

# Lecture 1 - 438

☰ Course	PH 438 - Stat Mech
📅 Date	@January 2, 2023
☑ Notes completed	☑
⚙ Status	Completed
📎 Materials	
☑ Reviewed	<input type="checkbox"/>
🕒 Created	@January 2, 2023 10:33 AM

Next:

Office hours: TBA, PH 229-D

Assessment:

- Quiz 1 - 15%
- Quiz 2 - 15%
- Midsem - 30%
- Endsem - 30%
- Assignments - 10%

References:

- Statistical Physics of Particles by Kardar
  - Terse and concise
- Statistical Physics - Swendsen
  - Expands more than Kardar
- Statistical ... - Kevsun Huang
- Statistical ... - Pathvia
  - A little more worked-out detail than Huang
- Entropy, order parameters, complexity - Sethna

- Not really a textbook, but gives good physical intuition.
- Not a lot of maths, nice to read.

## Storytelling

Stat Phys and Thermodynamics both developed from Thermal Physics, which began in the 1600s, studying the behaviour of gases especially with change in temperature. By the 1800s, people figured out how to use heat to do work, Thermodynamics. Then Boltzmann and Maxwell tried to understand where these laws come from, and came up with the Kinetic Theory of Gases and the molecular picture. This was a controversial theory, was not accepted for a long time. Why?

Science was thought to be a process which could allow deterministic answers to questions. The Kinetic Theory took a step away from it, to a probabilistic approach. Given a temperature, pressure, etc, the velocity of gas molecules cannot be determined - a probability distribution can be given. Some said this just means we aren't using enough information, aren't looking deeply enough at the problem. But today it is accepted that for macroscopic systems with a large number of degrees of freedom, probabilistic approaches are far more useful, and arguably, correct.

In this course, we'll be studying Equilibrium Statistical Mechanics.

## What is equilibrium?

Mechanically, it is generally being at rest. But for say, a gas, the molecules are always moving, so we need a different definition. We'll write one formally in terms of *phase-space densities*.

We could describe a system microscopically, a position and velocity for each particle, and theoretically solve the many  $F = ma$  coupled equations to obtain how the system will evolve, but that quickly becomes impossible. We rather describe systems macroscopically, writing measurables write pressure and temperature, and define equilibrium as these not changing. Through stat mech, we relate the macroscopic and microscopic points of view.

## Zeroth Law of Thermodynamics

- **Zeroth Law** - If pairs of systems A,C and B,C are in equilibrium, the pair A,B is also in equilibrium.
  - This law allows temperature to be well-defined.

Let there be an equilibrium between A and C, described by  $f_{AC}(A_1, A_2, \dots, C_1, C_2, \dots) = 0$  for some function  $f_{AC}$ . Similarly  $f_{BC}(B_1, B_2, \dots, C_1, C_2, \dots) = 0$ .

Therefore we can write:

$$\begin{aligned} C_1 &= F_{AC}(A_1, \dots, C_2, \dots) \\ C_1 &= F_{BC}(B_1, \dots, C_2, \dots) \\ \implies F_{AC}(A_1, \dots, C_2, \dots) &= F_{BC}(B_1, \dots, C_2, \dots) \end{aligned}$$

If we let  $C$  be a deep reservoir, i.e. a system which does not change even on interacting with and changing other systems, the  $C_i$  are constant, so we can conclude that  $\exists \Theta_A, \Theta_B$  s.t.  $\Theta_A(A_i) = \Theta_B(B_i)$ . These quantities  $\Theta$  are then defined as the intensive quantities - for thermal equilibrium, we call this temperature.

Note that this is a cyclical argument, in that thermal equilibrium is not well-defined here in the first place. There is a more formal approach, which is what stat mech is about.

## Entropy

Colloquially referred to as a measure of disorder, note the classic example of different gases in separate compartments, the partition is removed and they mix, and entropy is said to have increased - it is intuitively a more disordered system. But if the gases are the same, the entropy does not increase - Gibb's Paradox.

