 = \int d^3r \frac{\int d^3v}{h^3} J e^{-\beta \frac{m v^2}{2}}$$

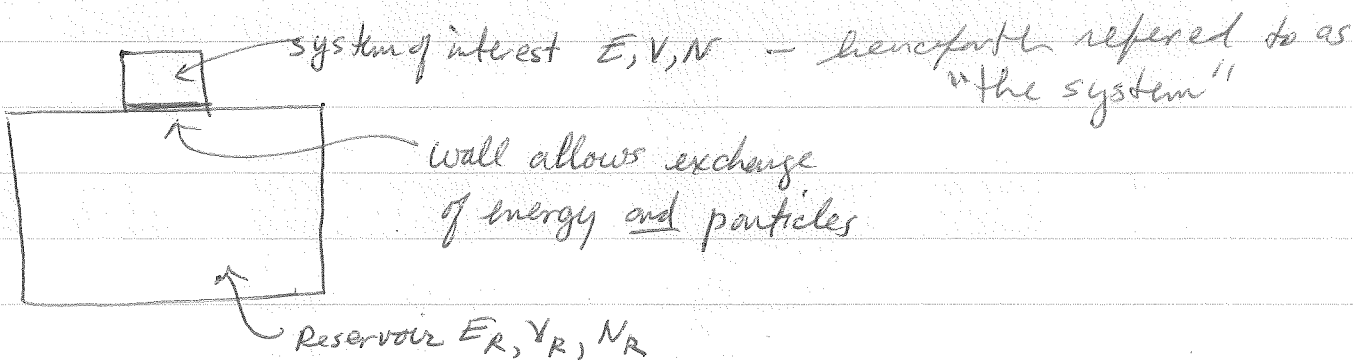
where  $J = m^3$  is the Jacobian of the transformation from  $\vec{r}, \vec{p}$  to  $\vec{r}, \vec{v}$ .

We can now do the integration over  $\vec{v}$  and get the same result for  $Q_1$  as for the case with no magnetic field. The

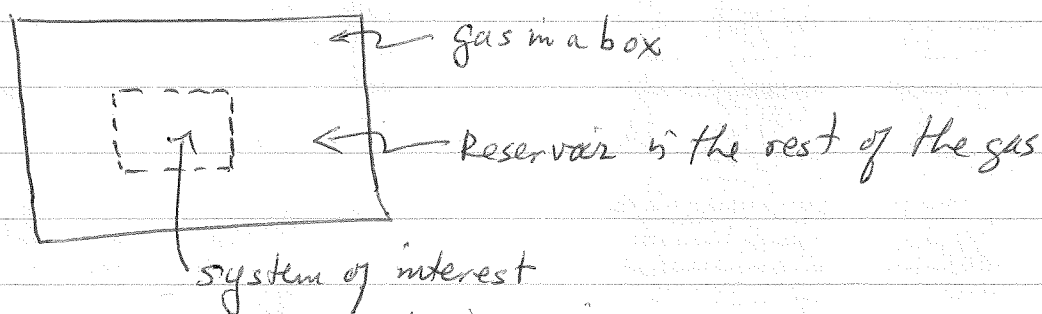
thing that made things work simply in this case was that the Jacobian  $J$  was a constant and not some function of  $\vec{r}, \vec{v}$ .

## Grand Canonical Ensemble

Consider a system of interest which is in contact with both a thermal and a particle reservoir



One way such a situation may arise physically is if the "system of interest" is just a certain volume immersed in a much larger volume of the same "stuff", and the walls ~~at~~ around the "system of interest" are just our mental constructs



system of interest is some interior region of the gas. Dashed lines are mental construct - not physical walls!

The energy  $E$  and number of particles  $N$  in the region of interest are not fixed but fluctuate as energy + particles flow between the region and the rest of the gas.

The reservoir is so large, that no matter how much energy or particles the system of interest transfers to it, its temperature  $T_R$  and chemical potential  $\mu_R$  do not change - this is what we mean by it being a reservoir.

