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# 1 Hamiltonian Dynamics

- The Hamiltonian is defined to be

$$\mathcal{H} := \sum_i p_i \dot{q}_i - \mathcal{L}(\{q_i, \dot{q}_i\}) \quad (1.1)$$

where  $q_i$  are the generalized coordinates and  $p_i = \partial \mathcal{L} / \partial \dot{q}_i$  are the generalized momenta.

- We can think of the Hamiltonian as a function of the momenta and coordinates  $\mathcal{H}(\{p_i, q_i\})$ .
- Q: What happens to the Hamiltonian if we make a differential change in  $p_i$ ,  $q_i$ , and  $\dot{q}_i$ ?

$$p_i \rightarrow p_i + dp_i \quad q_i \rightarrow q_i + dq_i \quad \dot{q}_i \rightarrow \dot{q}_i + d\dot{q}_i \quad (1.2)$$

- A: A differential change to the Hamiltonian gives us

$$d\mathcal{H} = \sum_i \left[ \left( \frac{\partial \mathcal{H}}{\partial p_i} \right) dp_i + \left( \frac{\partial \mathcal{H}}{\partial q_i} \right) dq_i \right] \quad (1.3)$$

when we think of the Hamiltonian as a function of the momenta and coordinates.

- Q: What happens if we now use the definition of the Hamiltonian to think about its differential change?
- A: In general we would have a term with

$$d(p_i \dot{q}_i) = p_i \dot{q}_i + dp_i \dot{q}_i + p_i d\dot{q}_i + dp_i d\dot{q}_i, \quad (1.4)$$

but we can neglect the last term because it is of the order  $(dx)^2$ . Since we want the change in  $\mathcal{H}$  we need to subtract off an  $p_i \dot{q}_i$ . The total change in the Hamiltonian can be written as

$$d\mathcal{H} = \sum_i (\dot{q}_i dp_i + p_i d\dot{q}_i) - d\mathcal{L}. \quad (1.5)$$

We still need to calculate the change in the Lagrangian, which is

$$d\mathcal{L}(\{q_i, \dot{q}_i\}) = \sum_i \left[ \left( \frac{\partial \mathcal{L}}{\partial q_i} \right) dq_i + \left( \frac{\partial \mathcal{L}}{\partial \dot{q}_i} \right) d\dot{q}_i \right] \quad (1.6)$$

We can now write the differential change in the Hamiltonian as

$$d\mathcal{H} = \sum_i \left[ \dot{q}_i dp_i + p_i d\dot{q}_i - \left( \frac{\partial \mathcal{L}}{\partial q_i} \right) dq_i - \left( \frac{\partial \mathcal{L}}{\partial \dot{q}_i} \right) d\dot{q}_i \right]. \quad (1.7)$$

We can replace  $\partial \mathcal{L} / \partial \dot{q}_i$  with  $p_i$  and so two of the terms cancel. We can also replace  $\partial \mathcal{L} / \partial q_i$  with  $d/dt(\partial \mathcal{L} / \partial \dot{q}_i) = \dot{p}_i$  using the Euler-Lagrange equation of motion. After implementing these two changes we can write the Hamiltonian as

$$d\mathcal{H} = \sum_i [\dot{q}_i dp_i - \dot{p}_i dq_i] \quad (1.8)$$

- Now let's compare Eq. (1.3) and Eq. (1.8). We can see that the two equations are equal only if the coefficients in front of each  $dq_i$  and each  $dp_i$  are equal. Equating these coefficients gives us Hamilton's Equations

$$\boxed{\frac{\partial \mathcal{H}}{\partial p_i} = \dot{q}_i \quad - \quad \frac{\partial \mathcal{H}}{\partial q_i} = \dot{p}_i} \quad (1.9)$$

- Hamilton's Equations are an alternative way to formulate mechanics. We can use the following steps to approach problems in the Hamiltonian formalism.
  - (1) Find  $\mathcal{L}$
  - (2) Find  $p_i$
  - (3) Find  $\mathcal{H}$
  - (4) Write  $\mathcal{H}(\{p_i, q_i\})$
  - (5) Use Hamilton's equations to describe the dynamics.

## 2 Liouville's Theorem

- Consider a system of  $N$  particles where  $N \gg 1$ . We then have coordinates  $\mathbf{r}_\alpha$  and generalized momenta  $\mathbf{p}_\alpha$ , where  $\alpha = 1, 2, \dots, N$ .
- Let's think of the Hamiltonian as a function of only  $\mathbf{p}$  and  $\mathbf{q}$ , where  $\mathbf{p}$  is a  $3N$  component vector that represents all of the particles' positions (with three degrees of freedom for the position of each particle), and where  $\mathbf{p}$  is a  $3N$  component vector that represents all of the particles' conjugate momenta (with their three degrees of freedom per particle). We write this as  $\mathcal{H}(\{\mathbf{p}, \mathbf{q}\})$  and represent the state of the system as a point in a higher dimensional space called phase space.

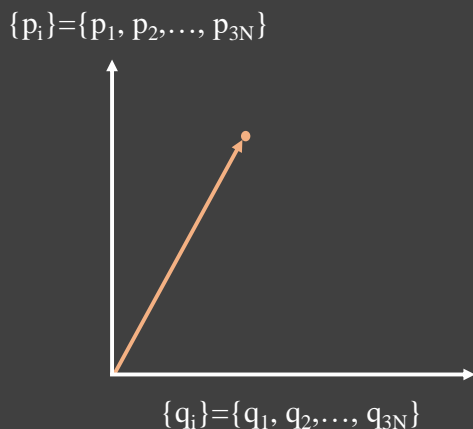


Figure 1: We can represent that state of the system as a point in phase space determined by  $\mathbf{p}$  and  $\mathbf{q}$ . This point moves in phase space according to Hamilton's equations.

- Hamilton's equations gives  $\dot{p}_i$  and  $\dot{q}_i$ , which in the phase space representation corresponds to a velocity vector  $\mathbf{v} = \{\dot{q}_i, \dot{p}_i\}$  that is  $6N$ -dimensional.
- Now consider a set of  $N_E \gg 1$  isolated systems with  $N$  particles that are identical, except for their initial conditions. Such a set is called an ensemble.
- In phase space this looks like a cloud of points, where each point is a different system in the ensemble.

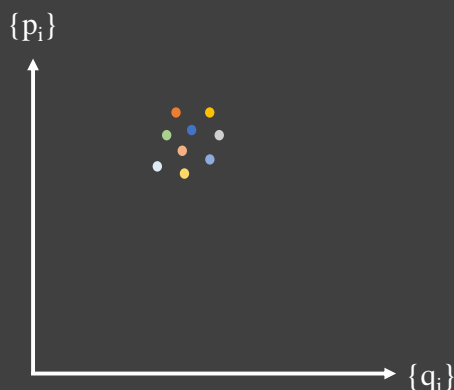


Figure 2: An ensemble of systems in phase space.

- Each system in the ensemble evolves according to Hamilton's equation.
- We are going to make the ergodic assumption. The ergodic assumption is that the average value of some quantity that characterizes the ensemble is approximately the experimental value that you would measure in any one system of the ensemble.

$$\langle f \rangle \approx f_{\text{exp}} \quad (2.1)$$

where  $\langle f \rangle$  is the average value of quantity  $f$  over all of the systems in the ensemble.

- We can take the ensemble to be so dense in phase space that a differential volume in phase space can be thought of as being a continuous density  $\rho(\{q_i, p_i\})$  multiplied by the volume of the differential box  $d^{3N}q d^{3N}p$ .
- If we want to compute the average value of some quantity  $f$  that characterizes the system we can use the standard definition of an average

$$\langle f(\{q_i, p_i\}) \rangle = \frac{\sum_i^{N_E} f_i}{N_E} \quad (2.2)$$

which can also be written in terms of integrals over a phase space density.

$$\langle f(\{q_i, p_i\}) \rangle = \frac{\int \rho(\{q_i, p_i\}) f(\{q_i, p_i\}) d^{3N}q d^{3N}p}{\int \rho(\{q_i, p_i\}) d^{3N}q d^{3N}p} \quad (2.3)$$

- Now let's consider a volume in phase space  $\Omega$ . The number of systems in the volume  $N_\Omega$  is

$$N_\Omega = \int_\Omega \rho dq dp \quad (2.4)$$

where I have dropped the notation that explicitly specifies the dimension of the differentials and the variables that  $\rho$  depends on.

- The only way the number of particles changes in  $\Omega$  is for particles to leave or enter the surface of  $\Omega$ , so we need to find the flux of particles leaving  $\Omega$ . The outgoing flux  $\Phi$  of the system is

$$\Phi = \oint_S \rho \mathbf{v} \cdot d\mathbf{S} \quad (2.5)$$

where  $S$  denotes the surface of  $\Omega$ .