# Lecture 2 - 438

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📅 Date	@January 9, 2023
☑ Notes completed	☑
⚙ Status	Completed
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☑ Reviewed	<input type="checkbox"/>
🕒 Created	@January 15, 2023 12:40 PM

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## Random Variables

- Discrete
  - $A = \{a_j\}$
  - Probabilities sum to one, can define joint probabilities for multiple RVs
- Continuous
  - $S_x = \{-\infty < x < \infty\}$ , for example
  - Probability density  $p(x)$ , which is the derivative of the cumulative probability density  $P(x)$  (or  $C(x)$ , a notation I prefer).
    - $p(x)dx$  is the probability of  $X \in (x, x + dx)$ .
  - Marginal prob  $\rightarrow P_A(a) = \sum_b P(a, b)$  (uncoditional)
  - Conditional prob  $\rightarrow P(a, b) = P(a|b)P_B(b) = P(b|a)P_A(a)$ 
    - $P(a|b) = \frac{P(b|a)P_A(a)}{\sum_a P(b|a)P_A(a)}$  is Bayes' Theorem for the conditional prob, derived from the above definition.

## Functions of Random Variables

$A = \{a_j\}$ ,  $F = \{F(a_j)\}$  is another random variable mapped to by the function  $F(a)$ .

$P_F(f) = \sum_a \delta_{f, F(a)} P(a)$  is the discrete probability distribution. For the continuous case, we have

$$P_F(f) = \int \delta(F(x) - f) p(x) dx$$

While this is the intuitive extension, we can arrive at the same more rigorously.

Let  $F(x) = f$  have solutions  $\{x_i^f\}$ . Then the probability of  $F \in (f, f + df)$  is:

$$\begin{aligned} P_F(f)df &= \sum_i p(x_i^f)dx \\ f &= F(x_i), \text{ hence } df = dF \\ \implies P_F(f) &= \sum_i p(x_i^f) \left| \frac{dx}{dF} \right|_{x_i^f} \end{aligned}$$

Which is exactly what evaluating the integral would give us. But there is a further extension of this - we can have functions from  $\mathbb{R}^n \rightarrow \mathbb{R}^m$ , so the derivative factors become the Jacobian associated with a change of variables from  $\vec{x}$  to  $\vec{F}$ .

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📅 Date	@January 10, 2023
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⚙ Status	Completed
📎 Materials	
☑ Reviewed	<input type="checkbox"/>
🕒 Created	@January 15, 2023 8:20 PM

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## Moments of Probability Distributions

$$\langle F \rangle = \sum_a F(a)P(a)$$

The  $n^{\text{th}}$  moment:

$$\langle F^n \rangle = \sum_a (F(a))^n P(a)$$

These are called raw moments. The  $n^{\text{th}}$  central moment is:

$$\langle (F - \langle F \rangle)^n \rangle$$

Generally we use  $F(a)$  to map the random variable's states to numbers, integers or a real interval, and write the raw moments as  $\mu'_n$ , and the central moments as  $\mu_n$ .

The variance is defined as  $\langle X^2 \rangle - \langle X \rangle^2$ .

The correlation function  $\rho_{XY} = \langle XY \rangle - \langle X \rangle \langle Y \rangle$ , and is 0 if the variables are independent, which is also equivalent to  $P(x, y) = P_X(x)P_Y(y)$ .

## Moment-Generating Functions

AKA Characteristic functions,

$$\tilde{p}(k) = \langle e^{-ikx} \rangle = \sum_n \frac{(-ik)^n}{n!} \langle x^n \rangle$$

$$\langle e^{-ik(x - \langle x \rangle)} \rangle = \sum_n \frac{(-ik)^n}{n!} \langle (x - \langle x \rangle)^n \rangle$$

Derivatives wrt  $k$  give the moments:

$$\mu'_n = i^n \frac{d^n \tilde{p}(k)}{dk^n}$$

For the Gaussian PDF,

$$p(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$

$$\tilde{p}_X(k) = e^{\mu k} e^{\frac{1}{2}\sigma^2 k^2}$$

## Cumulants of a PDF

$$K_X(k) = \ln \tilde{p}_X(k) = \sum_{n=1}^{\infty} \frac{(-ik)^n}{n!} \underbrace{\langle x^n \rangle_c}_{\text{The cumulants}}$$

$$= \ln \left[ 1 + \sum_{n=1}^{\infty} \frac{(-ik)^n}{n!} \langle x^n \rangle \right]$$

$$= \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} \left[ \sum_{m=1}^{\infty} \frac{(-ik)^m}{m!} \langle x^m \rangle \right]$$

$$\text{(Using } \ln(1 + \varepsilon) = \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} \varepsilon^n \text{)}$$

$$= \sum_{m=1}^{\infty} \frac{(-ik)^m}{m!} \langle x^m \rangle - \frac{1}{2} \sum_{m=1}^{\infty} \frac{(-ik)^m}{m!} \langle x^m \rangle \sum_{m'=1}^{\infty} \frac{(-ik)^{m'}}{m'!} \langle x^{m'} \rangle + \frac{1}{3} \dots$$