We see this as we argued before. If heat  $dQ = T dS$  is transferred to the reservoir then the change in  $T_R$  is

$$\Delta T_R = \frac{\partial T_R}{\partial S_R} dS = \left( \frac{\partial^2 E_R}{\partial S_R^2} \right) dS \sim \frac{N}{N_R} T_R \quad \text{as } E_R, S_R \sim N_R \\ dS \sim N \text{ at most}$$

so if  $N \ll N_R$ ,  $\Delta T_R \ll T_R$

Similarly, if  $dN$  is transferred to the reservoir

$$\Delta \mu_R = \frac{\partial \mu_R}{\partial N_R} dN = \left( \frac{\partial^2 E_R}{\partial N_R^2} \right) dN \sim \frac{N}{N_R} \mu_R \quad \text{as } E_R, N_R \sim N_R \\ \text{and } dN \sim N \text{ at most}$$

so if  $N \ll N_R$ ,  $\Delta \mu_R \ll \mu_R$

So we regard  $T_R$  and  $\mu_R$  of the reservoir as fixed

Now - because the "system of interest" is in equilibrium with the reservoir, we have  $T = T_R$ , and  $\mu = \mu_R$



Now  $N + N_R = N_T$  is fixed,  $E + E_R = E_T$  is fixed  
 $V, V_R$  are fixed

Similar to what we had for the canonical ensemble, the density of states for the total system of reservoir + system of interest is

$$g_T(E_T, V, V_R, N_T) = \int dE \sum_N g(E, V, N) g_R(E_T - E, V_R, N_T - N)$$

or for the number of states  $\Omega = g \Delta$  ( $\Delta$  is small energy interval as before)

$$\begin{aligned} \Omega_T(E_T, V, V_R, N_T) &= \int \frac{dE}{\Delta} \sum_N \Omega(E, V, N) \Omega_R(E_T - E, V_R, N_T - N) \\ &= \int \frac{dE}{\Delta} \sum_N \Omega(E, V, N) e^{S_R(E_T - E, V_R, N_T - N)/k_B} \end{aligned}$$

probability density for system to have  $E$  and  $N$  is proportional to the number of states that have the system with  $E$  and  $N$  (of the total system)

$$P(E, N) \propto \frac{\Omega(E, V, N) e^{S_R(E_T - E, V_R, N_T - N)/k_B}}{\Delta}$$

expand

$$S_R(E_T - E, V_R, N_T - N) \approx S_R(E_T, V_R, N_T) + \frac{\partial S_R}{\partial E_R} (-E) + \left( \frac{\partial S_R}{\partial N_R} \right) (-N)$$

$$\begin{aligned} &= S_R - \frac{E}{T} + \frac{\mu N}{T} \\ P(E, N) &\propto \frac{\Omega(E, V, N) e^{-(E - \mu N)/k_B T}}{\Delta} \end{aligned}$$

Normalize

$$P(E, N) = \frac{\Omega(E, V, N) e^{-(E - \mu N)/k_B T}}{\sum_N \int \frac{dE}{\Delta} \Omega(E, V, N) e^{-E/k_B T} e^{\mu N/k_B T}}$$

probability density for system to have  $E$  and  $N$

$$P(E, N) = \frac{\Omega(E, V, N)}{\Delta} e^{-(E - \mu N)/k_B T}$$

$$\sum_N \int \frac{dE}{\Delta} \Omega(E, V, N) e^{-(E - \mu N)/k_B T}$$

$P(E, N)$  is normalized, i.e.  $\sum_N \int dE P(E, N) = 1$

The denominator in the above expression for  $P(E, N)$  defines the grand canonical partition function

$$\begin{aligned} \mathcal{Z}(T, V, \mu) &\equiv \sum_N \left[ \int \frac{dE}{\Delta} \Omega(E, V, N) e^{-E/k_B T} \right] e^{\mu N/k_B T} \\ &= \sum_N Q_N(T, V) z^N \end{aligned}$$

where we define the fugacity  $z \equiv e^{\mu/k_B T}$

If we can label the microscopic states of the system by the index  $i$ , such that state  $i$  has total energy  $E_i$  and contains  $N_i$  particles, then we can write

$$Q_N(T, V) = \sum_{\substack{i \text{ such} \\ \text{that } N_i = N}} e^{-E_i/k_B T}$$

and so

$$\mathcal{Z} = \sum_N \left[ \sum_{\substack{i \text{ such that} \\ N_i = N}} e^{-E_i/k_B T} \right] e^{\mu N/k_B T}$$

$$\mathcal{Z} = \sum_i e^{-(E_i - \mu N_i)/k_B T}$$

where now sum over  $i$  is over all states with no restriction on  $N_i$

Return now to probability density

$$P(E, N) = \frac{\Omega}{\Delta} \frac{e^{-(E - \mu N)/k_B T}}{\mathcal{Z}}$$

since  $\Omega$  just counts the number of states <sup>of the system</sup> with energy  $E$  and number of particles  $N$ , and all these states are equally likely, the probability to be in any particular state  $i$  is just

$$P_i = \frac{e^{-(E_i - \mu N_i)/k_B T}}{\mathcal{Z}}$$

This is the obvious generalization of what we had earlier for the canonical ensemble

Note: these expressions for  $\mathcal{Z}$ ,  $P_i$ ,  $P(E, N)$  etc, make NO reference to the reservoir!