- The rate of change of the particles in  $\Omega$ ,  $d/dt(N_\Omega)$  is equal to the negative of flux of particles leaving  $\Omega$ :

$$\frac{d}{dt}N_\Omega = \frac{d}{dt} \int_\Omega \rho \, dq dp = - \oint_S \rho \, \mathbf{v} \cdot d\mathbf{S} \quad (2.6)$$

The total time derivative can be pulled inside the integral and becomes a partial time derivative of only  $\rho$  because we are holding the coordinates fixed along with the differential box we are considering. We can also apply Divergence theorem to convert the surface integral into a volume integral. These two steps give us

$$\frac{d}{dt}N_\Omega = \int_\Omega \frac{\partial \rho}{\partial t} dq dp = - \int_\Omega \nabla \cdot (\rho \mathbf{v}) dq dp \quad (2.7)$$

- Since this equation holds for *any* volume  $\Omega$ , we can use the same argument in the derivation of the Euler-Lagrange equations to conclude that the two integrands are equal. This gives us the continuity equation

$$\boxed{\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0} \quad (2.8)$$

- To be clear, the divergence in the continuity equation is the  $6N$  dimensional divergence.
- Let's ask what density configurations are static (i.e. do not evolve in time). To answer this question let's write out the divergence term in the continuity equation.

$$\begin{aligned} \nabla \cdot (\rho \mathbf{v}) &= \frac{\partial}{\partial q_1}(\rho \dot{q}_1) + \frac{\partial}{\partial q_1}(\rho \dot{q}_1) + \dots + \frac{\partial}{\partial q_{3N}}(\rho \dot{q}_{3N}) \\ &\quad + \frac{\partial}{\partial p_1}(\rho \dot{p}_1) + \frac{\partial}{\partial p_1}(\rho \dot{p}_1) + \dots + \frac{\partial}{\partial p_{3N}}(\rho \dot{p}_{3N}) \end{aligned} \quad (2.9)$$

If we group the terms with the same index together we can write the continuity equation as

$$\partial_t \rho + \sum_{i=1}^{3N} \left[ \frac{\partial}{\partial q_i}(\rho \dot{q}_i) + \frac{\partial}{\partial p_i}(\rho \dot{p}_i) \right] = 0 \quad (2.10)$$

When we expand out the partial derivatives we obtain

$$\partial_t \rho + \sum_{i=1}^{3N} \left[ \left( \frac{\partial \rho}{\partial q_i} \right) \dot{q}_i + \rho \left( \frac{\partial \dot{q}}{\partial q_i} \right) + \left( \frac{\partial \rho}{\partial p_i} \right) \dot{p}_i + \rho \left( \frac{\partial \dot{p}}{\partial p_i} \right) \right] = 0 \quad (2.11)$$

or equivalently

$$\partial_t \rho + \sum_{i=1}^{3N} \left[ \rho \left( \frac{\partial \dot{q}}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right) + \left( \frac{\partial \rho}{\partial q_i} \right) \dot{q}_i + \left( \frac{\partial \rho}{\partial p_i} \right) \dot{p}_i \right] = 0 \quad (2.12)$$

- Recall Hamilton's equations (Eq. (1.9)). We can use these equations to rewrite  $\dot{q}_i$  and  $\dot{p}_i$ , so that

$$\frac{\partial \dot{q}}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} = \frac{\partial^2 \mathcal{H}}{\partial q_i \partial p_i} - \frac{\partial^2 \mathcal{H}}{\partial p_i \partial q_i} = 0. \quad (2.13)$$

- The continuity equation can now be simplified to

$$\boxed{\partial_t \rho + \sum_{i=1}^{3N} \left[ \left( \frac{\partial \rho}{\partial q_i} \right) \left( \frac{\partial \mathcal{H}}{\partial p_i} \right) - \left( \frac{\partial \rho}{\partial p_i} \right) \left( \frac{\partial \mathcal{H}}{\partial q_i} \right) \right] = 0} \quad (2.14)$$

- Let's assume the ensemble of systems reaches a state of thermal equilibrium, which means that  $\rho(\{q_i, p_i\}, t) = \rho(\{q_i, p_i\})$ , which is to say that  $\rho$  has no explicit time dependence. In this case we need to look for solutions to the partial differential equation

$$\sum_{i=1}^{3N} \left[ \left( \frac{\partial \rho}{\partial q_i} \right) \left( \frac{\partial \mathcal{H}}{\partial p_i} \right) - \left( \frac{\partial \rho}{\partial p_i} \right) \left( \frac{\partial \mathcal{H}}{\partial q_i} \right) \right] = 0 \quad (2.15)$$

- We can guess that the functional dependence of  $\rho$  on the coordinates is a function of the Hamiltonian:  $\rho(\{q_i, p_i\}) = f(\mathcal{H}(\{q_i, p_i\}))$ . We can check that this guess satisfies Eq. (2.15)

$$\sum_{i=1}^{3N} \left[ \left( \frac{df}{d\mathcal{H}} \right) \left( \frac{\partial \mathcal{H}}{\partial q_i} \right) \left( \frac{\partial \mathcal{H}}{\partial p_i} \right) - \left( \frac{df}{d\mathcal{H}} \right) \left( \frac{\partial \mathcal{H}}{\partial p_i} \right) \left( \frac{\partial \mathcal{H}}{\partial q_i} \right) \right] \stackrel{?}{=} 0 \quad (2.16)$$

- This result means that *any*  $\rho$  that is only a function of  $\mathcal{H}$  satisfies this equation for thermal equilibrium. This is Liouville's Theorem.
- Different ensembles in statistical mechanics correspond to different choices of  $f(\mathcal{H})$ .

### 3 The Micro-Canonical Ensemble

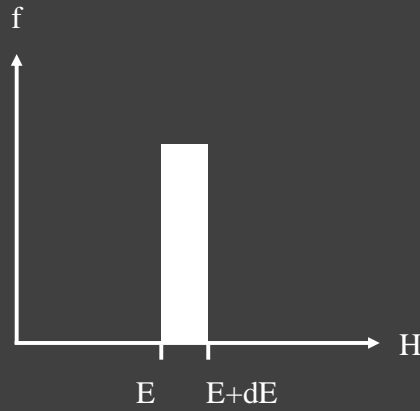


Figure 3: A graphical representation of the micro-canonical ensemble.

- The micro-canonical ensemble is the choice of  $f(\mathcal{H})$  such that  $f$  is a differential step function.
- In a phase space diagram the micro-canonical ensemble can be represented by two surfaces (one at  $E$  and one at  $E + dE$ ). Between the two surfaces the density  $\rho$  is a constant while outside of the two surfaces the density of systems is zero.
- Let  $d\Omega$  be the phase space volume between the two shells,  $\Omega_{<}(E)$  be the volume enclosed by the inner shell (the volume in phase space for which  $\mathcal{H} < E$ ), and  $\Omega_{<}(E + dE)$  be the volume enclosed by the outer shell ( $\mathcal{H} < E + dE$ ). With these definitions we can write

$$d\Omega = \Omega_{<}(E + dE) - \Omega_{<}(E) \quad (3.1)$$

or

$$\left( \frac{\partial \Omega_{<}}{\partial E} \right) dE = d\Omega \quad (3.2)$$

- We will define

$$\boxed{\Omega := \frac{\partial \Omega_{<}}{\partial E}} \quad (3.3)$$

so that

$$\boxed{d\Omega = \Omega(E)dE} \quad (3.4)$$

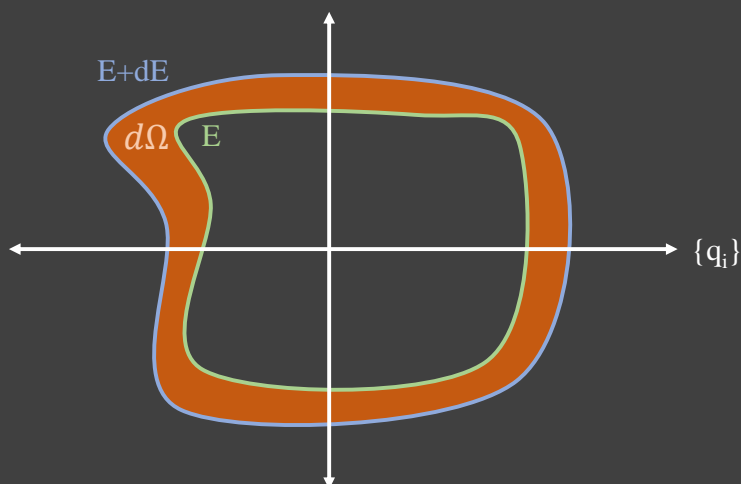


Figure 4: The micro-canonical ensemble can be represented in phase space by a region of constant density sandwiched between two shells.

### 3.1 Temperature

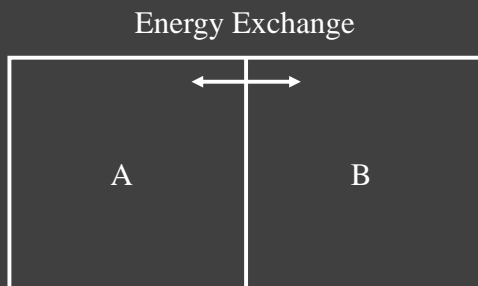


Figure 5: A closed box with a barrier that allows only energy exchange, no particle exchange between regions  $A$  and  $B$ .

- In defining temperature it will be helpful to consider a closed system with two regions  $A$  and  $B$  that are separated by a wall that only allows energy exchange. This means that  $E_A + E_B = E_T$ . Now consider a micro-canonical ensemble of such systems with  $E_T < \mathcal{H}_{A+B} < E_T + dE_T$
- Let's ask the following question: What is the probability  $P(E_A^0)dE$  that the energy of subsystem  $A$ ,  $\mathcal{H}_A$ , is between  $E_A^0$  and  $E_A^0 + dE_A$ ? Note that  $P(E_A^0)$  is the probability density whereas  $P(E_A^0)dE$  is the probability.
- Note that we are using  $E$  and  $\mathcal{H}$  interchangeably
- To find this probability it will be helpful to use the following diagram.

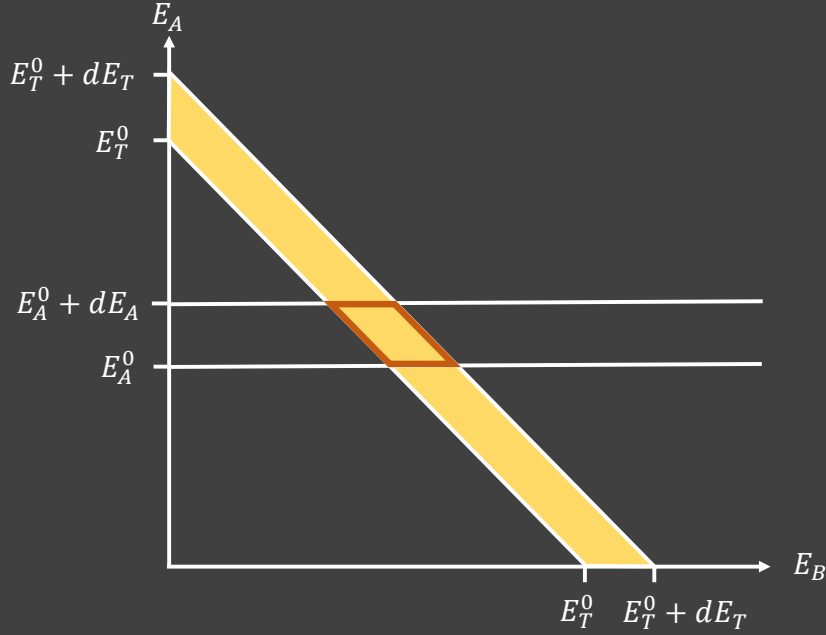


Figure 6: Since the total energy is fixed, we can plot  $E_A = -E_B + E_T$  and analyze the region shown in yellow. We are asking for the probability that the energy of system  $A$  is between  $E_A^0$  and  $E_A^0 + dE_A$ , and so we need to find the region outlined in orange on the graph.

