

# Equilibrium Statistical Mechanics

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## Chapter II

## Quantum Description

**Time evolution**

We have a complete set of state vectors

$$|\psi(t_o)\rangle = |a_1 \cdots a_N\rangle \quad (1)$$

Which are eigen vectors of a complete set of commuting operators

$$A_1 \cdots A_N$$

where

$$A_i |\psi(t_o)\rangle = a_i |\psi(t_o)\rangle \quad (2)$$

The time evolution of a state is governed by the Schrodinger equation

$$i\hbar \frac{\partial |\psi(\vec{x}, t)\rangle}{\partial t} = H(t) |\psi(\vec{x}, t)\rangle \quad (3)$$

- For an isolated system  $H$  is independent of time.

- ▶ However, if the system is in contact with the outside world with time dependent interactions  $H$  may be time dependent.
- ▶ The time evolution can also be represented by the time evolution operator  $U(t, t_0)$

$$|\psi(t)\rangle = U(t, t_0)|\psi(t_0)\rangle \quad (4)$$

which satisfies

$$i\hbar \frac{\partial U(t, t_0)}{\partial t} = H(t)U(t, t_0) \quad (5)$$

To see this we write

$$i\hbar \frac{\partial U(t, t_0)\psi(t_0)}{\partial t} = H(t)U(t, t_0)\psi(t_0) \quad (6)$$

or

$$\left[ i\hbar \frac{\partial U(t, t_0)}{\partial t} - H(t)U(t, t_0) \right] \psi(t_0) = 0 \quad (7)$$

- ▶ Since this is true for all  $\psi$  the term in the bracket must be zero. Remember  $U(t_0, t_0) = I$

The time evolution operator is unitary.

$$U^\dagger(t, t_0) = U^{-1}(t, t_0) \quad (8)$$

Here  $U^\dagger$  is the hermetian conjugate of  $U$

► In addition

$$U(t, t_0) = U(t, t_1)U(t_1, t_0) \quad (9)$$

If  $H$  is independent of time then

$$U(t, t_0) = \exp\left[-\frac{i}{\hbar}H(t - t_0)\right] \quad (10)$$

► This is the **Schrodinger picture**. We can also use the **Heisenberg picture**

In the Heisenberg picture the state vector is independent of time

$$|\psi_H\rangle = U^{-1}(t, t_0)|\psi(t)\rangle = |\psi(t_0)\rangle \quad (11)$$

While the dynamical variables represented by the operator  $A_i$  are now functions of time through.

$$A_H(t) = U^{-1}(t, t_0)A(t)U(t, t_0) \quad (12)$$

For generality we have displayed the possible time dependence of  $A$  but usually  $A$  is independent of time.

- The Hamiltonian in the Heisenberg picture is

$$H_H(t) = U^{-1}(t, t_0)H(t)U(t, t_0) \quad (13)$$

From eqs.(5)(and its hermetian conjugate) and (12)

$$i\hbar \frac{\partial A_H}{\partial t} = [A_H(t), H_H(t)] + i\hbar \left( \frac{\partial A(t)}{\partial t} \right)_H \quad (14)$$

- Note that the partials denote that the position variables are held constant and that if the Scrodinger operator is independent of time the second term on the right hand side is zero.
  - The brackets  $[ ]$  denote the commutator.
- The expectation values of dynamical variables are independent of representation.

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## Density operators and their time evolution

- ▶ The above description of a quantum state assumes a complete(quantum) knowledge of the system.
- ▶ Such a system is said to be in a pure state.  
In statistical mechanics we often only know the probability that the system be in a state.
- ▶ Consider the projection operator  $D = |\psi\rangle\langle\psi|$   
where  $\langle\psi|\psi\rangle = 1$   
Assume that we have a complete set of states so that

$$|\psi\rangle = \sum_i c_i |i\rangle \quad (15)$$

Hence

$$|\psi\rangle\langle\psi| = \sum_{i,j} c_i c_j^* |i\rangle\langle j| \quad (16)$$

and

$$D_{kl} = \langle k|D|l\rangle = c_k c_l^* \quad (17)$$

Suppose we know the probability  $p_n$  of finding the system in the state  $|\psi_n\rangle$  where

$$|\psi_n\rangle = \sum_i c_i^{(n)} |i\rangle \quad (18)$$

- ▶ The  $|\psi_n\rangle$  are normalized but not necessarily orthogonal.
- ▶ As usual

$$p_n \geq 0 \quad \sum_n p_n = 1 \quad (19)$$

- ▶ The system is now said to be in a mixed state or statistical mixture.
- ▶ We define the **density operator**  $D$  by

$$D = \sum_n |\psi_n\rangle p_n \langle \psi_n| \quad (20)$$

which is a generalization of the projection operator given above.

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- The expectation value of  $A$  is

$$\langle A \rangle = \sum_n p_n \langle \psi_n | A | \psi_n \rangle = \text{Tr} A D \quad (21)$$

The first equality is by definition. To see the second we expand

$$|\psi_n\rangle = \sum_l c_l |\phi_l\rangle \quad (22)$$

where the  $|\phi_l\rangle$  form an orthonormal basis.

- Inserting this expansion into the expression for  $|\psi_n\rangle$  in eq.(21)

$$\langle A \rangle = \sum_n p_n \sum_l c_l^{*(n)} \langle \phi_l | A \sum_m |\phi_m\rangle c_m^{(n)} \quad (23)$$

- Defining the matrix elements of  $A$  to be  $A_{ij} = \langle \phi_i | A | \phi_j \rangle$  we have

$$\langle A \rangle = \sum_n p_n \sum_l \sum_m c_l^{*(n)} c_m^{(n)} A_{lm} \quad (24)$$

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- We now insert the expansion in eq(22) into the definition of the density operator  $D$  in eq(20).

$$D = \sum_n \sum_m c_m^{(n)} |\phi_m\rangle p_n \sum_l c_l^{*(n)} \langle \phi_l| \quad (25)$$

or

$$D = \sum_m \sum_l |\phi_m\rangle \langle \phi_l| \sum_n c_m^{(n)} p_n c_l^{*(n)} \quad (26)$$

The operator formulation of  $A$  is

$$A = |\phi_i\rangle A_{ij} \langle \phi_j| \quad (27)$$

- The matrix representation of  $A$  is  $A_{ij}$ .
- The matrix representation of  $D$  is

$$D_{ij} = \langle \phi_i | D | \phi_j \rangle = \sum_n c_i^{(n)} p_n c_j^{*(n)} \quad (28)$$

- The  $ij$  matrix element of the product of  $A$  and  $D$  is

$$(AD)_{ij} = \sum_s A_{is} D_{sj} = \sum_s A_{is} \sum_n c_s^{(n)} p_n c_j^{*(n)} \quad (29)$$

The trace is then

$$\text{Tr}(AD)_{ij} = \sum_j \sum_s A_{js} \sum_n c_s^{(n)} p_n c_j^{*(n)} \quad (30)$$

- ▶ Remembering that the summation indices are arbitrary and that all of the terms in the sum are constants so they can be rearranged at will eqs.(30) and (24) are identical.

Hence

$$\langle A \rangle = \text{Tr} AD$$

- ▶ From eq(20) and the fact that  $p_n$  is real it is obvious that the density operator  $D$  is hermitian.
- ▶  $D$  has unit trace

To see this we use eq.(28)

$$D_{ij} = \sum_n c_i^{(n)} p_n c_j^{*(n)}$$

The trace is

$$\text{Tr} D = \sum_i D_{ii} = \sum_n \sum_i c_i^{(n)} c_i^{*(n)} p_n \quad (31)$$

- ▶ Since the  $c_i^{(n)}$  are the expansion coefficients in an orthonormal basis and the  $|\psi_n\rangle$  are normalized we have

$$\sum_i c_i^{(n)} c_i^{*(n)} = 1$$

- ▶ In addition  $p_n$  are probabilities of being in the  $n$ th state so that

$$\sum_n p_n = 1$$

and the trace of the  $D$  matrix is one.

- ▶  $D$  is a positive operator.

Using the definition of the density operator in eq.(20) we have for any vector  $|\phi\rangle$

$$\begin{aligned} \langle \phi | D | \phi \rangle &= \langle \phi | \sum_n |\psi_n\rangle p_n \langle \psi_n | \phi \rangle \\ &= \sum_n p_n |\langle \phi | \psi_n \rangle|^2 \geq 0 \end{aligned} \quad (32)$$

- ▶ A necessary and sufficient condition that the system be in a pure state is that  $D^2 = D$  Namely that  $D$  is a projection operator.
  - ▶ A pure state has  $p_n = 1$  for some value of  $n = n_o$  and  $p_n = 0$  for all  $n \neq n_o$
- ▶ For a pure state the density operator (from eq.(20))

$$D = |\psi_{n_o}\rangle \langle \psi_{n_o}| \quad (33)$$

- ▶ Since the  $|\psi_n\rangle$  are normalized  $\langle \psi_{n_o} | \psi_{n_o} \rangle = 1$ ,  $D^2 = D$

- ▶ Hence the equality  $D^2 = D$  is necessary if the system is in a pure state.

From eq.(28) the matrix form of  $D$  is

$$D_{ij} = \sum_n c_i^{(n)} p_n c_j^{*(n)} \quad (34)$$

Hence

$$D^2 = \sum_n \sum_m \sum_l c_i^{(n)} p_n c_l^{*(n)} c_l^{(m)} p_m c_j^{*(m)} \quad (35)$$

- ▶ The  $c_j^{(n)}$  are the coefficients of the expansion of  $|\psi_n\rangle$ . They are arbitrary because they depend on the basis used.  $\rightarrow$  if  $D^2 = D$  we must have  $p_n = 1$  for some  $n$  and zero for the rest.
  - ▶ Here we also use the fact that  $\sum_l c_l^{(n)} c_l^{*(n)} = 1$  since the  $|\psi_n\rangle$  are normalized.