Compare this with the definition of the cumulants, specifically using the powers of  $k$ , and obtain the following first few cumulants:

$$\langle x^1 \rangle_c = \langle x \rangle \quad (\text{Mean})$$

$$\langle x^2 \rangle_c = \langle x^2 \rangle - \langle x \rangle^2 \quad (\text{Variance})$$

$$\langle x^3 \rangle_c = \langle x^3 \rangle - 3\langle x \rangle \langle x^2 \rangle + \langle x \rangle^3 \quad (\text{Skewness})$$

$$\langle x^4 \rangle_c = \langle x^4 \rangle - 4\langle x^3 \rangle \langle x \rangle - 3\langle x^2 \rangle^2 + 12\langle x^2 \rangle \langle x \rangle^2 - 6\langle x \rangle^4 \quad (\text{Kurtosis})$$

For a gaussian,  $k_X = \mu k + \frac{\sigma^2 k^2}{2}$ , and all higher-order cumulants vanish.

## Sum of Independent Rand-Vars

$$S = \sum_j F_j$$

$$\langle S \rangle = \sum_j \langle F_j \rangle$$

$$\sigma_S^2 = \sum_j \sum_k \langle F_j F_k \rangle - \sum_j \sum_k \langle F_j \rangle \langle F_k \rangle = \sum_{j \neq k} \rho_{F_j F_k} + \sum_j \sigma_{F_j}^2$$

When they are also **identically distributed**,

$$\sigma_S^2 = N\sigma^2, \text{ and the relative SD } \frac{\sigma_S}{\langle S \rangle} = \frac{\sqrt{N}\sigma}{N\langle F \rangle} = \frac{1}{\sqrt{N}} \frac{\sigma}{\langle F \rangle}.$$

## Central Limit Theorem

$N$  independent and identically distributed (iid) rand-vars, then the PDF of their sum tends to a gaussian as  $N \rightarrow \infty$ .

$$S = \sum_i X_i$$

$$E[S] = N\mu$$

$$\text{Var}[S] = N\sigma^2$$

$$\text{Normalise : } S^* := \frac{S - E[S]}{\sqrt{\text{Var}[S]}} = \frac{\left(\frac{1}{N} \sum_i X_i\right) - \mu}{\sigma/\sqrt{N}}$$

## Properties of the generating function

AKA the convolution, for obvious reasons

### Addition



$$\begin{aligned}\tilde{p}_{X+Y}(k) &= \tilde{p}_X(k)\tilde{p}_Y(k) \\ K_{X+Y}(k) &= \ln(\tilde{p}_{X+Y}(k)) = K_X(k) + K_Y(k)\end{aligned}$$

## Scaling

$$\begin{aligned}\tilde{p}_{cX}(k) &= \tilde{p}_X(ck) \\ K_{cX}(k) &= K_X(ck)\end{aligned}$$

## Gaussian behaviour from cumulants

$$K_{\frac{1}{\sqrt{N}} \sum_i X_i} = \sum_i K_{X_i} \left( \frac{k}{\sqrt{N}} \right)$$

Thus the  $m^{\text{th}}$  cumulant  $k_m(\frac{1}{\sqrt{N}} \sum_i X_i) = \frac{1}{\sqrt{N}^m} \sum_i k_m(X_i)$ . Hence, for  $Z = \frac{1}{\sqrt{N}} \sum_i X_i$ ,

$$\begin{aligned}k_1(Z) &= 0 \\ k_2(Z) &= \frac{N\sigma^2}{N} = \sigma^2 \\ k_3(Z) &= \frac{Nc}{N^{3/2}} \xrightarrow{N \rightarrow \infty} 0 \\ \text{And similarly for all } m > 2\end{aligned}$$

Hence  $Z$  behaves like a gaussian centred at the origin, with variance  $\sigma^2$ . The normalised  $S^*$  behaves like it has a variance 1.

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📅 Date	@January 12, 2023
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⚡ Status	Doubts
📎 Materials	
☑ Reviewed	☐
🕒 Created	@January 16, 2023 2:55 AM

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## Deriving Stirling's Formula

Stirling's formula:  $\ln n! \approx n \ln n - n$

Gamma function:

$$\Gamma(n+1) = n! = \int_0^{\infty} e^{-x} x^n dx$$

We try to evaluate  $I = \int dx e^{n\phi(x)}$  as  $n \rightarrow \infty$ .