- The probability that the energy of system  $A$  is between  $E_A^0$  and  $E_A^0 + dE_A$  is given by

$$P(E_A^0)dE_A = \frac{d\Omega_T}{d\Omega_T(E_T, dE_T)} \quad (3.5)$$

where  $d\Omega_T$  is the phase space volume of the parallelogram region outlined in orange in Fig. 6, while  $\Omega_T(E_T, dE_T)$  is the total volume of the phase space region that has nonzero density.

- Since we can divide the phase space system into particles associated with subsystem  $A$  only and subsystem  $B$  only, we can rewrite  $d\Omega_T$  as an integral over the parallelogram of the product of these two subsystems (as they are orthogonal spaces)

$$P(E_A^0)dE_A = \frac{\int^\diamond \Omega_A(E_A^0)dE_A \Omega_B(E_B^0)dE_B}{\Omega(E_T)dE_T} \quad (3.6)$$

- Since the parallelogram is small,  $\Omega_A$  and  $\Omega_B$  are relatively constant over the integration region so we can pull them outside of the integral, and so

$$P(E_A^0)dE_A = \frac{\Omega_A(E_A^0)\Omega_B(E_B^0) \int^\diamond dE_A dE_B}{\Omega(E_T)dE_T} \quad (3.7)$$

- To compute the integral we just need to find the area of the parallelogram in the  $E_A$  vs  $E_B$  space (not phase space). The area is  $dE_T dE_A$ . When we plug this into our previous expression (and cancel the  $dE_T$  in the numerator and denominator, and the  $dE_A$  terms) we obtain

$$\boxed{P(E_A^0) = \frac{\Omega_A(E_A^0)\Omega_B(E_B^0)}{\Omega_T}} \quad (3.8)$$

where again  $P(E_A^0)$  is the probability density (per energy).

- To find the most likely value of  $E_A$  we can take the partial derivative of  $P(E_A^0)$  and set that equal to zero.

$$\begin{aligned}
 \left( \frac{\partial P_A}{\partial E_A} \right)_{E_T} &= \frac{1}{\Omega_T} \left[ \left( \frac{\partial \Omega_A}{\partial E_A} \right) \Omega_B + \left( \frac{\partial \Omega_B}{\partial E_B} \right) \frac{\partial E_B}{\partial E_A} \Omega_A \right] \\
 &= \frac{1}{\Omega_T} \left[ \left( \frac{\partial \Omega_A}{\partial E_A} \right) \Omega_B - \left( \frac{\partial \Omega_B}{\partial E_B} \right) \Omega_A \right] \\
 &\stackrel{!}{=} 0 \\
 \implies \left( \frac{\partial \Omega_A}{\partial E_A} \right) \Omega_B - \left( \frac{\partial \Omega_B}{\partial E_B} \right) \Omega_A &= 0
 \end{aligned} \tag{3.9}$$

This condition (most likely value of  $E_A$ ) can be written as

$$\frac{1}{\Omega_A} \frac{\partial \Omega_A}{\partial E_A} = \frac{1}{\Omega_B} \frac{\partial \Omega_B}{\partial E_B} \tag{3.10}$$

- Let's consider the derivative again

$$\left( \frac{\partial_A(E_A)}{\partial E_A} \right)_{E_T} = \frac{\Omega_A \Omega_B}{\Omega_T} \left( \frac{1}{\Omega_A} \frac{\partial \Omega_A}{\partial E_A} - \frac{1}{\Omega_B} \frac{\partial \Omega_B}{\partial E_B} \right) \tag{3.11}$$

- Suppose that

$$\frac{1}{\Omega_A} \frac{\partial \Omega_A}{\partial E_A} > \frac{1}{\Omega_B} \frac{\partial \Omega_B}{\partial E_B} \tag{3.12}$$

then energy moves from  $B$  to  $A$ . **I do not understand this. The best explanation I could think of is that the most likely state is when the two quantities are equal so the left-hand-side will tend to decrease, which occurs when  $E_A$  increases (because it is in the denominator of the partial derivative). If the energy increases subsystem  $A$ , then since the system is closed, the only place for the energy to come from is subsystem  $B$ , and we therefore have energy transfer (heat transfer) from  $B$  to  $A$ .**

- The zeroth law of thermodynamics is that heat flows from hot cold. Thus,  $B$  is the hot system.
- One definition of temperature (that assigns a relative number to systems  $A$  and  $B$  to characterize the direction of heat flow) is

$$\frac{1}{T_B} := \frac{1}{\Omega_B} \frac{\partial \Omega_B}{\partial E_B} \tag{3.13}$$

$$\frac{1}{T_A} := \frac{1}{\Omega_A} \frac{\partial \Omega_A}{\partial E_A} \tag{3.14}$$

- Traditionally, we include a multiplicative factor (Boltzmann's constant) to make the previous definition consistent with the historical temperature scale

$$\boxed{
 \begin{aligned}
 \frac{1}{k_B T_B} &:= \frac{1}{\Omega_B} \frac{\partial \Omega_B}{\partial E_B} \\
 \frac{1}{k_B T_A} &:= \frac{1}{\Omega_A} \frac{\partial \Omega_A}{\partial E_A}
 \end{aligned}
 } \tag{3.15}$$

- The Boltzmann's factor is the conversion factor between joules and degrees.



### 3.2 Other Thermodynamic Quantities

- We can write the definition of the temperature as

$$\frac{1}{T} = \frac{\partial}{\partial E}(k_B \ln \Omega) \quad (3.16)$$

and then define the entropy as

$$\boxed{S := k_B \ln \Omega} \quad (3.17)$$

- We can now write

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{N,V} \quad (3.18)$$

or

$$dE = TdS \quad (3.19)$$

with constant particle number and constant volume.

- Let's ask what else  $\Omega$  is a function of.  $\Omega$  depends on the Hamiltonian and so it also depends on the number of particles and the volume. It depends on the volume because there must be a potential to keep the particles in the box (potential energy is a part of the energy). Thus,  $\Omega$ , depends on the energy, number of particles, and volume.
- What happens to the entropy when we make a differential change in  $E$ ,  $V$ , and  $N$ ?

$$\begin{aligned} d(\ln(\Omega)) &= \left( \frac{\partial \ln \Omega}{\partial E} \right)_{N,V} dE + \left( \frac{\partial \ln \Omega}{\partial V} \right)_{E,N} dV + \left( \frac{\partial \ln \Omega}{\partial N} \right)_{E,V} dN \\ &= \frac{1}{k_B T} dE + \left( \frac{\partial \ln \Omega}{\partial V} \right)_{E,N} dV + \left( \frac{\partial \ln \Omega}{\partial N} \right)_{E,V} dN \end{aligned} \quad (3.20)$$

- If we solve this for

$$dE = TdS - k_B T \left[ \left( \frac{\partial \ln \Omega}{\partial V} \right)_{E,N} dV + \left( \frac{\partial \ln \Omega}{\partial N} \right)_{E,V} dN \right] \quad (3.21)$$

We can identify the prefactor in front of  $dV$  as the pressure  $P$  and the prefactor in front of  $dN$  as the chemical potential  $\mu$ .

- Let's find out why it is reasonable to use the term pressure to describe  $P$ . Consider a box with a single wall that can slide. Then  $dV = A dx$  where  $V$  is the volume,  $A$  is the area, and  $x$  is the distance the wall moved.
- We can then consider the differential energy, which is equal to the negative of the differential work

$$dE = -dW = -F dx = -\frac{F dV}{A} = -P dV \quad (3.22)$$

### 3.3 Ideal Gas

- An ideal gas is a system of  $N$  identical particles, of mass  $m$ , confined to a volume  $V$ , and there are no interactions.
- For each particle there is a position vector and so a set of coordinates  $\{q_i\}$  and momenta  $\{p_i\}$  (which is just the linear momenta). The Hamiltonian is the total kinetic energy

$$\mathcal{H} = \sum_{\alpha=1}^N \frac{|\mathbf{p}_{\alpha}|^2}{2m} \quad (3.23)$$

- To calculate  $\Omega_{<}$  we need to find the Hamiltonian less than some energy surface  $E$ . To find the volume  $\Omega_{<}$  we just integrate over all the coordinates

$$\Omega_{<}(E) = \int dx^{3N} dp^{3N} \quad (3.24)$$

- We also need to consider the physical box that the particles are confined to. Thus

$$\int dx_1 dy_1 dz_1 = V \quad (3.25)$$

and over the hypervolume we will get a factor of  $V^N$  once we take the integral over all of the position coordinates.

- We can write

$$\Omega_{<}(E) = V^N f(E, N) \quad (3.26)$$

because we know that the integral over the momenta coordinates only depends on the energy and particle number.

- We can write  $\Omega$  as

$$\Omega(E, V, N) = V^N \left( \frac{\partial f}{\partial E} \right)_N \quad (3.27)$$

and then take the logarithm of both sides

$$\ln \Omega = N \ln V + \ln \left( \frac{\partial f}{\partial E} \right)_N \quad (3.28)$$

- If we take the partial with respect to  $V$  with fixed  $N$  and  $E$ , then we obtain

$$\left( \frac{\partial}{\partial V} \ln \Omega \right)_{N,E} = \frac{\partial}{\partial V} (N \ln V)_{N,E} + 0 = \frac{N}{V} \quad (3.29)$$

- Now we can derive the ideal gas law

$$P = k_B T \left( \frac{\partial}{\partial V} \ln \Omega \right)_{N,E} = \frac{k_B N T}{V} \quad (3.30)$$

- Now let's go back and calculate  $f$  for a monatomic ideal gas (point particle). The constraint on the momenta are that

$$E > \frac{1}{2M} \sum_{\alpha}^N \mathbf{p}_{\alpha}^2 \quad (3.31)$$

- This shape in phase space is a  $3N$  dimensional hypersphere with radius  $\sqrt{2mE}$ . We then need to find the volume of this sphere to find  $f$

$$f(N, E) = g(N) (2mE)^{3N/2} V^N \quad (3.32)$$

where  $g(N)$  encompasses the constant prefactor in front of the sphere's volume that in principle can be calculated.