## Time evolution of the density operator

Suppose the density operator at time  $t_0$  is

$$D(t_0) = \sum_n |\psi_n(t_0)\rangle p_n \langle \psi_n(t_0)| \quad (36)$$

and  $|\psi_n(t)\rangle = U(t, t_0)|\psi_n(t_0)\rangle$  we have

$$D(t) = U(t, t_0)D(t_0)U^{-1}(t, t_0) \quad (37)$$

From eqs.(7) and (37) it is straightforward to obtain

$$i\hbar \frac{\partial D}{\partial t} = [H(t), D] \quad (38)$$

Note that the time evolution of  $D$  in eq.(37) and in eq.(12) have the time evolution operators  $U$  and  $U^{-1}$  in opposite order. This results in the commutators having the Hamiltonian and the operator reversed in the differential form of the time evolution equation.

- ▶ The density operator  $D$  acts like the state vector in that it contains the information about the system.
- ▶ In the Schrodinger representation  $D$  is time dependent. In the Heisenberg representation it is independent of time like the state vector.

$$D_H = U^{-1}(t, t_0)D(t)U(t, t_0) \quad (39)$$

Since the trace is invariant under cyclic permutation we have

$$\langle A \rangle(t) = \text{Tr} A(t)D(t) = \text{Tr} A_H(t)D_H \quad (40)$$

- ▶ If we could have complete (quantum) knowledge of a system we would have it's state vector.
- ▶ The best we can have is the probability that various microstates are realized.
- ▶ This implies that the density matrix is as complete a description of a quantum system that we can have.

- ▶ The simplest illustration of the density matrix uses the spin  $1/2$  system.
- ▶ Spin  $1/2$  systems are described by a set of 4  $2 \times 2$  matrices, the three Pauli matrices and the identity.
- ▶ In the basis in which the  $z$  component is diagonal they are

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (41)$$

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad (42)$$

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (43)$$

$$I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad (44)$$

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The eigenvectors of  $\sigma_z$  are

$$|+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad (45)$$

$$|-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (46)$$

- The vectors  $|+\rangle$  and  $|-\rangle$  are orthonormal and span the space of 2 component vectors.

It is simple to show that the eigenvectors of  $\sigma_y$  are

$$\frac{1}{\sqrt{2}}(|+\rangle + i|-\rangle) \quad \frac{1}{\sqrt{2}}(|+\rangle - i|-\rangle) \quad (47)$$

In matrix form this is

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix} \quad (48)$$

and

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix} \quad (49)$$

Now we assume that we have a number of spin 1/2 particles that have been polarized in the positive y direction by a Stern-Gerlach apparatus.

- ▶ Since the system is in a pure state it is described by the eigenvector of  $\sigma_y$  with the eigenvalue 1.
  - ▶ In matrix representation this is given in eq.(48).
  - ▶ In bra and ket notation this is  $\frac{1}{\sqrt{2}}(|+ > +i|- >)$

The density operator is

$$\frac{1}{\sqrt{2}}(|+ > +i|- >) \frac{1}{\sqrt{2}}(\langle +| - i \langle -|) \quad (50)$$

In matrix form

$$D_{ij} = \begin{pmatrix} \frac{1}{2} & -\frac{i}{2} \\ \frac{i}{2} & \frac{1}{2} \end{pmatrix} \quad (51)$$

- ▶ The trace is 1 and the matrix is Hermetian which are general properties of density matrices
- ▶ Since we have a pure state the average of e.g.  $\sigma_z$  is

$$\begin{aligned} \frac{1}{2} (<+|-i<-|) [|+><+|-|-><-|] (|+>+i|->) \\ &= 0 \end{aligned} \quad (52)$$

- ▶ The density matrix approach gives

$$<\sigma_z> = \text{Tr} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 & -i \\ i & 1 \end{pmatrix} = 0 \quad (53)$$

Now we have a mixture of spins oriented in the up or positive  $z$  direction with probability  $1/2$  and others oriented in the positive  $y$  direction with probability  $1/2$ .

The density operator is

$$|+\rangle \langle +| + \frac{1}{2}(|+\rangle + i|-\rangle)(\langle +| - i\langle -|) \quad (54)$$

In matrix form

$$D_{ij} = \begin{pmatrix} \frac{3}{4} & -\frac{i}{4} \\ \frac{i}{4} & \frac{1}{4} \end{pmatrix} \quad (55)$$

- The average of  $\sigma_z$  is

$$\langle \sigma_z \rangle = \text{Tr} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \frac{3}{4} & -\frac{i}{4} \\ \frac{i}{4} & \frac{1}{4} \end{pmatrix} = \frac{1}{2} \quad (56)$$

- This makes sense since we have half the spins with expectation value of 1 and half with expectation value of 0.
- From eq.(34) we can easily show that the density matrix is Hermetian and with unit trace.

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- Suppose we ask for the time evolution of the density matrix in the above problem in potential free space. From eq.(38)

$$i\hbar \frac{\partial D}{\partial t} = [H(t), D]$$

- In this case  $\frac{\partial D}{\partial t} = 0 \rightarrow$  and the initial value of  $D$  (eq.(55)) is constant.
- Suppose now that we have a constant(spatial and temporal) magnetic field  $\vec{B}$  in the  $z$  direction. The Hamiltonian is

$$H = -\gamma \vec{S} \cdot \vec{B} \quad (57)$$

where the vector

$$\vec{S} = \frac{1}{2} \vec{\sigma} \quad (58)$$

- The components of the vector  $\vec{\sigma}$  are the Pauli spin matrices in eqs.(41) - (43)

- If  $\vec{B}$  points in the  $z$  direction then the Hamiltonian is

$$H = -\gamma B \sigma_z \quad (59)$$

where  $B = |\vec{B}|$ . Using eq.(38) and setting  $\gamma B = 1$

$$-i\hbar \frac{\partial}{\partial t} \begin{pmatrix} a & b \\ c & d \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} a & b \\ c & d \end{pmatrix} - \begin{pmatrix} a & b \\ c & d \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (60)$$

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} a & b \\ c & d \end{pmatrix} = \begin{pmatrix} 0 & -2b \\ 2c & 0 \end{pmatrix} \quad (61)$$

Clearly  $b$  and  $d$  are temporal constants. Since  $D$  has a unit trace  $a + d = 1$  and are fixed by the initial conditions.

- If the system is initiated as in eq.(55) then  $a = 3/4$  and  $d = 1/4$ .
- In addition we have

$$i\hbar \frac{\partial b}{\partial t} = -2b \quad i\hbar \frac{\partial c}{\partial t} = 2c \quad (62)$$

$$b(t) = b(0)e^{i2t/\hbar} \quad c(t) = c(0)e^{-i2t/\hbar} \quad (63)$$

- ▶ With the same initiation as above  $b(0) = -i/4$  and  $c(0) = i/4$ .

Hence

$$D(t) = \begin{pmatrix} \frac{3}{4} & -i\frac{e^{i2\gamma Bt/\hbar}}{4} \\ i\frac{e^{-i2\gamma Bt/\hbar}}{4} & \frac{1}{4} \end{pmatrix} \quad (64)$$

where we have made the  $\gamma B$  dependence explicit.

- ▶ Note that  $D(t)$  is Hermetian with unit trace.

The average of  $\sigma_z$  is

$$\langle \sigma_z \rangle = \text{Tr} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \frac{3}{4} & -i\frac{e^{i2\gamma Bt/\hbar}}{4} \\ i\frac{e^{-i2\gamma Bt/\hbar}}{4} & \frac{1}{4} \end{pmatrix} = \frac{1}{2} \quad (65)$$

- ▶ Note that this is independent of time.

The average of  $\sigma_x$  is

$$\langle \sigma_x \rangle = \text{Tr} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \frac{3}{4} & -i\frac{e^{i2\gamma Bt/\hbar}}{4} \\ i\frac{e^{-i2\gamma Bt/\hbar}}{4} & \frac{1}{4} \end{pmatrix} \quad (66)$$

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$$\langle \sigma_x \rangle = \frac{\sin(2\gamma Bt/\hbar)}{2} \quad (67)$$

- ▶ This can be considered as a precessing of the spin about the  $z$  axis.
- ▶ A similar result is obtained for  $\langle \sigma_y \rangle$
- ▶ We will return to the density operator after we discuss ensembles.

## Quantum phase space

- ▶ In the following it will be important to know how to count energy levels.
- ▶ We start with the simplest case of a one dimensional box with end points  $[0, L]$
- ▶ The free particle of mass  $m$  is confined to the box and it has energy  $\varepsilon$

The Schrodinger equation is

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = \varepsilon \psi(x) \quad (68)$$

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- ▶ The boundary conditions are  $\psi(0) = \psi(L) = 0$
- ▶ The solutions are (with  $n \geq 0$ )

$$\psi_n(x) = A \sin(k_n x) \quad k_n = \frac{\pi n}{L} \quad (69)$$

- ▶ We want to count energy levels so for convenience we will take periodic boundary conditions  $\psi(x) = \psi(x + L)$ .

The solutions are

$$\psi_n(x) = \frac{1}{\sqrt{L}} e^{ik_n x} \quad k_n = \frac{2\pi n}{L} \quad (70)$$

where the  $1/\sqrt{L}$  is a normalization and the integer  $n$  takes on both positive and negative values.

- ▶ Since the number of states ( $n$ ) is doubled ( $n$  is not positive) but the  $k_n$  spacing is twice as big as the original the number of states will be the same.
- ▶ Since  $L$  is macroscopic the spacing between energy levels is small  $\rightarrow$  continuum approximation for the counting.

To do this we introduce the density of states  $\rho(k)$

- ▶ The number of states in the interval  $[k, k + \Delta K]$  is  $\rho(k)\Delta k$
- ▶ Since  $k_n = \frac{2\pi}{L}$  we have

$$\Delta n = \frac{L}{2\pi} \Delta k = \rho(k) \Delta k \quad (71)$$

Hence

$$\rho(k) = \frac{L}{2\pi} \quad (72)$$

In  $d = 3$  for a particle confined to a rectangular box with sides  $(L_x, L_y, L_z)$

$$\vec{k} = \left( \frac{2\pi n_x}{L_x}, \frac{2\pi n_y}{L_y}, \frac{2\pi n_z}{L_z} \right) \quad (73)$$

$$\rho(\vec{k}) = \frac{L_x L_y L_z}{(2\pi)^3} = \frac{V}{(2\pi)^3} \quad (74)$$

The number of states then is

$$\rho(\vec{k})d^3k = \frac{V}{(2\pi)^3}d^3k \quad (75)$$

We can also use the momentum  $\vec{p} = \hbar\vec{k}$

$$\rho(\vec{p})dp^3 = \frac{V}{h^3}dp^3 \quad (76)$$

- ▶ This result is independent of kinematic regime (relativistic and non-relativistic)
- ▶ We now consider the density of energy levels i.e. the number of levels per unit energy.