**Method of steepest descent**, AKA the **Saddle-point approximation**  $\rightarrow \phi(x) = \phi_{\max} - \frac{1}{2} \left| \frac{d^2\phi}{dx^2} \right|_{\max} (x - x_{\max})^2 + \dots$ , Taylor expand around maxima.

$$\begin{aligned} I &\approx e^{n\phi_{\max}} \int_{\mathbb{R}} dx e^{-\frac{n}{2} |\phi''_{\max}| (x - x_{\max})^2} \\ &= \sqrt{\frac{2\pi}{n |\phi''_{\max}|}} e^{n\phi_{\max}} \end{aligned}$$

$\phi(x) = \ln x - \frac{x}{N}$  gives  $I_N = N!$ , then

$$I_N \approx \sqrt{2\pi N} e^{N \ln N} e^{-N}$$

$$\implies \ln N! \approx N \ln N - N + \ln \sqrt{2\pi N}$$

(An improved approximation)

## Back to Physics

A microstate is the complete specification of all the microscopic variables of a system. A macrostate only describes some macroscopic parameters, thermodynamic coordinates or state functions. Many micros correspond to a single macro.

**State functions** can be

- Generalised Displacements
  - Extensive
  - Eg. V, S, N
- Generalised Forces
  - Intensive
  - Eg. P, T,  $\mu$

**doubt** - unclear which is an example of which

So how should equilibrium be defined?

Microstates exist in  $6N$  dimensional phase space  $\Gamma$  - they have  $\{\vec{q}_i(t), \vec{p}_i(t)\}$  each.

Recall that

$$\dot{q}_i = \frac{\partial H}{\partial p_i}$$

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

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📅 Date	@January 16, 2023
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⚡ Status	Completed
📎 Materials	
☑ Reviewed	<input type="checkbox"/>
🕒 Created	@January 16, 2023 3:16 AM

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## A continued study of microstates

Let's assume  $\mathcal{N}$  microstates (or rather,  $\mathcal{N}$  copies of my system) correspond to the same macrostate - call this the ensemble of microstates.

$d\Gamma = \prod_{\alpha=1}^{3N} dq_{\alpha} dp_{\alpha}$  is an infinitesimal volume in phase space, let  $d\mathcal{N}$  be the number of microstates in  $d\Gamma$  (i.e. around a given  $\vec{p}, \vec{q}$ ) given a particular macrostate.

Density of microstates  $\rho$  :

$$\rho(\vec{p}, \vec{q}, t) d\Gamma = \lim_{\mathcal{N} \rightarrow \infty} \frac{d\mathcal{N}}{\mathcal{N}}$$

This definition is chosen to be able to later use  $\rho$  as a probability density.

We'll try to define the equilibrium of a system through the time evolution of  $\rho$ .

If we know  $\mu$  (microstate) for a system, call it a pure state, else a mixed state.

## Liouville's Theorem

$\rho$  behaves like an incompressible fluid:

Consider a collection of microstates occupying  $d\Gamma$  volume in phase space - post time-evolution, this collection still occupies the same volume, though perhaps in a different shape/region. This is not limited to the microstates for a particular macrostate either.

▼ Proof (Physicist style)

After  $\delta t$  :

$$\begin{aligned} q'_\alpha &= q_\alpha + \dot{q}_\alpha \delta t + \Theta(\delta t^2) \\ p'_\alpha &= p_\alpha + \dot{p}_\alpha \delta t + \Theta(\delta t^2) \\ dq'_\alpha &= dq_\alpha + \frac{\partial \dot{q}_\alpha}{\partial q_\alpha} dq_\alpha \delta t + \Theta(\delta t^2) \\ dp'_\alpha &= dp_\alpha + \frac{\partial \dot{p}_\alpha}{\partial p_\alpha} dp_\alpha \delta t + \Theta(\delta t^2) \end{aligned}$$

Where  $dq_\alpha$  is one edge length of the volume  $d\Gamma = \prod_{\alpha=1}^{3N} dq_\alpha dp_\alpha$ , and we want to show that  $d\Gamma' = d\Gamma$ .