- We can then write

$$\Omega_{<} = g(N) (2mE)^{3N/2} V^N \quad (3.33)$$

and

$$\Omega = \left( \frac{\Omega_{<}}{\partial E} \right)_{N,V} = (2mE)^{3N/2-1} 2m \frac{3N}{2} V^N g(N) \quad (3.34)$$

- Now lets calculate

$$\ln \Omega = \left( \frac{3N}{2} - 1 \right) \ln(E) + h(N, V) \quad (3.35)$$

If  $N \gg 1$  then we can discard the minus one. We can use this result to find

$$\frac{1}{k_B T} = \left( \frac{\partial \ln \Omega}{\partial E} \right)_{N, V} = \frac{3N}{2E} \quad (3.36)$$

or

$$E = \frac{3}{2} k_B N T \quad (3.37)$$

- adiabatic cooling is when there is constant entropy (no heat exchange)
- We can write  $\Omega$  as

$$\Omega = \left[ (k_B T)^{3/2} V \right]^N g(N) = \text{const} \quad (3.38)$$

using the equation we just derived in the last section and the fact that for an adiabatic process  $\ln \Omega = \text{const}$ . If we fix  $N$ , then we can say that

$$T^{3/2} V = \text{const} \quad (3.39)$$

### 3.4 Thermodynamics

- Let's summarize the thermodynamic quantities

$$\begin{aligned} S &= k_B \ln \Omega \\ P &= k_B T \left( \frac{\partial \ln \Omega}{\partial V} \right)_{N, E} \\ \mu &= k_B T \left( \frac{\partial \ln \Omega}{\partial N} \right)_{E, V} \\ T &= \frac{1}{k_B} \left( \frac{\partial \ln \Omega}{\partial E} \right)_{N, V} \end{aligned} \quad (3.40)$$

where again

$$\Omega = \left( \frac{\partial \Omega}{\partial E} \right)_{N, V} \quad (3.41)$$

- The three ways to change the energy are encompassed in

$$dE = TdS - PdV + \mu dN \quad (3.42)$$

- Specific heat is defined as

$$C_V := T \left( \frac{\partial S}{\partial T} \right)_{V, N} \quad C_P := T \left( \frac{\partial S}{\partial T} \right)_{P, N} \quad (3.43)$$

- We can use Legendre transformations in thermodynamics. One is the enthalpy

$$H = E + PV \quad (3.44)$$

or

$$dH = dE + PdV + VdP = TdS + VdP + \mu dN \quad (3.45)$$

- We can then write

$$C_P = \left( \frac{\partial H}{\partial T} \right)_{P,N} \quad (3.46)$$

- Another useful quantity is the Helmholtz free energy

$$F = E - TS \quad (3.47)$$

or in differential form

$$dF = E - TdS - SdT = -SdT - PdV + \mu dN \quad (3.48)$$

and so

$$-S = \left( \frac{\partial F}{\partial T} \right)_{N,V} \quad (3.49)$$

and

$$C_V = -T \left( \frac{\partial^2 F}{\partial T^2} \right)_{N,V} \quad (3.50)$$

- If we know the Helmholtz free energy we can also see that

$$-P = \left( \frac{\partial F}{\partial V} \right)_{T,N} \quad (3.51)$$

and

$$\mu = \left( \frac{\partial F}{\partial N} \right)_{T,V} \quad (3.52)$$

- If we know  $P(N, V, T)$ , which is the equation of state, then we can find the entropy via

$$\left( \frac{\partial^2 F}{\partial T \partial V} \right) = \left( \frac{\partial^2 F}{\partial V \partial T} \right) \implies \left( \frac{\partial S}{\partial V} \right)_{T,N} = \left( \frac{\partial P}{\partial T} \right)_{V,N} \quad (3.53)$$

- We can relate  $C_P$  and  $C_V$  if we know the equation of state, using

$$(\bar{d}Q)_P = (\bar{d}Q_1)_V + (\bar{d}Q_2)_T \quad (3.54)$$

Here the  $\bar{d}$  just denotes a small change and we can see that this equation holds by considering a constant pressure curve on a volume vs. temperature graph. The the two terms on the right reach the same point along the constant pressure curve but via a two step process (one at constant volume and one at constant temperature).

- We can rewrite the previous relationship as

$$C_P dT = D_V dT + (\bar{d}Q_2)_T \quad (3.55)$$

or

$$C_P = C_V + \left( \frac{\bar{d}Q_2}{dT} \right)_T \quad (3.56)$$

where the temperature is only fixed for the second step. We can make a few more simplifications

$$C_P = C_V + T \frac{(dS)_T}{dT} \quad (3.57)$$

and since

$$(dS)_T = \left( \frac{\partial S}{\partial V} \right)_{T,N} dV \quad (3.58)$$

we can write

$$C_P = C_V + T \left( \frac{\partial S}{\partial V} \right)_{T,N} \left( \frac{dV}{dT} \right) \quad (3.59)$$

- The slope

$$\frac{dV}{dT} = \left( \frac{\partial V}{\partial T} \right)_{P,N} \quad (3.60)$$

and so

$$C_P = C_V + T \left( \frac{\partial S}{\partial V} \right)_{T,N} \left( \frac{\partial V}{\partial T} \right)_{P,N} \quad (3.61)$$

To put this in terms of the quantities we can obtain directly from the equation of state we can make one last substitution

$$C_P = C_V + \left( \frac{\partial P}{\partial T} \right)_{N,V} T \left( \frac{\partial V}{\partial T} \right)_{P,N} \quad (3.62)$$

- Example: Ideal gas (not necessarily monoatomic)
- We have the equation of state

$$P = \frac{Nk_B T}{V} \implies \left( \frac{\partial P}{\partial T} \right)_{N,V} = \frac{Nk_B}{V} \quad (3.63)$$

and if we rearrange the equation of state

$$V = \frac{Nk_B T}{P} \implies \left( \frac{\partial V}{\partial T} \right)_{P,N} = \frac{Nk_B}{P} \quad (3.64)$$

- When we plug these two partial derivatives into our equation for  $C_P$  or  $C_V$  we obtain

$$C_V + Nk_B = C_P \quad (3.65)$$

- Maxwell's Relations

$$\left( \frac{\partial x}{\partial y} \right)_z \left( \frac{\partial y}{\partial z} \right)_x \left( \frac{\partial z}{\partial x} \right)_y = -1 \quad (3.66)$$

- To show this we can consider the differentials

$$dx = \left( \frac{\partial f}{\partial y} \right)_z dy + \left( \frac{\partial f}{\partial z} \right)_y dz \quad (3.67)$$

At constant  $z$  we obtain

$$\left( \frac{\partial x}{\partial y} \right)_z = \left( \frac{\partial f}{\partial y} \right)_z \quad (3.68)$$

and similarly when we hold  $y$  and  $x$  constant

$$\left( \frac{\partial z}{\partial x} \right)_y = \frac{1}{(\partial f / \partial z)_y} \quad (3.69)$$

and

$$\left( \frac{\partial y}{\partial z} \right)_x = - \frac{(\partial f / \partial y)_x}{(\partial f / \partial z)_y} \quad (3.70)$$

When we plug in all of these partials we see that Maxwell's Relations hold.

- Adiabatic Law
- Consider a sealed container (entropy and particle number constant), and let's move one of the sides of the container.

- The speed of sound is given by

$$c_s \propto \sqrt{\left(\frac{\partial P}{\partial V}\right)_S} \quad (3.71)$$

so we need the quantity inside of the square root.

- Use Maxwell's relation to write

$$\left(\frac{\partial T}{\partial P}\right)_S \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_P = -1 \quad (3.72)$$

and

$$\left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial V}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_V = -1 \quad (3.73)$$

If we divide these two equations

$$\frac{(\partial T/\partial P)_S (\partial P/\partial S)_T (\partial S/\partial T)_P}{(\partial T/\partial V)_S (\partial V/\partial S)_T (\partial S/\partial T)_V} = 1 \quad (3.74)$$

we can take the ratio of differentials for ratios with the same variable held fixed

$$\frac{1}{(\partial P/\partial V)_S} \left(\frac{\partial P}{\partial V}\right)_T \frac{C_P}{C_V} = 1 \quad (3.75)$$

Rearranging gives

$$\left(\frac{\partial P}{\partial V}\right)_S = \left(\frac{\partial P}{\partial V}\right)_T \frac{C_P}{C_V} \quad (3.76)$$

- It turns out that  $C_P > C_V$
- We can consider a monotonic ideal gas so that  $C_P = C_V + Nk_B$  and  $C_V = (3/2)Nk_B$ . Thus,  $C_P = (5/2)Nk_B$  and

$$\frac{C_P}{C_V} = \frac{5}{3} \quad (3.77)$$

- Toner made a few more points about how you could determine that air was not a monoatomic gas using methods like these

## 4 The Canonical Ensemble

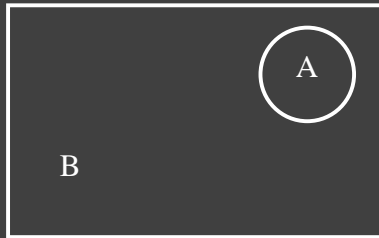


Figure 7: The canonical ensemble involves a system of interest  $A$ , and a “bath”  $B$  that is much larger than the system of interest ( $V_B \gg V_A$ ,  $E_B \gg E_A$ ,  $N_B \gg N_A$ ). The bath and system  $A$  are in the micro-canonical ensemble (i.e. the combined system is isolated.) In the canonical ensemble there is heat exchange between  $A$  and  $B$  and the temperature is fixed.

- Question: What is the probability that system  $A$  is in quantum state  $i$  (not energy  $i$ )? That is what is  $P_i(E_i)$ .
- In the micro-canonical ensemble the probability is given by

$$P_i(E_i) = \frac{\Omega_B(E_B)\Omega_A(\text{"conditions"})}{\Omega_T} \quad (4.1)$$

where  $E_T = E_A + E_B$ . The "conditions" are that subsystem  $A$  is in quantum state  $i$ . If we know what  $E_i$  is and  $E_T$ , then we know  $E_B$ .