Let  $\Phi(\varepsilon)$  be the number of levels whose energy is  $\leq \varepsilon$

We use the non-relativistic dispersion relation

$p = \sqrt{2m\varepsilon}$  and the continuum approximation.

$$\Phi(\varepsilon) = \int_{p \leq \sqrt{2m\varepsilon}} \rho(\vec{p}) d^3 p = \frac{V}{h^3} \int_{p \leq \sqrt{2m\varepsilon}} d^3 p \quad (77)$$

where we have used the density of states in eq.(76).

$$\Phi(\varepsilon) = \frac{4\pi V}{h^3} \int_0^{\sqrt{2m\varepsilon}} p^2 dp \quad (78)$$

where the last expression is obtained by going to spherical coordinates. Evaluating the integral

$$\Phi(\varepsilon) = \frac{4\pi V}{3h^3} (2m\varepsilon)^{3/2} = \frac{V}{6\pi^2 \hbar^3} (2m\varepsilon)^{3/2} \quad (79)$$

$$\rho(\varepsilon) = \Phi'(\varepsilon) = \frac{Vm}{2\pi^2 \hbar^3} (2m\varepsilon)^{1/2} \quad (80)$$

In  $d = 2$  in a box with area  $S$

$$\rho(\varepsilon) = \frac{Sm}{2\pi \hbar^2} \quad (81)$$

## Classical description **Liouville's theorem**

- ▶ In classical mechanics the system is described microscopically by the Hamiltonian which depends on the  $2N$  coordinates  $q_i$  and  $p_i$   
 $N$  is the number of **degrees of freedom** In  
 $d = 3$ ,  $N = 3\bar{N}$  where  $\bar{N}$  is the number of particles.
- ▶ We assume a Hamiltonian of the form

$$H = \sum_{i=1}^{\bar{N}} \frac{p_i^2}{2m} + U(\{q_i\}) \quad (82)$$

- ▶  $H$  is not an explicit function of time and  $U$  depends only on the set  $\{q_i\}$ .  
 Hamilton's equations

$$\frac{\partial H}{\partial p_i} = \dot{q} \quad \frac{\partial H}{\partial q_i} = -\dot{p} \quad (83)$$

where the dot denotes the time derivative.

- ▶ The set of coordinates  $\{q_i, p_i\}$  constitutes the **phase space**.
- ▶ The trajectory in phase space is uniquely determined by Hamilton's equations and the initial conditions  $q_i(0)$  and  $p_i(0)$  so that the trajectories do not intersect.
  - ▶ If the trajectories intersect they would not be unique.
- ▶ Defining a microstate in classical mechanics corresponds to knowing all the coordinates  $\{q_i(t), p_i(t)\}$  at an arbitrary time  $t$ .

### Liouville's Theorem

Consider two times  $t$  and  $t + dt$  and define  $q = q(t)$  and  $q' = q(t + dt)$ ,  $p = p(t)$  and  $p' = p(t + dt)$

$$q' = q + \dot{q}dt = q + \frac{\partial H}{\partial p}dt \quad (84)$$

$$p' = p + \dot{p}dt = p - \frac{\partial H}{\partial q}dt \quad (85)$$

where we have used eq.(83).

- ▶ The differential volume  $dqdp$  evolves under the natural motion dictated by Hamilton's equations.
- ▶ This implies that  $dqdp \rightarrow dq'dp'$  where  $dq'$  and  $dp'$  are specified in eqs.(84) and (85)
- ▶ The relation between the primed and unprimed volumes in phase space involves the Jacobian  $J(t)$  where

$$\frac{\partial(q', p')}{\partial(q, p)} = \det \begin{pmatrix} 1 + \frac{\partial^2 H}{\partial p \partial q} dt & \frac{\partial^2 H}{\partial p^2} dt \\ -\frac{\partial^2 H}{\partial q^2} dt & 1 - \frac{\partial^2 H}{\partial p \partial q} dt \end{pmatrix} \quad (86)$$

where we have assumed that the order of the partials is not relevant.

Hence

$$\frac{\partial(q', p')}{\partial(q, p)} = 1 + O(dt)^2 \quad (87)$$

- ▶  $\rightarrow$  The Jacobian is 1 independent of time or

$$dpdq = dp'dq' \quad (88)$$

(incompressible fluid)

- ▶ With  $N$  degrees of freedom we generalize the previous result to

$$d^3 r_1 \cdots d^3 r_N d^3 p_1 \cdots d^3 p_N = d^3 r'_1 \cdots d^3 r'_N d^3 p'_1 \cdots d^3 p'_N \quad (89)$$

The integration volume(measure) then is

$$d\Gamma = C \prod_{i=1}^N d^3 p_i d^3 r_i \quad (90)$$

The constant  $C$  is arbitrary in classical mechanics but it can be fixed, as we will see, by quantum considerations.

### Density in phase space

A classical system has a set of positions and momenta  $\vec{p}_i(0), \vec{q}_i(0)$  at time  $t = 0$ .

- ▶ A microstate is specified by the set of variables  $\{\vec{r}_i, \vec{p}_i\}$  at any time  $t$  including  $t = 0$ .

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The probability of observing this microstate will be denoted by  $D(\vec{r}_i, \vec{p}_i)$ . At  $t = 0$  by  $D_0(\vec{r}_i, \vec{p}_i)$ .

$$D(\vec{r}_i, \vec{p}_i) \geq 0 \text{ and}$$

$$\int d\Gamma D_0(\vec{r}_i, \vec{p}_i) = C \int \prod_{i=1}^N d^3 p_i d^3 r_i D_0(\vec{r}_i, \vec{p}_i) = 1 \quad (91)$$

- ▶ The probability density plays the same role in classical statistical physics that the density operator plays in quantum statistical physics.
- ▶ The normalization in eq.(91) is the analog of  $\text{Tr} D = 1$  in quantum systems.

We adopt the notation

$$x = \{\vec{p}_1 \cdots \vec{p}_N; \vec{r}_1 \cdots \vec{r}_N\} \quad (92)$$

As time  $t$  evolves

$$\vec{p}_i \rightarrow \vec{p}_i(t) \quad \vec{r}_i \rightarrow \vec{r}_i(t) \quad (93)$$

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- This evolution is governed by Hamilton's equations. With the above notation the time evolution can be denoted by

$$x \rightarrow y = \phi_t(x) \quad (94)$$

Since the trajectories are unique we can write

$$x = \phi_t^{-1}(y) \quad (95)$$

From Liouville's theorem  $dx = dy$  where these are the integration measures.

- Let  $A$  be a classical variable which depends only on the coordinates with no explicit time dependence. We have

$$A(t=0) = A(\vec{p}_i, \vec{r}_i) = A(x) \quad (96)$$

$$A(t) = A(\vec{p}_i(t), \vec{r}_i(t)) = A(\phi_t(x)) \quad (97)$$

At  $t=0$

$$\langle A \rangle (t=0) = \int dx D_0(x) A(x) \quad (98)$$

- ▶ At time  $t$

$$\langle A \rangle(t) = \int dx D_0(x) A(\phi_t(x)) \quad (99)$$

- ▶ In this formulation we use the assumption of equal a priori probability.
  - ▶ That is the probability of each **micro state**  $(\{\vec{p}_i, \vec{r}_i\})$  is the same.
- ▶ Equation (99) is analogous to the expectation value in the Heisenberg picture.
  - ▶  $D$  is independent of time (state vectors) while the dynamical variables (operators) depend on time
- ▶ This is the usual picture in classical mechanics  
The analog of the Schrodinger picture is found by changing variables  $x \rightarrow \phi_t(x) = y$  and Liouville's theorem.

$$\langle A \rangle(t) \int dy D_0(\phi_{-t}(y)) A(y) = \int dx D(x(t), t) A(x) \quad (100)$$

Where

$$D(x(t), t) = D_0(\phi_{-t}(x)) \quad (101)$$

- Here the phase space density  $D$  depends on time but the dynamical variables do not. **Evolution of  $D$  with time** We consider one degree of freedom to obtain

$$D(q(t+dt), p(t+dt), t+dt) dq' dp' = D(q(t), p(t), t) dq dp \quad (102)$$

- Using eq.(102), Liouville's theorem  $dpdq = dp'dq'$  and the expansion of  $D$  as a function of  $q'$  and  $p'$  in a Taylor series

$$D(q(t+dt), p(t+dt), t+dt) = D(q(t), p(t), t) + \left( \frac{\partial D}{\partial q} \dot{q} + \frac{\partial D}{\partial p} \dot{p} + \frac{\partial D}{\partial t} \right) dt = D(q(t), p(t), t) \quad (103)$$

Since  $dt$  is arbitrary

$$\left( \frac{\partial D}{\partial q} \dot{q} + \frac{\partial D}{\partial p} \dot{p} + \frac{\partial D}{\partial t} \right) = 0 \quad (104)$$

- ▶ This clearly implies that  $\frac{dD}{dt} = 0$  where this is the total derivative.
  - ▶ This implies that  $D$  is a constant along a trajectory defined by the natural motion (Hamilton's eqs.)
  - ▶ Note that the partial derivative is taken at a fixed point in phase space.

Generalizing this to  $N$  particles and 3 dimensions we have

$$\{H, D\} + \frac{\partial D}{\partial t} = 0 \quad (105)$$

Where the Poisson bracket is

$$\{A, B\} = \sum_{i,\alpha} \left( \frac{\partial A}{\partial p_{i,\alpha}} \frac{\partial B}{\partial q_{i,\alpha}} - \frac{\partial A}{\partial q_{i,\alpha}} \frac{\partial B}{\partial p_{i,\alpha}} \right) \quad (106)$$

where  $\alpha$  labels the components of  $\vec{q}_i$  or  $\vec{p}_i$  and  $i$  labels the particle.