$$\begin{aligned} \dot{q}_i &= \frac{\partial \mathcal{H}}{\partial p_i}, \quad \frac{\partial \dot{q}_\alpha}{\partial q_\alpha} = \frac{\partial^2 \mathcal{H}}{\partial q_\alpha \partial p_\alpha} \\ \dot{p}_i &= -\frac{\partial \mathcal{H}}{\partial q_i}, \quad \frac{\partial \dot{p}_\alpha}{\partial p_\alpha} = -\frac{\partial^2 \mathcal{H}}{\partial q_\alpha \partial p_\alpha} \end{aligned}$$

Hence

$$\begin{aligned} d\Gamma' &= \prod dq'_\alpha dp'_\alpha \\ &= \prod_\alpha dq_\alpha dp_\alpha \left( 1 + \left( \frac{\partial \dot{q}_\alpha}{\partial q_\alpha} + \frac{\partial \dot{p}_\alpha}{\partial p_\alpha} \right) \delta t \right) = d\Gamma \end{aligned}$$

Furthermore, we're looking at a fixed collection of microstates,  $d\mathcal{N}$  and  $\mathcal{N}$  do not change, and neither does  $d\Gamma$  as we showed, so we can conclude that  $\rho(p', q', t + \delta t) = \rho(p, q, t)$ . Since  $p' = p(t + \delta t)$  and so for  $q'$ , hence this is equivalent to saying  $\frac{d\rho}{dt} = 0$ .

Hence (not completely rigorously) proved.

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📅 Date	@January 17, 2023
☑ Notes completed	☑
⚙ Status	Completed
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☑ Reviewed	☐
🕒 Created	@January 17, 2023 11:39 AM

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## The evolution of a system

Phase space density remains unchanged:

$$\begin{aligned}
 \frac{d\rho(\vec{p}, \vec{q}, t)}{dt} &= 0 \\
 \Rightarrow \frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial p_\alpha} \dot{p}_\alpha + \frac{\partial \rho}{\partial q_\alpha} \dot{q}_\alpha &= 0 \\
 \Rightarrow \frac{\partial \rho}{\partial t} - \frac{\partial \rho}{\partial p_\alpha} \frac{\partial \mathcal{H}}{\partial q_\alpha} + \frac{\partial \rho}{\partial q_\alpha} \frac{\partial \mathcal{H}}{\partial p_\alpha} &= 0
 \end{aligned}$$

The poisson bracket is  $\{A, B\} = \frac{\partial A}{\partial q_\alpha} \frac{\partial B}{\partial p_\alpha} - \frac{\partial A}{\partial p_\alpha} \frac{\partial B}{\partial q_\alpha}$ , hence

$$\frac{\partial \rho}{\partial t} + \{\rho, \mathcal{H}\} = 0$$

The average value of an observable is

$$\begin{aligned}
 \langle \Theta(\vec{p}, \vec{q}) \rangle &= \int d\Gamma \rho(\vec{p}, \vec{q}, t) \Theta(\vec{p}, \vec{q}) \\
 \text{Using the Leibniz integral rule,} \\
 \frac{d}{dt} \langle \Theta(\vec{p}, \vec{q}) \rangle &= \int d\Gamma \frac{\partial \rho}{\partial t} \Theta(\vec{p}, \vec{q}) = \int d\Gamma \left( \frac{\partial \rho}{\partial p_\alpha} \frac{\partial \mathcal{H}}{\partial q_\alpha} - \frac{\partial \rho}{\partial q_\alpha} \frac{\partial \mathcal{H}}{\partial p_\alpha} \right) \Theta(\vec{p}, \vec{q})
 \end{aligned}$$

Now since  $d\Gamma = \prod_\alpha dp_\alpha dq_\alpha$ , we can use integration by parts to remove the derivative from the  $\rho$  and put it on the  $\Theta$ . We will obtain some terms outside the integral, but since we're integrating over all coordinate and momentum space, and since for real situations  $\rho = 0$  for momenta and coordinates larger than some maximum, these "surface terms" go to 0.