- $\Omega_B$  is the number of states in subsystem  $B$  with  $E_B$  obeying  $E_T = E_i + E_B$ .  $\Omega_A$  is the number of states in subsystem  $A$  allowed by the condition. The condition is that  $\Omega_A$  is only in one state so  $\Omega_A(\text{"conditions"})$  is just one.
- This means the that the probability that subsystem  $A$  is in state  $E_i$  is

$$P_i(E_i) = \frac{\Omega(E_B)}{\Omega_T(E_T)} = \frac{\Omega_B(E_T - E_i)}{\Omega_T} \quad (4.2)$$

- Let compute

$$\begin{aligned} \left( \frac{\partial P_i}{\partial E_i} \right)_{N_A, N_B, V_A, V_B} &= \frac{1}{\Omega_T} \left( \frac{\partial \Omega_B(E_T - E_i)}{\partial E_B} \right)_{N_A, N_B, V_A, V_B} \\ &= \frac{\Omega_B(E_T - E_i)}{\Omega_T} \left[ \frac{1}{\Omega_B} \left( \frac{\partial \Omega_B(E_T - E_i)}{\partial E_B} \right)_{N_A, N_B, V_A, V_B} \right] \\ &= -P_i(E_i) \left( \frac{\partial \ln \Omega_B(E_T - E_i)}{\partial E_B} \right)_{N_A, N_B, V_A, V_B} \\ &= -\frac{P_i(E_i)}{k_B T_B(E_T - E_i)} \end{aligned} \quad (4.3)$$

- This is a differential equation for  $P_i(E_i)$ . To solve this equation we use the fact that  $B \gg A$ , so that  $E_i \ll E_T$ . This means  $T_B(E_T - E_i) \approx T_B(E_T) = \text{const}$ . We will just call  $E_B = T$  and it will be the temperature of of  $A$  and  $B$ .
- The solution to this equation is

$$P_i(E_i) = e^{-E_i/k_B T} \times \text{const}(N_A, V_A, T) \quad (4.4)$$

- We will stop using the subscript  $A$ , and because we will only work with the system of interest  $A$ . This distribution is called the Boltzmann distribution and the constant that is a function of  $N$ ,  $V$ , and  $T$  is called the partition function.

$$\text{const} = \frac{1}{Z(N, V, T)} \quad (4.5)$$

- The system must be in some state must be one so

$$\frac{\sum_i^{\text{all states}} e^{-E_i/k_B T}}{Z} = 1 \quad (4.6)$$

thus

$$Z = \sum_i^{\text{all states}} e^{-E_i/k_B T} \quad (4.7)$$

- For a system in a box the energy depends on the number of particles and the volume of the box, so the partition is a function of the number of particles, the volume, and the temperature.

- To go from quantum mechanics to classical mechanics we convert a sum over states to an integral over phase space. The classical probability density is

$$P(\{r_i, p_i\}) = \frac{e^{-\beta\mathcal{H}}}{Z} \quad (4.8)$$

where  $\beta := 1/k_B T$  and

$$Z_{\text{classical}} = \int d^{3N} q d^{3N} p e^{-\beta\mathcal{H}} \quad (4.9)$$

- Now suppose we have  $N$  particles that are classical and non-ideal (so they can interact). Let the potential depend only on the coordinates. The Hamiltonian is

$$\mathcal{H} = \sum_i^N \frac{p_i^2}{m_i} + U(\{r_i\}) \quad (4.10)$$

- How do we figure out the probability density of the velocity for a single particle  $j$ ;  $P(v_j)$ ?
- To approach this question let's consider a simpler case in which we have the probability density for a two coordinate system  $P(x, y)$ . To find the probability that some particle lies between  $x$  and  $x + dx$  we can integrate  $P(x, y)dx$  over  $dy$

$$\int_{-\infty}^{\infty} dy P(x, y) dx = P_x(x) dx \quad (4.11)$$

- If we cancel off the  $dx$  term we obtain

$$P_x(x) = \int_{-\infty}^{\infty} dy P(x, y) \quad (4.12)$$

- We can generalize this idea to higher dimensional spaces. In the case of the Boltzmann distribution we have

$$\begin{aligned} P(p_j) &= \frac{\int (\prod_i d^3 r_i) \left( \prod_{i \neq j} d^3 p_i \right) e^{i\beta\mathcal{H}}}{Z} \\ &= \frac{\int (\prod_i d^3 r_i) \left( \prod_{i \neq j} d^3 p_i \right) \exp[-\beta \sum_i p_i^2 / 2m_i] \exp[-\beta U(\{r_i\})]}{\int (\prod_i d^3 r_i) (\prod_i d^3 p_i) \exp[-\beta \sum_i p_i^2 / 2m_i] \exp[-\beta U(\{r_i\})]} \end{aligned} \quad (4.13)$$

This fraction can be simplified greatly by making the following observations. We are integrating in both the numerator and denominator over all of the spatial coordinates, with the same bounds (all space), the same function of the spatial coordinates  $U(\{r_i\})$ . This allows us to cancel off spatial integrals. Similarly we can cancel off all but the  $j^{\text{th}}$  component of the momenta coordinates leaving us with our probability density

$$P(p_j) = \frac{\exp[-\beta p_j^2 / 2m_j]}{\int (d^3 p_j) \exp[-\beta p_j^2 / 2m_j]} \quad (4.14)$$

We have a Gaussian distribution in the numerator along with a normalization factor in the denominator.

## 4.1 Thermodynamics and the Partition Function

- We can obtain all of the thermodynamic quantities from the partition function  $Z(N, V, T)$ .
- Let's consider the average energy

$$\langle E \rangle = \sum_i P_i E_i \quad (4.15)$$



- If we plug in the probability  $P_i$  in the canonical ensemble we obtain

$$\langle E \rangle = \frac{\sum_i \exp[-\beta E_i] E_i}{\sum_i \exp[-\beta E_i]} \quad (4.16)$$

- If we notice that

$$\left( \partial_\beta \sum_i e^{-\beta E_i} \right)_{N,V} = - \sum_i E_i e^{-\beta E_i} \quad (4.17)$$

we can rewrite the average energy as

$$\langle E \rangle = - (\partial_\beta \ln Z)_{N,V} \quad (4.18)$$

- Recall the Helmholtz free energy

$$F = \langle E \rangle - TS \quad (4.19)$$

- Let's compute

$$\begin{aligned} \left( \frac{\partial \ln Z}{\partial \beta} \right)_{N,V} &= \left( \frac{\partial \ln Z}{\partial T} \right)_{N,V} \frac{dT}{d\beta} \\ &= \left( \frac{\partial \ln Z}{\partial T} \right)_{N,V} (-k_B T^2) \end{aligned} \quad (4.20)$$

to can now find the average energy

$$\langle E \rangle = k_B T^2 \left( \frac{\partial \ln Z}{\partial T} \right)_{N,V} \quad (4.21)$$

- Now let's find  $C_V$ . Recall that the heat capacity at constant volume is defined as

$$C_V = \left( \frac{\partial \langle E \rangle}{\partial T} \right)_{N,V} \quad (4.22)$$

When we take this partial derivative we find that

$$C_V = 2k_B T \left( \frac{\ln Z}{\partial T} \right)_{N,V} + k_B T^2 \left( \frac{\partial^2 \ln Z}{\partial T^2} \right)_{N,V} \quad (4.23)$$

- The heat capacity can also be written as

$$C_V = T \left( \frac{\partial S}{\partial T} \right)_{N,V} \quad (4.24)$$

This comes from the first law of thermodynamics

$$dE = TdS - PdV + \mu dN \quad (4.25)$$

when  $V$  and  $N$  are held fixed and we have divided through by  $dT$

- If we equate these two expressions for  $C_V$  we obtain

$$\begin{aligned} 2k_B T \left( \frac{\ln Z}{\partial T} \right)_{N,V} + k_B T^2 \left( \frac{\partial^2 \ln Z}{\partial T^2} \right)_{N,V} &= C_V = T \left( \frac{\partial S}{\partial T} \right)_{N,V} \\ \implies 2k_B \left( \frac{\ln Z}{\partial T} \right)_{N,V} + k_B T \left( \frac{\partial^2 \ln Z}{\partial T^2} \right)_{N,V} &= \left( \frac{\partial S}{\partial T} \right)_{N,V} \end{aligned} \quad (4.26)$$

- This expression can be manipulated further to yield

$$\begin{aligned}
 \left(\frac{\partial S}{\partial T}\right)_{N,V} &= k_B \left(\frac{\ln Z}{\partial T}\right)_{N,V} + k_B \left[ \left(\frac{\partial \ln Z}{\partial T}\right)_{N,V} + T \left(\frac{\partial^2 \ln Z}{\partial T^2}\right)_{N,V} \right] \\
 &= k_B \left(\frac{\ln Z}{\partial T}\right)_{N,V} + k_B \left[ \frac{\partial}{\partial T} \left( T \left(\frac{\partial \ln Z}{\partial T}\right)_{N,V} \right) \right]_{N,V} \\
 &= k_B \left[ \frac{\partial}{\partial T} \left( \ln Z + T \left(\frac{\partial \ln Z}{\partial T}\right)_{N,V} \right) \right]_{N,V}
 \end{aligned} \tag{4.27}$$

- We can integrate this last expression to find the entropy

$$S = k_B \left[ \ln Z + T \left(\frac{\partial \ln Z}{\partial T}\right)_{N,V} \right] + f(N, V) \tag{4.28}$$

We will show late in this section that  $f(N, V) = 0$  and so the entropy is

$$S = k_B \frac{\partial}{\partial T} (T \ln Z)_{N,V} \tag{4.29}$$

- Going back to Helmholtz free energy

$$dF = -SdT - PdV + \mu dN \tag{4.30}$$

we can see that

$$\left(\frac{\partial F}{\partial T}\right)_{N,V} = -S = -k_B \frac{\partial}{\partial T} (T \ln Z)_{N,V} \tag{4.31}$$

- If we integrate this last expression we can find the Helmholtz free energy

$$F = -k_B T \ln Z + g(N, V) \tag{4.32}$$

- Again, we will show later that  $g(N, V) = 0$  and so we are just left with

$$F = -k_B T \ln Z \tag{4.33}$$

- Now to show that  $f(N, V)$  and  $g(N, V)$  are zero let's consider the low temperature limit  $T \rightarrow 0$  or  $k_B T \ll E_1 - E_0$ . The ground state dominates the partition function so

$$\begin{aligned}
 Z &\approx e^{-E_0/k_B T} + e^{-E_1/k_B T} \\
 &= e^{-E_0/k_B T} \left( 1 + e^{(E_1 - E_0)/k_B T} \right) \\
 &\approx e^{-E_0/k_B T}
 \end{aligned} \tag{4.34}$$

- In the micro-canonical ensemble the entropy is

$$S = k_B \ln \Omega = 0 \quad \text{for } T \rightarrow 0 \tag{4.35}$$

because  $\Omega$  is the number of states and at low temperatures there is only the ground state so we have  $\ln(1) = 0$ .