If we have a dynamical variable  $A(\{p_{i,\alpha}(t), q_{i,\alpha}(t)\}, t)$  then the total time derivative of  $A$  is

$$\frac{dA}{dt} = \sum_{i,\alpha} \left( \frac{\partial A}{\partial q_{i,\alpha}} \dot{q}_{i,\alpha} + \frac{\partial A}{\partial p_{i,\alpha}} \dot{p}_{i,\alpha} \right) + \frac{\partial A}{\partial t} \quad (107)$$

From Hamilton's equations

$$\frac{\partial H}{\partial p_{i,\alpha}} = \dot{q}_{i,\alpha} \quad \frac{\partial H}{\partial q_{i,\alpha}} = -\dot{p}_{i,\alpha} \quad (108)$$

we have

$$\frac{dA}{dt} = \sum_{i,\alpha} \left( \frac{\partial A}{\partial q_{i,\alpha}} \frac{\partial H}{\partial p_{i,\alpha}} - \frac{\partial A}{\partial p_{i,\alpha}} \frac{\partial H}{\partial q_{i,\alpha}} \right) + \frac{\partial A}{\partial t} \quad (109)$$

$$\frac{dA}{dt} = \sum_{i,\alpha} \left( \frac{\partial H}{\partial p_{i,\alpha}} \frac{\partial A}{\partial q_{i,\alpha}} - \frac{\partial H}{\partial q_{i,\alpha}} \frac{\partial A}{\partial p_{i,\alpha}} \right) + \frac{\partial A}{\partial t} \quad (110)$$

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$$\frac{dA}{dt} = \{H, A\} + \frac{\partial A}{\partial t} \quad (111)$$

- ▶ In the usual case  $\frac{\partial A}{\partial t} = 0$ . Therefore

$$\frac{dA}{dt} = \{H, A\} \quad (112)$$

- ▶ The time dependence of  $D$  is

$$\frac{\partial D}{\partial t} = -\{H, D\} \quad (113)$$

- ▶ The difference in the sign in the Poisson bracket is similar to the different signs in the time evolution of the dynamical operators and the density matrix in quantum mechanics
- ▶ Note that  $\frac{\partial D}{\partial t} = 0$  if  $D$  is only a function of  $H$ . This is easy to see by substitution.

## Statistical Entropy

Let  $\{e_m\}$  be a set of possible events with  $m = 1 \cdots M$  and the probability of  $e_m$  be  $P_m$  with

$$P_m \geq 0 \quad \sum_{m=1}^M P_m = 1 \quad (114)$$

**Definition** The entropy of the probability distribution  $P$  defined by the  $P_m$  is defined by

$$S[P] = - \sum_{m=1}^M P_m \ln P_m \quad (115)$$

- ▶ Clearly if  $P_m = 0$  then this term does not contribute to the entropy.
- ▶ If  $P_m = 1$  for some  $m$  and zero for all others then  $S[P] = 0$

- ▶ If all events have the same probability  $M^{-1}$  then we have the minimum of information and  $S[P] = \ln M$
- ▶ We have that

$$0 \leq S[P] \leq \ln M \quad (116)$$

- ▶ To see this we look for the extrema of  $S[P]$  with the constraint that  $\sum_m P_m = 1$ .
  - ▶ We deal with the constraint by using the Lagrange multiplier.

We define

$$\tilde{S}[P] = - \sum_{m=1}^M P_m \ln P_m - \lambda \left( \sum_{m=1}^M P_m - 1 \right) \quad (117)$$

$$\frac{\partial \tilde{S}}{\partial P_m} = -(\ln P_m + 1 + \lambda) = 0 \quad (118)$$

$$\rightarrow P_m = e^{-(1+\lambda)} \quad (119)$$

Since  $\sum_{m=1}^M P_m = 1 \rightarrow M e^{-(\lambda+1)} = 1$  or

- ▶  $P_m = 1/M$ .

- ▶ Hence  $P_m = 1/M$  is an extremum of  $S$  that satisfies the normalization constraint.
- ▶ The second derivative of  $\tilde{S}$  or  $S$  is  $-\frac{1}{P_m} \rightarrow P_m = 1/M$  is a maximum.
- ▶ This implies that the maximum of the entropy is  $\ln M$
- ▶ Since  $P_m \geq 0$  by definition, the inequality in eq.(116) is satisfied.

### The entropy of a probability distribution is additive

Let there be two sets of independent events  $\{e'_{m'}\}$  and  $\{e_m\}$

- ▶ The probability of observing the pair  $\{e_m, e'_{m'}\}$   
 $P_{m,m'} = P_m P_{m'}$

$$S[P_{m,m'}] = \sum_m \sum_{m'} P_m P_{m'} (\ln P_m + \ln P_{m'}) \quad (120)$$

Since  $\sum_{m'} P_{m'} = 1$

$$\sum_m \sum_{m'} P_m P_{m'} \ln P_m = \sum_m P_m \ln P_m \quad (121)$$

Therefore

$$S[P_{m,m'}] = S[P_m] + S[P_{m'}] \quad (122)$$

We state without proof the general inequality

$$S[P \times P'] \leq S[P] + S[P'] \quad (123)$$

## Statistical entropy of a mixed quantum state

The definition of the entropy in a mixed quantum state is modeled after that of the probability distribution.

Let  $D$  be the density operator of a mixture

$$D = \sum_m |\psi_n\rangle p_n \langle \psi_n| \quad (124)$$

If we now switch to an ortho-normal basis  $|m\rangle$

$$D = \sum_m |m\rangle P_m \langle m| \quad (125)$$

The statistical entropy  $S_{st}$  of the mixed state described by  $D$  is defined as

$$S_{st}[D] = -k \sum_m P_m \ln P_m = -k \text{Tr} D \ln D \quad (126)$$

The last step can be seen in the following way.

- ▶ Since the basis is ortho-normal  $D$  is diagonal with the diagonal elements  $\leq 1$
- ▶ We can write  $D = I + \alpha$  where  $I$  is the identity matrix and  $\alpha$  is diagonal where  $\alpha_j \leq 1$
- ▶ The operator  $\ln I + \alpha$  is a diagonal matrix with elements equal to  $\sum_{n=1}^{\infty} (-1)^{n+1} \frac{(\alpha_j)^n}{n}$
- ▶  $D \ln D$  is then a diagonal matrix with elements  $P_m \ln P_m$  so the trace of  $D \ln D$  is  $\sum_n P_n \ln P_n$
- ▶  $k$  is Boltzmann's constant which is introduced so that this definition of entropy will correspond, as we will see, to the thermodynamic entropy in equilibrium.

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- ▶ The additivity property of the statistical entropy is obtained by examining a system made of two non-interacting sub systems.
- ▶ Let  $H^{(a)}$  be the Hilbert space of the first system and  $H^{(\alpha)}$  of the second.
- ▶ The total Hilbert space is the tensor product  $H^{(a)} \times H^{(\alpha)}$

- ▶ Operators in this product space are of the form (each Hilbert space is two dimensional in this example) of a 4 index tensor. Symbolically we can write

$$D_{a\alpha;b\beta} = D_{ab}^{(a)} D_{\alpha\beta}^{(\alpha)} \quad (127)$$

- ▶ We assume that we can diagonalize the sub-matrices so that the product operator can be put in diagonal form.

In diagonal form

$$D_{a\alpha;b\beta} = D_{aa}^{(a)} D_{\alpha\alpha}^{(\alpha)} \delta_{ab} \delta_{\alpha\beta} \quad (128)$$

Therefore the entropy is

$$Tr D \ln D = \sum_{a,\alpha} D_{aa}^{(a)} D_{\alpha\alpha}^{(\alpha)} (\ln D_{aa}^{(a)} + D_{\alpha\alpha}^{(\alpha)}) \quad (129)$$

$$Tr D \ln D = Tr D^{(a)} \ln D^{(a)} + Tr D^{(\alpha)} \ln D^{(\alpha)} \quad (130)$$

Therefore

$$S_{st}[D] = S_{st}[D^{(a)}] + S_{st}[D^{(\alpha)}] \quad (131)$$

- ▶ The entropy is additive when the systems do not interact
- ▶ When the systems are not independent the density operator of one system is defined by taking the trace of the total density operator with respect to the indicies that define the other system.
  - ▶ We will refer to this as a partial trace.

That is

$$D^{(\alpha)} = Tr_{\alpha} D = D_{ab}^{(a)} = \sum_{\alpha} D_{a\alpha; b\alpha} \quad (132)$$

Suppose  $A$  is an operator that acts only on the  $a$  part of Hilbert space.  $A = A^{(a)} \times I^{(\alpha)}$

$$\langle A \rangle = \text{Tr}AD = \sum_{a,\alpha,b,\beta} A_{ab}^{(a)} \delta_{\alpha\beta} D_{b\beta;a\alpha} \quad (133)$$

$$\langle A \rangle = \sum_{ab} A_{ab}^{(a)} \sum_{\alpha} D_{b\alpha;a\alpha} = \text{Tr}A^{(a)}D^{(a)} \quad (134)$$

- Note that the average reduces to the trace using the reduced density operator generated from the partial trace.

We now state two theorems without proof.

- In analogy with the entropy of a probability distribution (eq.(123)) when two systems interact the statistical entropy satisfies

$$S_{st}[D] \leq S_{st}[D^{(a)}] + S_{st}[D^{(\alpha)}] \quad (135)$$

- If  $X$  and  $Y$  are two positive Hermetian operators

$$\text{Tr}X \ln Y - \text{Tr}X \ln X \leq \text{Tr}Y - \text{Tr}X \quad (136)$$

where the equality only holds if  $X = Y$

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## Time evolution of the statistical entropy

To calculate the time evolution we need to calculate the time derivative of  $-K_B \text{Tr} D \ln D$ .