- Now recall our expression for the entropy

$$S = k_B \left[ \ln Z + T \left(\frac{\partial \ln Z}{\partial T}\right)_{N,V} \right] + f(N, V) \tag{4.36}$$

- If we set the entropy to zero and plug in  $Z$  for low temperatures we find that

$$\begin{aligned} 0 &= -k_B \left( \partial_T \left( T \frac{-E_0}{k_B T} \right) \right) + f(N, V) \\ \implies 0 &= f(N, V) \end{aligned} \quad (4.37)$$

- Now to show that  $g(N, V) = 0$ , we can note that  $F \rightarrow E_0$  as  $T \rightarrow 0$  and  $S \rightarrow 0$ .
- We then have

$$F = E_0 = -k_B T \left( -\frac{E_0}{k_B T} \right) + g(N, V) \quad (4.38)$$

which implies that  $g(N, V) = 0$ .

## 4.2 Energy Fluctuations

- We would like to show that the fluctuations in the energy are much less than the average energy if the number of particles is large.
- To do this we can consider the standard deviation

$$\sqrt{\langle (E - \langle E \rangle)^2 \rangle} = \sqrt{\langle E^2 \rangle - \langle E \rangle^2} = \delta E \quad (4.39)$$

- The average of the energy and the average of the square are given by

$$\langle E \rangle = \frac{\sum_i e^{-\beta E_i} E_i}{\sum_i e^{-\beta E_i}} \quad (4.40)$$

$$\langle E^2 \rangle = \frac{\sum_i e^{-\beta E_i} E_i^2}{\sum_i e^{-\beta E_i}} \quad (4.41)$$

- Let's compute

$$\frac{\partial \langle E \rangle}{\partial \beta} = -\langle E^2 \rangle + \langle E \rangle^2 \quad (4.42)$$

- For a system with many particles we expect  $\langle E \rangle \propto N$  (i.e.  $E$  is extensive). Temperature on the other hand is intensive. The derivative  $\partial \langle E \rangle / \partial \beta$  is then proportional to  $N$ .
- The standard deviation of the energy,  $\sqrt{-\partial \langle E \rangle / \partial \beta}$ , which characterizes the energy fluctuations, goes like the square root of  $N$ .
- The ratio

$$\frac{\delta E}{\langle E \rangle} \propto \frac{1}{\sqrt{N}} \quad (4.43)$$

shows that in the thermodynamics limit  $N \rightarrow \infty$  that the energy is constant. This allows us to perform calculations in the micro-canonical ensemble in the canonical ensemble.

- We can also write

$$\left( \frac{\partial \langle E \rangle}{\partial \beta} \right)_{N, V} = - \left( \frac{\partial \langle E \rangle}{\partial T} \right)_{N, V} k_B T^2 \quad (4.44)$$

so that

$$\delta T = k_B T^2 \left( \frac{\partial \langle E \rangle}{\partial T} \right)_{N, V} = k_B T^2 C_V \quad (4.45)$$

## Probabilities

- Q: What is the probability of measuring a certain energy?
- This probability is given by

$$P(E)dE = e^{-\beta E}g(E)dE \quad (4.46)$$

where

$$g(E) := \frac{(\text{number of states with } E < E_0 < E + dE)}{Z} \quad (4.47)$$

- The probability density is

$$\boxed{P(E) = e^{-\beta E}g(E)} \quad (4.48)$$

- If we take the logarithm of both sides we obtain

$$\ln P(E) = \ln g(E) - \beta E \quad (4.49)$$

- To find the most likely energy we can take a derivative of the previous expression and set that derivative equal to zero. This gives us

$$\frac{\partial}{\partial E} \ln g(E_m) = \beta \quad (4.50)$$

where  $E_m$  is the most likely energy. From this we can see that  $\ln(g(E)) \propto N$ .

- If we expand  $\ln P(E)$  about  $E_M$  and neglect terms above second order we get

$$\ln P(E) = \text{const} + \frac{1}{2} \left( \frac{\partial^2 \ln P}{\partial E^2} \right)_{E=E_m} (E - E_M)^2 \quad (4.51)$$

If we exponentiate both sides we obtain

$$P(E) = \text{const} \times \exp \left[ -\frac{a}{2} (E - E_m)^2 \right] \quad (4.52)$$

where  $a$  is the the constant that comes from the second derivative evaluated at  $E = E_m$ .

- We know the standard deviation already so  $1/a = (\delta E)^2$ , which gives

$$P(E) = \text{const} \times \exp \left[ -\frac{(E - \langle E \rangle)^2}{2\langle (E - \langle E \rangle)^2} \right] \quad (4.53)$$

- All higher order terms are negligible in the thermodynamic limit.
- We can write the final result as

$$\boxed{P(E) = \text{const} \times \exp \left[ e^{-\frac{(E - \langle E \rangle)^2}{2k_B T^2 C_V}} \right]} \quad (4.54)$$

- Let's find the most likely energy for an ideal gas
- For an ideal gas in a box the Hamiltonian is

$$\mathcal{H} = \sum_i \frac{|\mathbf{p}_i|^2}{2m} \quad (4.55)$$

and so the partition function is

$$Z = \int \prod_{i=1}^N d^3 p_i \exp \left[ -\beta \sum_i \frac{|\mathbf{p}_i|^2}{2m} \right] \int \prod_{\mathbf{r}_i \in V} d^3 r_i \quad (4.56)$$

where  $V$  is the volume of the box. This integral simplifies to

$$Z = V^N (2\pi m k_B T)^{3N/2} \quad (4.57)$$

- Due to indistinguishability in quantum mechanics we need to alter this last equation to

$$Z = \frac{1}{N!} V^N (2\pi m k_B T)^{3N/2} \quad (4.58)$$

- Now let's find thermodynamic quantities. To do this we can start by finding the Helmholtz's free energy

$$F = -k_B T \ln Z = -k_B T \left[ \frac{3N}{2} \ln(m k_B T) + \frac{3N}{2} \ln(2\pi) - \ln N! \right] \quad (4.59)$$

- If we use Stirling's approximation

$$\ln(N!) = N \ln N - N \quad (4.60)$$

we obtain

$$F = N k_B \ln \left( \frac{N}{V (m k_B T)^{3/2}} \right) + \text{const} \quad (4.61)$$

- To make the dimensions work out we need a fudge constant  $h$  (which turns out to be Planck's constant)

$$F = N k_B \ln \left( \frac{N h^3}{V (m k_B T)^{3/2}} \right) + \text{const} \quad (4.62)$$

- Note that

$$\frac{N}{V} \left( \frac{h}{\sqrt{m k_B T}} \right)^3 \sim \frac{N}{V} \left( \frac{h}{p_{\text{typ}}} \right)^3 = \frac{N}{V} \lambda_{\text{TdB}}^3 \quad (4.63)$$

where  $p_{\text{typ}}$  is the typical momentum which is proportional to  $\sqrt{k_B T/2}$ , and

$$\lambda_{\text{TdB}} = \frac{h}{\sqrt{m k_B T}} \quad (4.64)$$

is the thermal deBroglie wavelength.

- To find the other thermodynamic quantities we can use

$$dF = -S dT - P dV + \mu dN \quad (4.65)$$

- The pressure is

$$P = - \left( \frac{\partial F}{\partial V} \right)_{T,N} = \frac{N k_B T}{V} \quad (4.66)$$

- The entropy is

$$S = - \left( \frac{\partial F}{\partial T} \right)_{V,N} = -N k_B \left( -\frac{3}{2} \ln T + \ln \left( \frac{N h^3}{V (m k_B)^{3/2}} \right) \right) + \frac{3}{2} N k_B \quad (4.67)$$

- The heat capacity at constant volume is

$$C_V = T \left( \frac{\partial S}{\partial T} \right)_{N,V} = \frac{3}{2} N k_B \quad (4.68)$$

### 4.3 Diatomic Gas

- The energy levels of a rotating dumbbell (which is a model for a diatomic gas) is given classically by

$$E = \frac{L^2}{2I} \quad (4.69)$$

where  $I$  is the moment of inertia  $I = mR^2/2$  (where  $R$  is the separation between the masses  $m$ ).

- The quantum mechanic expression for the energy is

$$E = \frac{l(l+1)\hbar^2}{2I} \quad (4.70)$$

- The partition function is

$$Z_{\text{rot}} = \sum_{l=0}^{\infty} (2l+1) e^{-\beta l(l+1)\hbar^2/2I} \quad (4.71)$$

because there are  $(2l+1)$  states with the same energy.

- Treat the position and momentum degrees of freedom classically for the center of mass. This gives the following expression for  $N$  diatomic molecules

$$Z = Z_{\text{mono}} Z_{\text{rot}}^N = \left( \int d^3N d^3p e^{-\beta \mathcal{H}(\mathbf{r}, \mathbf{p})} \right) \left( \prod_{\alpha=1}^N Z_{\text{rot}} \right) \quad (4.72)$$

- The Helmholtz free energy is

$$\begin{aligned} F &= -k_B T \ln Z \\ &= -k_B T \ln Z_{\text{mono}} - k_B T \ln Z_{\text{rot}} \\ &= F_{\text{mono}} - k_B T \ln Z_{\text{rot}} \end{aligned} \quad (4.73)$$

- Let's define the following quantity in the exponent of the rotational partition function, which is a characteristic temperature

$$T_r = \frac{\hbar^2}{2Ik_B} \quad (4.74)$$

- If we are in the limit where  $T \gg T_r$  then we can approximate the sum in the partition function as an integral

$$Z_{\text{rot}} \approx \int_0^{\infty} (2l+1) e^{-l(l+1)T_r/T} dl \quad (4.75)$$

This integral can be evaluated using a substitution of  $u := l(l+1)$ , which gives

$$Z_{\text{rot}} = \frac{T}{T_r} \quad (4.76)$$

- Let's now use what we just calculated to write the Helmholtz free energy as

$$F = F_{\text{mono}}(N, T, V) - k_B T \ln(T/T_r) \quad (4.77)$$

- We can find other thermodynamic quantities

$$P = - \left( \frac{\partial F}{\partial V} \right)_{N, T} = \frac{Nk_B T}{V} \quad (4.78)$$

$$S = - \left( \frac{\partial F}{\partial T} \right)_{N, V} = S_{\text{mono}} + Nk_B (\ln(T/T_r) + 1) \quad (4.79)$$

$$C_V = T \left( \frac{\partial S}{\partial T} \right)_V = \frac{3}{2} Nk_B + Nk_B = \frac{5}{2} Nk_B \quad (4.80)$$

$$C_p = C_V + Nk_B = \frac{7}{2} Nk_B \quad (4.81)$$

- Now suppose that  $T \ll T_r$ . In this limit the rotation partition function can be approximated (to first order) by

$$Z_{\text{rot}} \approx 1 + 3e^{-2T_r/T} \quad (4.82)$$

The log of this is approximately

$$\ln(1 + 3e^{-2T_r/T}) \approx 3e^{-2T_r/T} \quad (4.83)$$

- The Helmholtz free energy is then

$$F = F_{\text{mono}} - 3Nk_B T e^{-2T_r/T} \quad (4.84)$$

and the entropy is

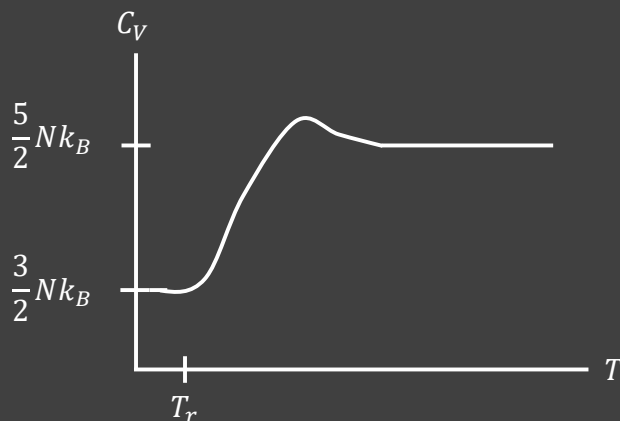
$$\begin{aligned} S &= S_{\text{mono}} - 3Nk_B (e^{-2T_r/T} + (2T_r/T)e^{-2T_r/T}) \\ &\approx S_{\text{mono}} - 3Nk_B \left( \frac{2T_r}{T} e^{-2T_r/T} \right) \end{aligned} \quad (4.85)$$

and the heat capacity at constant volume is

$$\begin{aligned} C_V &= \frac{3}{2}Nk_B + 6NT_r k_B T e^{-2T_r/T} \left( \frac{2T_r}{T^3} - \frac{1}{T^2} \right) \\ &\approx \frac{3}{2}Nk_B + \frac{12Nk_B T_r^2}{T^2} e^{-2T_r/T} \end{aligned} \quad (4.86)$$

The second term goes to zero as  $T$  approaches zero.

- We can plot specific heat as a function of temperature.



- Model vibrational modes of diatomic molecule as a harmonic oscillator. The energy is

$$E_n = \hbar\omega(n + 1/2) \quad (4.87)$$

- The vibrational partition function is

$$Z_{\text{vib}} = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+1/2)} \quad (4.88)$$

We can evaluate this sum using a geometric series to obtain

$$Z_{\text{vib}} = \frac{1}{e^{\beta\hbar\omega/2} - e^{-\beta\hbar\omega/2}} = \frac{1}{2 \sinh(\beta\hbar\omega/2)} \quad (4.89)$$

- There is a characteristic temperature

$$T_c = \hbar\omega/k_B \quad (4.90)$$

which in the limit of  $T \gg T_c$  (or  $\hbar\omega/k_B T \ll 1$ ) gives us an approximate expression for  $Z_{\text{vib}}$

$$Z_{\text{vib}} \approx \frac{k_B T}{\hbar\omega} \quad (4.91)$$

- In the opposite limit  $T \ll T_c$  we obtain

$$Z_{\text{vib}} \approx e^{-\beta\hbar\omega/2} \quad (4.92)$$

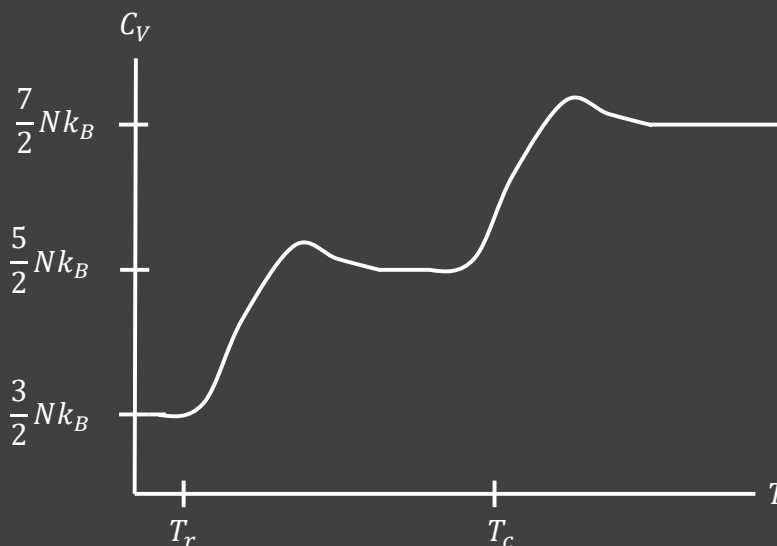
- The Helmholtz free energy is

$$F_{\text{vib}} = -k_B T \ln Z_{\text{vib}} = k_B T (\ln 2 + \ln \sinh(\hbar\omega/2k_B T)) \quad (4.93)$$

and the energy is

$$E = - \left( \frac{\partial \ln Z}{\partial \beta} \right)_{N,V} = \frac{\hbar\omega}{2} \coth(\beta\hbar\omega/2) \quad (4.94)$$

- We can now compute the heat capacity by taking a derivative of the energy with respect to temperature. If we do this we can plot the full graph of the heat capacity for a diatomic molecule.



## 5 The Grand Canonical Ensemble

- In the grand canonical ensemble we have a big system in the micro-canonical system which is divided into a reservoir  $R$  and subsystem  $S$ , where the both heat (and so energy not constant) and particles can be exchanged between  $S$  and  $R$ .
- Think about the probability  $P_i$  that  $S$  is in  $n$  particle quantum state  $i$ . To find this probability we can compute

$$P_i = \frac{\Omega_R(E_R)\Omega_S(E_S)}{\Omega_T(E_T)} \quad (5.1)$$



where the  $T$  stands for the total system. Now because we are asking for the probability of a single state  $i$  in the subsystem  $S$ , then  $\Omega_S(E_S) = 1$ , and so

$$P_i = \frac{\Omega_R(E_R, N_R)}{\Omega_T(E_T)} \quad (5.2)$$

- Now note that  $E_R = E_T - E_S$  and  $N_R = N_T - N_S$ , so

$$P_i = \frac{\Omega_R(E_T - E_S, N_T - N_S)}{\Omega_T(E_T, N_T)} \quad (5.3)$$

- If we compute

$$\left( \frac{\partial \ln P_i}{\partial E_S} \right)_{N_S} = - \frac{\partial \ln \Omega_R(E_R, N_R)}{\partial E_R} = - \frac{1}{k_B T_R(E_R, N_R)} \approx \frac{1}{k_B T} \quad (5.4)$$

where the second to last expressions follow from the definition of temperature and the approximation is valid (i.e. that  $T$  is constant) in the limit that the reservoir is much greater than the subsystem

- The solution to this partial differential equation is

$$\ln P_i = - \frac{E_S}{k_B T} + g(N_S) \quad (5.5)$$

- To find  $g(N_S)$  we can compute

$$\left( \frac{\partial \ln P_i}{\partial N_S} \right)_{E_S} = \frac{dg}{dN_S} = \left( \frac{\partial \ln \Omega_R}{\partial N_S} \right)_{E_S} = - \left( \frac{\partial \ln \Omega_R}{\partial N_R} \right)_{E_R} \quad (5.6)$$

- We can recall from the microcanonical ensemble that

$$\left( \frac{\partial \ln \Omega_R}{\partial N_S} \right)_{E_S} = \frac{\mu}{k_B T} =: -\alpha \quad (5.7)$$

where  $\alpha$  is a constant in the limit that the reservoir is very large compared to the subsystem

- We now have an ODE with a solution

$$g = -\alpha N_S + \text{const} \quad (5.8)$$

and we can use this result to write

$$\ln P_i = -\beta E_i - \alpha N_i + \text{const} \quad (5.9)$$

- If we define the constant as  $\mathcal{Q}$  we can solve for the probability

$$P_i = \frac{e^{-\alpha N_i - \beta E_i}}{\mathcal{Q}} \quad (5.10)$$

where

$$\mathcal{Q} = \sum_i e^{-\alpha N_i - \beta E_i} \quad (5.11)$$

- Note that in the grand canonical ensemble  $T$ ,  $\mu$ , and  $V$  are fixed.
- The grand canonical partition function can get us all of the thermodynamic properties of a system

- The average number of particles in the system is

$$\langle N \rangle = \frac{\sum_i e^{-\beta E_i - \alpha N_i} N_i}{\mathcal{Q}} = - \left( \frac{\partial \ln \mathcal{Q}}{\partial \alpha} \right)_{T,V} \quad (5.12)$$

and the average is

$$\langle E \rangle = \frac{\sum_i e^{-\beta E_i - \alpha N_i} E_i}{\mathcal{Q}} = - \left( \frac{\partial \ln \mathcal{Q}}{\partial \beta} \right)_{V,\alpha} \quad (5.13)$$

- From the grand canonical partition function we can obtain the equation of state. Let's consider

$$q := \ln(\mathcal{Q}(\beta, \alpha, V)) \quad (5.14)$$

so that

$$dq = \left( \frac{\partial q}{\partial \beta} \right)_{\alpha,V} d\beta + \left( \frac{\partial q}{\partial \alpha} \right)_{\beta,V} d\alpha + \left( \frac{\partial q}{\partial V} \right)_{\alpha,\beta} dV \quad (5.15)$$

- We know what the first two terms are

$$dq = -\bar{E}d\beta - \bar{N}d\alpha + \left( \frac{\partial q}{\partial V} \right)_{\alpha,\beta} dV \quad (5.16)$$

where the overbar denotes an average.