To see that this is not straightforward we note that functions of operators are defined by Taylor series. That is

$$f(A) = \sum_{n=0}^{\infty} \frac{1}{n!} f^{(n)}(0) A^n \quad (137)$$

$$\frac{d}{dt} A^n = \frac{dA}{dt} A^{n-1} + A \frac{dA}{dt} A^{n-2} + \dots + A^{n-1} \frac{dA}{dt} \quad (138)$$

This cannot be regrouped to give  $nA^{n-1} dA/dt$  unless  $A$  commutes with  $dA/dt$ . In general this is not true.

- The trace is invariant under cyclic permutations so

$$\text{Tr} A \frac{dA}{dt} A^{n-1} = \text{Tr} A^n \frac{dA}{dt} \quad (139)$$

- The operators  $A$  and  $dA/dt$  can be treated as commuting within the trace.

Hence

$$\text{Tr}\left(\frac{d}{dt}A^n\right) = n\text{Tr}\left(A^{n-1}\frac{dA}{dt}\right) \quad (140)$$

Hence by re-summing the series

$$\text{Tr}\left(\frac{d}{dt}f(A)\right) = \text{Tr}\left(f'(A)\frac{dA}{dt}\right) \quad (141)$$

We can also write since the derivative commutes with the trace (do  $2 \times 2$ )

$$d(\text{Tr } f(A)) = \text{Tr}(f'(A)dA) \quad (142)$$

$$\frac{dS_{st}}{dt} = -K_B \frac{d}{dt} \text{Tr} D \ln D = -K_B \text{Tr} \ln D \frac{dD}{dt} \quad (143)$$

where

$$\text{Tr} \frac{dD}{dt} = \frac{d\text{Tr} D}{dt} = \frac{d}{dt} 1 = 0 \quad (144)$$

Since (eq.(38))

$$\frac{dD}{dt} = -\frac{1}{i\hbar}[H(t), D] \quad (145)$$

Hence

$$\frac{dS_{st}}{dt} = \frac{K_B}{i\hbar} \text{Tr} \ln D [H(t), D] \quad (146)$$

Since the trace is invariant under cyclic permutation we have

$$\ln \text{Tr} D [H(t), D] = \text{Tr} [\ln D (H(t)D - DH(t))] \quad (147)$$

$$= \text{Tr} [H(t)D \ln D - H(t) \ln DD] \quad (148)$$

$$= \text{Tr} (H(t)[D, \ln D]) = 0 \propto \frac{dS_{st}}{dt} \quad (149)$$

→ For a system evolving under Hamiltonian motion the entropy is conserved

## Boltzmann Distribution

We now address the question of the probability of the microscopic state  $P_m$  consistent with the specified macroscopic constraints that give rise to the (probability) density (operator)  $D$ .

- ▶ If there is no information that constrains the probability then we know that each of the  $M$  accessible states is equally probable so that  $P_m = 1/M$ .
  - ▶ We want to generalize this to the case where we have partial information.
- ▶ The partial information can be of two types.
  - ▶ We have data that puts definite constraints on the microscopic states. For example we might know that the energy is constrained to be between  $E$  and  $E + \Delta E$ .
  - ▶ We have data that puts statistical constraints on the microscopic variables. For example we might know the average energy so that  $\langle H \rangle = TrDH$  is fixed.

In the case of definite microscopic constraints; If the energy uncertainty  $\Delta E$  is small compared with the energy  $E$  ( $\Delta E \ll E$ ) but  $\Delta E \gg 1/\rho(E)$  ( $\rho(E)$  is the energy level density) so that  $\Delta E$  is much greater than the energy level spacing, we call this constraint micro canonical.

- ▶ Then the only acceptable states  $|r\rangle$  are the eigenvectors of  $H$  such that  $H|r\rangle = E_r|r\rangle$  and

$$E \leq E_r \leq E + \Delta E \quad (150)$$

- ▶ If there are no other constraints then each allowed microscopic state will be equally probable and  $P_r = 1/M$  where  $M = \rho(E)\Delta E$  is the number of states that satisfy eq(150).
- ▶ The density operator is then

$$D = \sum_r |r\rangle \frac{1}{M} \langle r| \quad E \leq E_r \leq E + \Delta E \quad (151)$$

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- ▶ The entropy is (eq(126))

$$S_{st}[D] = -K_B \text{Tr} D \ln D \quad (152)$$

- ▶ Since the  $|r\rangle$  are energy eigen-states they are ortho-normal(or can be made so) so that the density matrix is diagonal and

$$S_{st} = K_B \ln M \quad (153)$$

- ▶ The micro-canonical ensemble is not very convenient and in general does not reflect the usual experimental constraints. We turn to statistical constraints.
- ▶ To express these constraints conveniently we adopt the notation that

$$\bar{A}_i = \langle A_i \rangle = \text{Tr} D A_i \quad (154)$$

- ▶ We adopt the principle of equal a priori probability. That is: Consistent with constraints, each micro-scopic state is equally likely.
  - ▶ This is reasonable in that if there is no reason to prefer one state over the other they are equally likely.
  - ▶ Since the equally probable micro-states maximize the entropy this leads to the postulate

### **Postulate of maximum statistical entropy**

Among all the density operators consistent with the macroscopic constraints, we must choose the density operator  $D$  that gives the maximum statistical entropy  $S_{st}$ . At equilibrium, a macro-state will be represented by this density operator.

(Remember the definition of equilibrium in chapter 1.)

- ▶ This means that we choose the most disordered macro-state consistent with the available information
- ▶ The density operator contains no information beyond what is necessary to satisfy the macroscopic constraints.

## Equilibrium distribution

Statistical constraints define various ensembles. The two most common examples are

- ▶ If we impose the constraint on the average energy  $\langle H \rangle = \text{Tr}DH$  this will be referred to as the canonical ensemble.
- ▶ If, **in addition**, one is given the particle number operator  $N$  and  $\langle N \rangle = \text{Tr}DN$  is fixed we have the grand canonical ensemble.
- ▶ In addition to these statistical constraints we also have the constraint

$$\text{Tr}D = 1 \quad (155)$$

The method for finding the equilibrium distributions is to maximize the entropy subjects to the above constraints. That is

$$\frac{1}{K_B} \tilde{S}_{st}[D] = -\text{Tr} D \ln D + \sum_i \lambda_i (\text{Tr} D A_i - \bar{A}_i) - \lambda_o (\text{Tr} D - 1) \quad (156)$$

- ▶ We want to maximize  $\tilde{S}_{st}$  with respect to  $D$ .  $\rightarrow$   
Take the differential with respect to  $D$ .
- ▶ We use eq.(142)

$$d(\text{Tr} f(A)) = \text{Tr}(f'(A) dA) \quad (157)$$

$$\text{Tr} \left[ dD \left( \ln D + 1 - \sum_i \lambda_i A_i + \lambda_o \right) \right] \quad (158)$$

- ▶ Since  $dD$  is arbitrary the term in the () must be zero.  $\rightarrow$

$$D_B = \frac{1}{Z} \exp\left(\sum_i \lambda_i A_i\right) \quad (159)$$

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- $Z^{-1} = \exp[1 + \lambda_o]$  is chosen to obtain  $Tr D = 1$ .

$$\rightarrow Z = Tr \exp\left(\sum_i \lambda_i A_i\right) \quad (160)$$

- $D_B$  is referred to as the Gibbs or Gibbs-Boltzmann distribution and  $Z$  is the partition function.  
Clearly

$$S_B = S_{st}[D_B] = -K_B Tr D_B \ln D_B \quad (161)$$

$$S_B = -K_B \ln Z - \sum_i \lambda_i \bar{A}_i \quad (162)$$

where we have used eq.(159) in eq.(161).

- The entropy is an extremum by construction. We now show it is a maximum.  
Let  $D$  be a density operator that satisfies

$$Tr D A_i = \bar{A}_i \quad Tr D = 1 \quad (163)$$

Using eq.(136)

$$\text{Tr} X \ln Y - \text{Tr} X \ln X \leq \text{Tr} Y - \text{Tr} X$$

and substituting  $Y \rightarrow D_B$  and  $X \rightarrow D$  we obtain

$$\text{Tr} D \ln D_B - \text{Tr} D \ln D \leq \text{Tr} D_B - \text{Tr} D \quad (164)$$

Since

$$\text{Tr} D_B = \text{Tr} D = 1 \quad (165)$$

we have

$$- \text{Tr} D \ln D \leq - \text{Tr} D \ln D_B \quad (166)$$

$$- \text{Tr} D \ln D \leq \text{Tr} D \ln Z - \text{Tr} D \sum_i \lambda_i A_i \quad (167)$$

$$- \text{Tr} D \ln D \leq \ln Z - \sum_i \lambda_i \bar{A}_i \quad (168)$$

where we have used  $\text{Tr} D A_i = \bar{A}_i$  and  $\text{Tr} D = 1$ .

Since  $S_{st} = K_B \text{Tr} D \ln D$  and from eq.(162) we have

$$S_{st}[D] \leq S_{st}[D_B] = S_B \quad (169)$$

- ▶ Clearly if a distribution satisfies the conditions in eq.(163) then the form  $D_B$  in eq.(159) maximizes the entropy.
- ▶ Also the fact that eq.(136) is only satisfied as an equality when  $X = Y$  means that the solution to the maximization equation is unique.

### **Legendre transformation**

- ▶ The average values of the operators  $A_i$  can be related to the derivatives of the partition function with respect to the Lagrange multipliers  $\lambda_i$   
Using eq.(157)

$$d(\text{Tr} f(A)) = \text{Tr}(f'(A)dA)$$

or alternatively we can assume that we can exchange the derivative with respect to  $\lambda_i$  with the trace.

$$\frac{1}{Z} \frac{\partial}{\partial \lambda_j} \text{Tr} \exp \left[ \sum_i \lambda_i A_i \right] = \frac{1}{Z} \text{Tr} (A_j \exp \left[ \sum_i \lambda_i A_i \right]) \quad (170)$$

$$= \text{Tr} (D_B A_j) = \bar{A}_j \quad (171)$$

In other words

$$\bar{A}_j = \frac{\partial}{\partial \lambda_j} \ln Z[\lambda_j] \quad (172)$$

- Equation(172) indicates that the partition function  $Z$  should be considered a function of the Legendre multipliers  $\{\lambda_i\}$ .

From eq.(162)

$$S_B = -K_B \ln Z - \sum_i \lambda_i \bar{A}_i$$

and eq.(172) we have

$$\frac{1}{K_B} S_B = \ln Z - \sum_i \lambda_i \frac{\partial \ln Z}{\partial \lambda_i} \quad (173)$$

- ▶ As we will see eq.(173) is a Legendre transformation equivalent to the Legendre transformations discussed in the section on thermodynamics.
- ▶ Since the partition function is to be considered a function of the  $\lambda_i$  we have

$$d \ln Z = \sum_i \frac{\partial \ln Z}{\partial \lambda_i} d\lambda_i = \frac{1}{Z} \frac{\partial}{\partial \lambda_i} \text{Tr} \exp \left[ \sum_i \lambda_i A_i \right] d\lambda_i \quad (174)$$

$$= \sum_i \text{Tr} \frac{1}{Z} A_i \exp \left[ \sum_i \lambda_i A_i \right] d\lambda_i \quad (175)$$

$$d \ln Z = \sum_i \bar{A}_i d\lambda_i \quad (176)$$

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Hence from eqs.(173) - (176)

$$dS_B = d \ln Z - \sum_i \lambda_i d\bar{A}_i - \sum_i \bar{A}_i d\lambda_i \quad (177)$$

$$dS_B = -K_B \sum_i \lambda_i dA_i \quad (178)$$

- ▶ In general it is the partition function we use to calculate the properties of the system rather than the density operator
- ▶ We want to look at the response of the system to changes in the Legendre multipliers  $\lambda_j$ .
- ▶ We begin by assuming that the operators  $A_j$  and  $A_i$  commute  $\forall i$  and  $j$ .

If the operators commute then we can take the derivative of the partition function and treat the  $A_i$  as scalars. Hence

$$\frac{\partial^2 Z}{\partial \lambda_i \partial \lambda_j} = \text{Tr} [A_i A_j \exp(\sum_k \lambda_k A_k)] = Z \langle A_i A_j \rangle \quad (179)$$

or

$$\frac{1}{Z} \frac{\partial^2 Z}{\partial \lambda_i \partial \lambda_j} - \left( \frac{1}{Z} \frac{\partial Z}{\partial \lambda_i} \right) \left( \frac{1}{Z} \frac{\partial Z}{\partial \lambda_j} \right) = \frac{\partial^2 \ln Z}{\partial \lambda_i \partial \lambda_j} \quad (180)$$

As we have shown (eq.(172))

$$\frac{\partial \ln Z}{\partial \lambda_i} = \bar{A}_i \quad (181)$$

So

$$\frac{\partial^2 \ln Z}{\partial \lambda_i \partial \lambda_j} = \frac{\partial \bar{A}_i}{\partial \lambda_j} \quad (182)$$

We have then

$$\frac{\partial^2 \ln Z}{\partial \lambda_i \partial \lambda_j} = \frac{\partial \bar{A}_i}{\partial \lambda_j} = \langle A_i - \bar{A}_i \rangle \langle A_j - \bar{A}_j \rangle = \langle A_i A_j \rangle - \bar{A}_i \bar{A}_j \quad (183)$$

- This is called the fluctuation-response theorem since  $\langle A_i A_j \rangle - \bar{A}_i \bar{A}_j$  measures the fluctuations in the dynamical variable  $A_i$  and  $\frac{\partial \bar{A}_i}{\partial \lambda_j}$  is the response of  $\bar{A}_i$  to a change in the Legendre multiplier  $\lambda_j$  and eq.(183) relates them..
- We can use this result to prove an important positivity result  
Define an operator

$$B = \sum_k a_k (A_k - \bar{A}_k) \quad (184)$$

where the  $a_k$  are real numbers.

From eq.(183) we have

$$\sum_{i,j} a_i a_j \frac{\partial^2 \ln Z}{\partial \lambda_i \partial \lambda_j} = \sum_{i,j} a_i C_{ij} a_j = \langle B^2 \rangle \geq 0 \quad (185)$$

- Note that  $\sum_{i,j} a_i C_{ij} a_j \geq 0$  along with the fact that the  $\{a_i\}$  are arbitrary and real implies that

$$C_{ij} = \frac{\partial^2 \ln Z}{\partial \lambda_i \partial \lambda_j} \quad (186)$$

is a positive definite matrix and  $\ln Z$  is a convex function of the  $\{\lambda_i\}$ . Also  $\rightarrow$  the diagonal elements  $C_{ii} \geq 0$ .

- This is the same condition we saw in the discussion of stability in chapter 1.
- This implies (as we have seen) that  $S_B$ , the Legendre transform of  $\ln Z$  is a concave function of the  $\{A_i\}$ .

## Canonical and Grand Canonical Ensemble

We now want to introduce the canonical and grand canonical ensemble. We will treat them in more detail later.

- ▶ In the canonical ensemble the volume  $V$  and the number of particles  $N$  are controlled and hence are known precisely.
- ▶ The energy is not controlled but its average value is  $\rightarrow A_{i=1} = H; A_i = 0 \quad \forall i \neq 1$ .

It is conventional to write  $\lambda_1 = \beta$  and we will see that  $\beta = 1/K_B T$ .

The partition function is then

$$Z = \text{Tr} \exp[-\beta H] \quad (187)$$

and the density operator  $D_B$  is

$$D_B = \frac{1}{Z} \exp[-\beta H] = \frac{1}{Z} \sum_r |r\rangle e^{-\beta E_r} \langle r| \quad (188)$$

Where  $H|r\rangle = E_r|r\rangle$  and the  $|r\rangle$  are an ortho-normal basis.

To see the second equality we have

$$e^{-\beta H}|\psi\rangle = \sum_r e^{-\beta H} a_r |r\rangle = \sum_r a_r \sum_n \frac{(-\beta H)^n}{n!} |r\rangle \quad (189)$$

$$= \sum_r a_r \sum_n \frac{(-\beta E_r)^n}{n!} |r\rangle = \sum_r a_r e^{-\beta E_r} |r\rangle \quad (190)$$

We also have

$$\sum_r |r\rangle e^{-\beta E_r} \langle r|\psi\rangle = \sum_r |r\rangle e^{-\beta E_r} \sum_n \langle r|a_n|n\rangle \quad (191)$$

$$= \sum_r |r\rangle e^{-\beta E_r} \sum_n a_n \delta_{nr} = \sum_r a_r |r\rangle e^{-\beta E_r} \quad (192)$$

as in eq.(190).

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If the system is composed of two non-interacting subsystems then

$$H = H^{(a)} + H^{(b)} \quad [H^{(a)}, H^{(b)}] = 0 \quad (193)$$

- ▶ We saw in the previous discussion that operators on spaces that are the sum of two independent systems are tensor products of operators acting independently of the sub-systems
- ▶ The basis in Hilbert space is factorized so we have

$$|I\rangle = |a\rangle \times |\alpha\rangle \quad |m\rangle = |b\rangle \times |\beta\rangle \quad (194)$$

where  $\{|a\rangle\}$  and  $\{|\alpha\rangle\}$  are the eigen vectors of  $H^{(a)}$  and  $H^{(\alpha)}$  respectively and are ortho-normal bases vectors of the Hilbert spaces.

Hence we have

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$$\begin{aligned}
 \langle I | H | m \rangle &= \langle a | \times \langle \alpha | (H^{(a)} + H^{(\alpha)}) | \alpha \rangle \times | a \rangle \\
 &= (H_{ab}^{(a)} + H_{\alpha\beta}^{(\alpha)}) \delta_{ab} \delta_{\alpha\beta}
 \end{aligned} \tag{195}$$

- Since  $H^{(a)}$  and  $H^{(\alpha)}$  commute we have from the Taylor series expansion

$$\langle I | e^{-\beta H} | m \rangle = \exp[-\beta H_{ab}^{(a)}] \exp[-\beta H_{\alpha\beta}^{(\alpha)}] \delta_{ab} \delta_{\alpha\beta} \tag{196}$$

Therefore

$$\begin{aligned}
 Z &= \text{Tre}^{-\beta H} = \left( \sum_a e^{-\beta H_{aa}^{(a)}} \right) \left( \sum_{\alpha} e^{-\beta H_{\alpha\alpha}^{(\alpha)}} \right) \\
 &= Z^{(a)} Z^{(\alpha)}
 \end{aligned} \tag{197}$$

**The partition function of two non-interacting systems is the product of the partition functions of each system**

In the grand canonical ensemble we have  $A_1 = H$  and  $A_2 = N$  and all the other operators  $A_i = 0$

- ▶ It is customary to write  $\lambda_1 = \beta$  as in the canonical ensemble and  $\lambda_2 = \alpha$
- ▶ We will see that  $\alpha = \beta\mu$  where  $\mu$  is the chemical potential.

The grand canonical or grand partition function is

$$Q = \text{Tr} \exp[-\beta H + \alpha N] \quad (198)$$

and the density operator is

$$D_B = \frac{1}{Q} \exp[-\beta H + \alpha N] \quad (199)$$

## Thermodynamics Revisited

### Heat and work: first law

We now want to relate the thermodynamic quantities that we considered in the first two weeks to the statistical concepts we just discussed.

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We now consider a system  $A$  that can exchange heat with a reservoir  $R$ .

- ▶ The combined system  $R + A$  is thermally isolated from the outside world
- ▶  $A$  is connected to a piston so that work can be done on or by the system.
- ▶ We only consider quasi static processes so that the process can be described by a Hamiltonian
- ▶ The systems walls are impermeable so that the number of particles is fixed.

The Hamiltonian of the system is

$$H_{tot} = H + H_R + V \quad (200)$$

where  $H$  is the Hamiltonian of the system  $A$ ,  $H_R$  is that of the reservoir and  $V$  is interaction between the system and the reservoir.

- ▶ Since we will assume that the interaction between  $A$  and  $R$  is a surface effect we can assume it to be negligible. However it is not zero.