- We can compute the last derivative by noting that only the energy is a function of volume, so

$$\left( \frac{\partial q}{\partial V} \right)_{\alpha,\beta} = \beta \sum_i \left[ - \left( \frac{\partial E_i}{\partial V} \right) \right] \left( \frac{e^{-\alpha N_i - \beta E_i}}{\mathcal{Q}} \right) = \beta \sum_i \left( - \frac{\partial E_i}{\partial V} \right) P_i \quad (5.17)$$

where  $P_i$  is the probability of being in state  $i$ . Now note that the term in parentheses in the expression on the right is the pressure of state  $i$ ,  $\mathcal{P}$ , and so

$$\left( \frac{\partial q}{\partial V} \right)_{\alpha,\beta} = \beta \bar{\mathcal{P}} \quad (5.18)$$

- The differential of  $q$  is then

$$\boxed{dq = -\bar{E}d\beta - \bar{N}d\alpha + \beta \bar{\mathcal{P}}dV} \quad (5.19)$$

- Now let's consider

$$d(q + \bar{E}\beta + \alpha\bar{N}) = dq + \bar{E}d\beta + \beta d\bar{E} + \bar{N}d\alpha + \alpha d\bar{N} \quad (5.20)$$

and once we plug in  $d\bar{E}$  we find that

$$d(q + \bar{E}\beta + \alpha\bar{N}) = \beta T dS = \frac{1}{k_B} S \quad (5.21)$$

- This last line means that

$$q + \bar{E}\beta + \alpha\bar{N} = \frac{S}{k_B} + \text{const} \quad (5.22)$$

- The Gibbs free energy is defined as

$$\boxed{G = \bar{E} - TS + PV} \quad (5.23)$$

so that

$$\boxed{dG = -SdT + VdP + \mu dN} \quad (5.24)$$

- The Gibbs free energy is extensive so it can be written as

$$G = \bar{N}f(T, P) \quad (5.25)$$

- The chemical potential is

$$\mu = \left( \frac{\partial G}{\partial N} \right)_{T,P} = f(T, P) \quad (5.26)$$

so

$$G = \bar{N}\mu \quad (5.27)$$

- Since  $\alpha = -\beta\mu$  we can rewrite Eq. (5.22) as

$$q + \bar{E}\beta - \beta\mu\bar{N} = \frac{S}{k_B} + \text{const} \quad (5.28)$$

or

$$q + \beta\bar{E} - \beta G = \frac{S}{k_B} + \text{const} \quad (5.29)$$

If we substitute in our definition for the Gibbs free energy we find that

$$q - \beta\bar{\mathcal{P}}V = \text{const} \quad (5.30)$$

- If we evaluate this last equation at  $\alpha \rightarrow \infty$ ,  $N_i \rightarrow 0$ , then both  $q$  and  $\bar{\mathcal{P}}$  go to zero, so the constant is zero.
- We have thus recovered the equation of state in the grand canonical ensemble

$$q = \frac{PV}{k_B T} \quad (5.31)$$

- We can obtain the Helmholtz free energy as follows

$$F = E - TS = G - PV = N\mu - k_B T q \quad (5.32)$$

and from this other thermodynamic quantities

- Now let's relate the canonical partition function to the grand canonical partition function

$$\mathcal{Q} = \sum_{n=0}^{\infty} \sum_{i_n} e^{-\alpha n - \beta E_i} = \sum_{n=0}^{\infty} e^{-\alpha n} \sum_{i_n} e^{i\beta E_i} \quad (5.33)$$

and so

$$\mathcal{Q} = \sum_{N=0}^{\infty} e^{-\alpha N} Z(T, N, V) \quad (5.34)$$

- This is sometimes written as

$$\mathcal{Q} = \sum_{N=0}^{\infty} Y^N Z(N, T, V) \quad (5.35)$$

where

$$Y := e^{-\alpha} \quad (5.36)$$

- Did not take notes on rest of section (covered ideal gas in grand canonical ensemble and fluctuations in particle number)

## 5.1 Non-Interacting Quantum Particles and Quantum Statistics

- Change notation so that the label “ $i$ ” refers to single particle states (previously it had been used to label the states of a many particle system).
- How do we characterize a many particle system with identical Hamiltonians
- To specify a many particle state we just need to specify how many particles are in each single particle states.
- In this formalism we have that

$$N = \sum_i n_i \quad E = \sum_i n_i \epsilon_i \quad (5.37)$$

which we need to compute probabilities

$$P(\{n_i\}) = \frac{e^{-\alpha N - \beta E}}{\mathcal{Q}} \quad (5.38)$$

where

$$\mathcal{Q} = \sum_{\text{many particle}} e^{-\alpha N - \beta E} \quad (5.39)$$

or explicitly

$$\mathcal{Q} = \sum_{n_0=0}^{N_{\max}} \sum_{n_1=0}^{N_{\max}} \dots \sum_{n_{N_{\max}}=0}^{N_{\max}} e^{-\alpha N - \beta E} \quad (5.40)$$

- In quantum mechanics, Fermions can only have 1 particle per state ( $N_{\max} = 1$ ), whereas Bosons can have an arbitrary number of particles in a state ( $N_{\max} = \infty$ ).
- We can factor  $\mathcal{Q}$  as

$$\begin{aligned} \mathcal{Q} &= \sum_{n_0=0}^{N_{\max}} \sum_{n_1=0}^{N_{\max}} \dots \sum_{n_{N_{\max}}=0}^{N_{\max}} e^{-\alpha \sum_i n_i - \beta \sum_i n_i \epsilon_i} \\ &= \prod_i \left( \sum_{n_i=0}^{N_{\max}} e^{-(\alpha + \beta \epsilon_i) n_i} \right) \end{aligned} \quad (5.41)$$

- Now if we evaluate the sum in the previous expression for Fermions we obtain

$$\sum_{n_i=0}^1 e^{-(\alpha + \beta \epsilon_i) n_i} = 1 + e^{-(\alpha + \beta \epsilon_i)} \quad (5.42)$$

while for Bosons we obtain

$$\sum_{n_i=0}^{\infty} e^{-(\alpha + \beta \epsilon_i) n_i} = \frac{1}{1 - e^{-(\alpha + \beta \epsilon_i)}} \quad (5.43)$$

- The grand canonical partition function can be written as

$$\mathcal{Q} = \prod_i (1 + \sigma e^{-(\alpha + \beta \epsilon_i)})^\sigma \quad (5.44)$$

where  $\sigma$  is 1 for Fermions and -1 for Bosons.

- We can ask what the average number of particles in state  $i$ . It is the sum over the many body states multiplied by the probability of being in the many body state. This can be written as

$$\langle n_i \rangle = -\frac{1}{\beta} \frac{\partial \ln \mathcal{Q}}{\partial \epsilon_i} \quad (5.45)$$

- In order to evaluate this derivative we can note that the logarithm can be simplified to

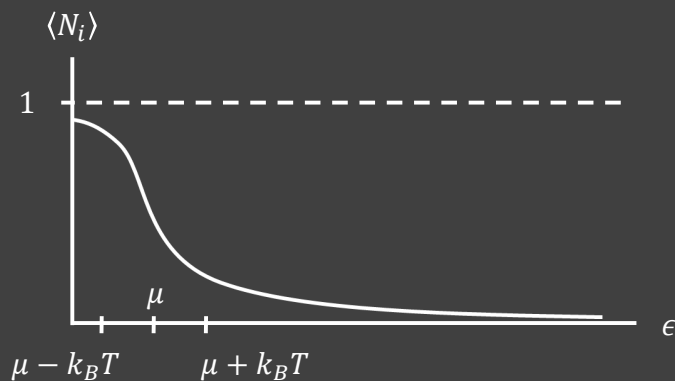
$$\ln \mathcal{Q} = \sum_j \ln \left( (1 + \sigma e^{-(\alpha + \beta \epsilon_j)})^\sigma \right) \quad (5.46)$$

and so

$$\langle n_i \rangle = \frac{1}{e^{\alpha + \beta \epsilon_i} + \sigma} \quad (5.47)$$

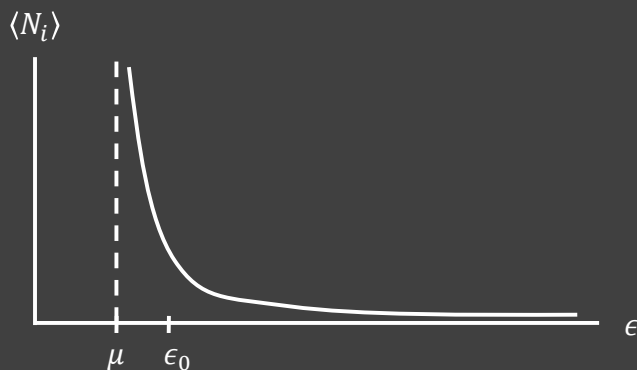
- So in the case of Fermions we have

$$\langle n_i \rangle = \frac{1}{e^{\alpha + \beta \epsilon_i} + 1} \quad (5.48)$$



- In the case of Bosons we have

$$\langle n_i \rangle = \frac{1}{e^{\alpha + \beta \epsilon_i} - 1} \quad (5.49)$$



- The average number of particles in the system is

$$\langle N \rangle = \sum_i \langle n_i \rangle \quad (5.50)$$

whereas the average energy of the system is

$$\langle E \rangle = \sum_i \langle n_i \rangle \epsilon_i \quad (5.51)$$