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Let  $D_{tot}$  be the density operator of the system/reservoir combination. We have for the time evolution

$$i\hbar \frac{dD_{tot}}{dt} = [H, D_{tot}] + [H_R, D_{tot}] + [V, D_{tot}] \quad (201)$$

- ▶ The density operator of the system is obtained by taking the partial trace over the reservoir variables. Defining  $Tr_R D_{tot} = D$  we have (since  $H$  does not depend on the reservoir variables)

$$i\hbar \frac{dD}{dt} = [H, D] + Tr_R[V, D_{tot}] + Tr_R[H_R, D_{tot}] \quad (202)$$

- ▶ Remember that the total density operator  $D_{tot}$  operates on the product Hilbert space and hence is a four index tensor  $D_{a\gamma; b\alpha}$
- ▶  $H_R$  is a four index operator or tensor acting non-trivially only on the reservoir Hilbert space. Hence

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$$H_{R:a\alpha;c\gamma} = H_{R:\alpha\gamma}\delta_{ac} \quad (203)$$

- We now take the partial trace with respect to the reservoir variables

$$\begin{aligned} \text{Tr}_R(H_R D_{\text{tot}}) &= \sum_{\alpha} (H_R D_{\text{tot}})_{a\alpha;b\alpha} = \\ &= \sum_{\alpha,\gamma} H_{R:\alpha,\gamma} D_{\text{tot}:a,\gamma;b,\alpha} \end{aligned} \quad (204)$$

- The  $H_{R:\alpha,\gamma}$  and  $D_{\text{tot}:a,\gamma;b,\alpha}$  terms and the summation indicies can be interchanged to give

$$\sum_{\gamma,\alpha} D_{\text{tot}:a,\alpha;b,\gamma} H_{R:\gamma,\alpha} \quad (205)$$

This is simply  $\text{Tr}_R(D_{\text{tot}} H_R)$  so that

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$$\text{Tr}_R(H_R D_{\text{tot}}) = \text{Tr}_R(D_{\text{tot}} H_R) \rightarrow \text{Tr}_R[H_R, D_{\text{tot}}] = 0 \quad (206)$$

Hence

$$i\hbar \frac{dD}{dt} = [H, D] + \text{Tr}_R[V, D_{\text{tot}}] \quad (207)$$

This equation is not closed.  $dD/dt$  does not depend only on the system variables

- This implies that there is no Hamiltonian that governs the evolution of  $D$ .

The time change of the average energy  $E$  is given by

$$\frac{dE}{dt} = \frac{d}{dt} \text{Tr}(DH) = \text{Tr}\left(H \frac{dD}{dt}\right) + \text{Tr}\left(D \frac{dH}{dt}\right) \quad (208)$$

- The trace is over the system variables.

The first term on the right hand side describes the interaction with the reservoir since it depends on  $V$ .  
From eq.(207) we have

$$\text{Tr}(H \frac{dD}{dt}) = \frac{1}{i\hbar} \text{Tr}(H[H, D]) + \frac{1}{i\hbar} \text{Tr} \text{Tr}_R(H[V, D_{\text{tot}}]) \quad (209)$$

- The trace is invariant under cyclic permutation

$$\begin{aligned} \text{Tr}(H[HD - DH]) &= \text{Tr}(HHD) - \text{Tr}(HDH) \\ &= \text{Tr}(HHD) - \text{Tr}(HHD) = 0 \end{aligned} \quad (210)$$

Hence

$$\text{Tr}(H \frac{dD}{dt}) = \frac{1}{i\hbar} \text{Tr} \text{Tr}_R H[V, D_{\text{tot}}] \quad (211)$$

From  $\text{Tr} \text{Tr}_R = \text{Tr}_{\text{tot}}$  (the trace over all degrees of freedom) and the invariance of the trace under cyclic permutation

$$\text{Tr}(H \frac{dD}{dt}) = \frac{1}{i\hbar} \text{Tr}_{\text{tot}}(D_{\text{tot}}[H, V]) \quad (212)$$

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Therefore

$$\frac{dE}{dt} = \frac{1}{i\hbar} \text{Tr}_{tot}(D_{tot}[H, V]) + \text{Tr}(D \frac{dH}{dt}) \quad (213)$$

Since  $D = \text{Tr}_R D_{tot}$  and  $H$  is the system Hamiltonian they do not depend on the properties of the reservoir.

- ▶ The second term on the right hand side of eq.(213) then cannot describe heat transfer since it is independent of the reservoir.
- ▶ The heat transfer is described by the first term on the right hand side of eq.(213) which depends on  $V$ .
- ▶ The second term on the right hand side of eq.(213) describes the energy change in the form of work.

To see this we note that the time dependence of the Hamiltonian depends on the **controllable** external parameters.

- ▶ We have assumed that the Hamiltonian is time independent if the system is isolated  $\rightarrow$  the time dependence is in the external parameters.

- ▶ For example in the Ising model the Hamiltonian

$$H = -J \sum_{ij} s_i s_j - h \sum_j s_j \quad (214)$$

depends on the magnetic field  $h$  and the coupling constant  $J$ .

- ▶ We will take the coupling constant  $J$  to be independent of the time.
  - ▶ In most cases of interest the interaction is independent of the time but it can happen in for example very high pressure.
- ▶ This means that the work will come from the time dependence of  $h$
- ▶ In a fluid the controllable external variable is the volume. The simplest way to see this is the quantum Hamiltonian

$$H = \sum_n |n\rangle E_n \langle n| \quad (215)$$

The  $|n\rangle$  are the eigen-vectors of the Hamiltonian and the  $E_n$  are eigen-values.

- Consider a free particle. The eigen-values and eigen-vectors depend on the system size.

Since the potential of interaction will (usually) not change, the Hamiltonian will change with the volume.

We have with these examples

$$\text{Tr}\left(D\frac{dH}{dt}\right) = \sum_i \left(D\frac{\partial H}{\partial x_i}\bigg|_{x_j \neq i}\right) \frac{dx_i}{dt} \quad (216)$$

This implies that

$$dE = d(\text{Tr}(DH)) = \text{Tr}(HdD) + \text{Tr}(DdH) = dQ + dW \quad (217)$$

- We identify

$$dQ = \text{Tr}(HdD) \quad dW = \text{Tr}(DdH) \quad (218)$$

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- With these considerations we can say that the transfer of heat changes the occupation of energy levels and the work modifies the levels themselves (Hamiltonian). This is true for quasi static transformations.

## Entropy and Temperature

We now show that the Lagrange multiplier  $\beta$  is an inverse temperature. We begin with the Boltzmann entropy (eq.(161))

$$S_B = -K_B \text{Tr}(D_B \ln D_B)$$

$$dS_B = -K_B \text{Tr}(dD_B (\ln D_B + 1)) \quad (219)$$

where we have used eq.(157). Using the fact that again from eq.(157)

$$\text{Tr} dD_B = d \text{Tr} D_B = d1 = 0 \quad (220)$$

From the form  $D_B = e^{-\beta H}/Z$  (eqs.(187 and (188))

$$dS_B = K_B \text{Tr}(dD_B[\ln Z + \beta H]) = K_B \beta \text{Tr}(H dD_B) \quad (221)$$

where we again have used the fact that  $\text{Tr} dD_B = 0$  and  $Z$  is already traced over.

- From eq.(218) we have

$$dS_B = K_B \beta dQ \quad (222)$$

Remembering that  $S_B$  is the statistical entropy and  $S$  is the thermodynamic entropy we have

$$dS = \frac{dQ}{T} \quad (223)$$

so

$$dS_B = K_B \beta T dS \quad (224)$$

- Dividing both sides of eq.(224) by  $d\beta$  and taking the limit  $d\beta \rightarrow 0$  keeping the external parameters constant we have

$$\frac{\partial S_B}{\partial \beta} = K_B \beta T \frac{\partial S}{\partial \beta} \quad (225)$$

Doing the same thing for the external parameters

$$\frac{\partial S_B}{\partial x_i} = K_B \beta T \frac{\partial S}{\partial x_i} \quad (226)$$

Differentiating eq.(225) with respect to  $x_i$  and using the facts that the partials can be exchanged and that  $T$  is independent of  $x_i$ .

$$\frac{\partial^2 S_B}{\partial \beta \partial x_i} = K_B \beta T \frac{\partial^2 S}{\partial \beta \partial x_i} \quad (227)$$

Differentiating eq.(226) with respect to  $\beta$  and exchanging the partials we have

$$\frac{\partial^2 S_B}{\partial \beta \partial x_i} = K_B \beta T \frac{\partial^2 S}{\partial \beta \partial x_i} + \frac{\partial(K_B \beta T)}{\partial \beta} \frac{\partial S}{\partial x_i} \quad (228)$$

Equating eqs.(227) and (228) we see that  $K_B\beta T$  must be a constant.

- ▶ We can always choose units where  $\beta = 1/K_B T$  so that  $S_B - S = \text{constant}$ . (Integrate both sides of  $dS_B = dS$ )
- ▶ The constant of integration is zero since  $S$  and  $S_B$  vanish at  $T = 0$ .
  - ▶ The thermodynamic entropy goes to zero as  $T \rightarrow 0$  (see chapter 1)
  - ▶ The Boltzmann entropy also goes to zero since at  $T = 0$  the system is in its (energy) ground state.

## Entropy of Mixing

We discuss the entropy of mixing which illustrates that entropy increase is not always associated with heat.

- ▶ We will use as an example the ideal gas in the canonical ensemble.
- ▶ We begin with the Hamiltonian for a system of  $N$  particles

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$$H = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} \quad (229)$$

where  $\vec{p}$  is the momentum operator. For the ideal gas the partition function is the product of the individual partition functions  $\zeta$ . We have then

$$\zeta = \sum_{\vec{p}} \langle \vec{p} | \exp(-\beta \frac{\vec{p}^2}{2m}) | \vec{p} \rangle \quad (230)$$

$$\zeta = \frac{V}{h^3} \int d^3p \exp(-\beta \frac{\vec{p}^2}{2m}) = V \left( \frac{2\pi m}{\beta h^2} \right)^{3/2} \quad (231)$$

where we have used eq.(76)

- Therefore the partition function of the ideal gas with  $N$  particles in  $d = 3$  is

$$Z_N = V^N \left( \frac{2\pi m}{\beta h^2} \right)^{3N/2} \quad (232)$$

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This expression needs to be modified.

- ▶ Note that this expression leads to a free energy ( $\ln Z$ ) that is not extensive since it will have a term of order  $N \ln V$
- ▶ To correct this problem we note that in quantum systems the particles are indistinguishable which means that the number of configurations (example: lattice gas) is over counted and we must divide by  $N!$
- ▶ Hence the partition function becomes

$$Z_N = \frac{V^N}{N!} \left( \frac{2\pi m}{\beta h^2} \right)^{3N/2} \quad (233)$$

- ▶ Note that this will also be the case in the classical limit of the quantum systems which we will see later in the semester.
  - ▶ The classical limit of the quantum case (either fd or be) will be referred to as Maxwell-Boltzmann statistics.

- Note that in the limit  $N \gg 1$  we can use Stirling approximation  $N! \sim N \ln N - N$

In the limit  $N \rightarrow \infty$

$$N! \sim N^N \exp(-N) \sim N^N \quad (234)$$

Hence

$$Z_N \sim \left( \frac{V^N}{N^N} \right) \left( \frac{2\pi m}{\beta h^2} \right)^{3N/2} \quad (235)$$

so the free energy will be extensive.

- From eq.(173) with the Legendre multiplier  $\lambda = -\beta$  (since we are in the canonical ensemble) the entropy is

$$S = K_B \ln Z_N - K_B \beta \left. \frac{\partial \ln Z_N}{\partial \beta} \right|_V \quad (236)$$

$$S = K_B \left[ \ln \frac{V}{N} + \frac{3}{2} \ln \left( \frac{2\pi m K_B T}{h^2} \right) + \frac{5}{2} \right] \quad (237)$$

Where we have used eq.(235) for  $Z_N$  in eq.(236).

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Note that we could have done the entire calculation classically by replacing quantum operators with classical vectors in eq.(231).

- That is

$$Z_N^{class} = C \int \prod_{i=1}^N d^3 r_i d^3 p_i \exp\left(-\sum_i \frac{\vec{p}_i^2}{2m}\right) \quad (238)$$

where we have used the integration measure in eq.(90).

- As mentioned previously we cannot determine the constant  $C$  from purely classical arguments but must go to quantum mechanics.
- Comparing the results of the integral in eq.(238) with eq.(233 we can see that the constant  $C$  contains quantum effects and

$$C = \frac{1}{N! h^{3N}} \quad (239)$$

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- ▶ The classical expression for the phase space measure is

$$d\Gamma = \frac{1}{N!} \prod_{i=1}^N \frac{d^3 r_i d^3 p_i}{h^3} \quad (240)$$

- ▶ Since the free energy is  $F = E - TS$  and (as we will see) the free energy is proportional to the  $\frac{1}{T} \ln Z$  we have

$$S = K_B \ln Z_N - K_B \beta \left. \frac{\partial \ln Z_N}{\partial \beta} \right|_V \quad (241)$$

- ▶ We can also see this from eq.(173) with the Lagrange multiplier  $\lambda_1 = -\beta$   
Using eq.(233) and Stirling approximation we obtain

$$S = K_B N \left[ \ln \frac{V}{N} + \frac{3}{2} \ln \left( \frac{2\pi m K_B T}{h^2} \right) + \frac{5}{2} \right] \quad (242)$$

- ▶ Consider now two different, classical, ideal gases in two compartments of a rigid adiabatic chamber (volume  $V$ ) with volumes  $V_1$  and  $V_2$  where  $V = V_1 + V_2$

- ▶ Each chamber has the same pressure  $P$  and temperature  $T$  and the number of molecules is  $N_1$  and  $N_2$  with  $N = N_1 + N_2$ .
- ▶ Since the gasses in the two chambers are not interacting the initial partition function of the combined system is the product

$$Z_N^{(in)} = Z_{N_1}(T, V_1) Z_{N_2}(T, V_2) \quad (243)$$

$$= \frac{V_1^{N_1}}{N_1!} \left( \frac{2\pi m_1 K_B T}{h^2} \right)^{3N_1/2} \frac{V_2^{N_2}}{N_2!} \left( \frac{2\pi m_2 K_B T}{h^2} \right)^{3N_2/2} \quad (244)$$

In the final partition function the two types of particles also do not interact but both types fill the volume  $V$ . Hence

$$Z_N^{(fin)}(T, V) = Z_{N_1}(T, V) Z_{N_2}(T, V) \quad (245)$$

$$= \frac{V^{N_1}}{N_1!} \left( \frac{2\pi m_1 K_B T}{h^2} \right)^{3N_1/2} \frac{V^{N_2}}{N_2!} \left( \frac{2\pi m_2 K_B T}{h^2} \right)^{3N_2/2} \quad (246)$$

- ▶ Since the term  $-K_B\beta(\partial \ln Z_N/\partial\beta)|_V$  in eq(241) is the energy, which is a function only of the temperature in an ideal gas, and the temperature remains constant, the term gives the same contribution to the initial and final entropies.

Therefore

$$\begin{aligned}
 S_{fin} - S_{in} \\
 = K_B \ln \frac{Z_N^{(fin)}}{Z_N^{(in)}} &= K_B \left[ N_1 \ln \frac{V}{V_1} + N_2 \ln \frac{V}{V_2} \right] \geq 0
 \end{aligned}
 \tag{247}$$

- ▶ Note that this means that the mixing of two gasses increases the entropy and hence the process is irreversible.
- ▶ Once the gasses are mixed they will not return to their initial compartments.
- ▶ The final state is more disordered than the initial state
- ▶ The increase in entropy is called the entropy of mixing.

- ▶ If the two gases are identical there is no entropy of mixing.
- ▶ Since the pressure and temperature are the same and we have an ideal gas then  $N_1/V_1 = N_2/V_2 = N/V$
- ▶ This means that the final partition function is

$$Z_N^{(fin)} = \frac{V^N}{N!} \left( \frac{2\pi m K_B T}{h^2} \right)^{3N/2} \quad (248)$$

- ▶ Note that this is not the expression we get if we simply put  $m_1 = m_2$  in eq(246).
- ▶ We can easily show that in the case of identical particles that the entropy difference is given by

$$S_{fin} - S_{in} = K_B \left[ N_1 \ln \frac{N_1 V}{N V_1} + N_2 \ln \frac{N_2 V}{N V_2} \right] \quad (249)$$

However, from above the argument of both  $\ln$  terms is one so that the entropy change is zero.

## Pressure and Chemical Potential

We now evaluate the energy exchanged in the form of work during a quasi-static process.

From eq(218) we have that  $dW = Tr(DdH)$   
Therefore

$$dW = Tr \left[ D_B \sum_i \frac{\partial H}{\partial x_i} dx_i \right] = \sum_i X_i dx_i \quad (250)$$

- ▶ We will refer to  $X_i$  as the conjugate variable to  $x_i$  calculated at equilibrium
- ▶ From eq(188) we have that

$$X_j = \left\langle \frac{\partial H}{\partial x_j} \right\rangle = \frac{1}{Z} Tr \left[ \frac{\partial H}{\partial x_j} e^{-\beta H} \right] = - \frac{1}{\beta} \frac{\partial \ln Z}{\partial x_j} \bigg|_{\beta, x_i \neq j} \quad (251)$$

In particular we can look at the variable conjugate to the volume, i.e. the pressure.

We have

$$P = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} \bigg|_{\beta, N} \quad (252)$$

Consider now that our system is connected to both a heat and particle reservoir. The volume, chemical potential and temperature are now the control parameters. The energy and the number of particles are only known on the average. The change in the Boltzmann entropy is given by eq.(219)

$$dS_B = -K_B \text{Tr}(dD_B(\ln D_B + 1))$$

which we have rewritten for convenience. The operator  $D_B$  is now the density operator in the grand canonical ensemble.(eq.(199))

$$D_B = \frac{1}{Q} \exp(-\beta H + \alpha N)$$

and  $Q$  is the partition function. Using the fact that  $\text{Tr} dD_B = 0$  (eq.(220)) we have

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$$\begin{aligned}
 dS_B &= K_B \beta \text{Tr}(H dD_B) - K_B \alpha \text{Tr}(N dD_B) \\
 &= K_B \beta dE - K_B \alpha dN
 \end{aligned} \tag{253}$$

Where we used eq(220) so that

$$\text{Tr}(H dD_B) = d\text{Tr}(H D_B) = dE$$

and the same for  $dN$ . Note that we have also used

$$\text{Tr}(dH D_B) = 0 \tag{254}$$

- Note that since  $H$  is a fluctuating variable the average of the difference  $\langle dH \rangle = 0$  as is  $\langle dN \rangle = 0$

Using these results we have from eq(253)

$$T dS_B = K_B T \beta dE - K_B T \alpha dN \tag{255}$$

If we demand that the Boltzmann entropy and the thermodynamic entropy are the same then

$$\beta = \frac{1}{K_B T} \quad \alpha = \frac{\mu}{K_B T} \quad (256)$$

## Irreversibility and the Growth of Entropy

- ▶ The equations of motion of classical physics are time reversal invariant.
  - ▶ This follows from the fact that there is a second derivative with respect to time.
- ▶ A movie run backwards will look physically reasonable.
- ▶ A counter example is a damped harmonic oscillator e.g. A pendulum in a viscous fluid.

$$m \frac{d^2 x(t)}{dt^2} + \alpha \frac{dx(t)}{dt} + m \omega_o^2 x(t) = 0 \quad (257)$$

- ▶ The first time derivative changes the sign of the friction term and the resulting equation has the friction accelerate the motion rather than de-accelerate it.

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- ▶ The macroscopic world is irreversible. Particles spread out from a small space to a larger space and do not return.
- ▶ Microscopic reversibility will not return system to its original state due to chaos.
- ▶ Poincare recurrence time for a macroscopic system is longer than the lifetime of the universe.
- ▶ The thermodynamic limit makes the recurrence time infinite and we do not need to consider it.