$$\begin{aligned}
\frac{d\langle\Theta\rangle}{dt} &= \int d\Gamma \left( \frac{\partial\rho}{\partial p_\alpha} \frac{\partial\mathcal{H}}{\partial q_\alpha} - \frac{\partial\rho}{\partial q_\alpha} \frac{\partial\mathcal{H}}{\partial p_\alpha} \right) \Theta(\vec{p}, \vec{q}) \\
\int dp_\alpha \frac{\partial\rho}{\partial p_\alpha} \frac{\partial\mathcal{H}}{\partial q_\alpha} \Theta(\vec{p}, \vec{q}) &= \left[ \rho \frac{\partial\mathcal{H}}{\partial q_\alpha} \Theta(\vec{p}, \vec{q}) \right]_{\text{boundary}} - \int dp_\alpha \rho \left( \frac{\partial^2\mathcal{H}}{\partial p_\alpha \partial q_\alpha} \Theta + \frac{\partial\mathcal{H}}{\partial q_\alpha} \frac{\partial\Theta}{\partial p_\alpha} \right) \\
\text{Similarly } \int dq_\alpha \frac{\partial\rho}{\partial q_\alpha} \frac{\partial\mathcal{H}}{\partial p_\alpha} \Theta &= \left[ \rho \frac{\partial\mathcal{H}}{\partial p_\alpha} \Theta \right]_{\text{boundary}} - \int dq_\alpha \rho \left( \frac{\partial^2\mathcal{H}}{\partial q_\alpha \partial p_\alpha} \Theta + \frac{\partial\mathcal{H}}{\partial p_\alpha} \frac{\partial\Theta}{\partial q_\alpha} \right) \\
\text{Hence } \frac{d\langle\Theta\rangle}{dt} &= \int d\Gamma \left( \frac{\partial\rho}{\partial p_\alpha} \frac{\partial\mathcal{H}}{\partial q_\alpha} - \frac{\partial\rho}{\partial q_\alpha} \frac{\partial\mathcal{H}}{\partial p_\alpha} \right) \Theta \\
&= \int d\Gamma \rho \left( \frac{\partial^2\mathcal{H}}{\partial p_\alpha \partial q_\alpha} \Theta + \frac{\partial\mathcal{H}}{\partial q_\alpha} \frac{\partial\Theta}{\partial p_\alpha} - \frac{\partial^2\mathcal{H}}{\partial q_\alpha \partial p_\alpha} \Theta - \frac{\partial\mathcal{H}}{\partial p_\alpha} \frac{\partial\Theta}{\partial q_\alpha} \right) \\
&= \int d\Gamma \rho(\vec{p}, \vec{q}, t) \{\Theta, \mathcal{H}\} = \langle \{\Theta, \mathcal{H}\} \rangle
\end{aligned}$$

## Equilibrium Condition

We want to impose that the macroscopic variables do not change for the equilibrium condition, which is done via  $\frac{d\langle\Theta\rangle}{dt} = 0$ , for all observables - and that will happen only when  $\frac{\partial\rho}{\partial t} = 0$ , i.e.  $\{\rho_{eq}(\vec{p}, \vec{q}), \mathcal{H}(\vec{p}, \vec{q})\} = 0$ .

Hence we have determined that  $\rho_{eq} \equiv \rho_{eq}(\vec{p}, \vec{q})$ .

## The form of the phase space density

While we do not know it explicitly, we can derive some results about it, notably that  $\rho_{eq}(\vec{p}, \vec{q}) = \rho_{eq}(\mathcal{H}(\vec{p}, \vec{q}))$  automatically satisfies the equilibrium condition. What that means is that  $\rho$  should be a function of  $\vec{p}, \vec{q}$  only through the hamiltonian, i.e. be expressible as a function of only the hamiltonian.

$$\begin{aligned}
\{\rho_{eq}(\mathcal{H}), \mathcal{H}\} &= \frac{\partial\rho}{\partial q_\alpha} \frac{\partial\mathcal{H}}{\partial p_\alpha} - \frac{\partial\rho}{\partial p_\alpha} \frac{\partial\mathcal{H}}{\partial q_\alpha} \\
&= \frac{\partial\rho}{\partial\mathcal{H}} \left( \frac{\partial\mathcal{H}}{\partial q_\alpha} \frac{\partial\mathcal{H}}{\partial p_\alpha} - \frac{\partial\mathcal{H}}{\partial p_\alpha} \frac{\partial\mathcal{H}}{\partial q_\alpha} \right) = 0
\end{aligned}$$

This is a sufficient but not necessary condition - however, it is the simplest assumption we can make such that the equilibrium condition is satisfied.

In what is called the microcanonical ensemble, the energy is fixed, and so the hamiltonian is, and hence  $\rho_{eq}$  is a constant, and also all accessible microstates are equally likely.

In the canonical ensemble, the temperature is fixed but energy can be exchanged with the surroundings. Then  $\rho_{eq}(\mathcal{H}) = e^{-\beta\mathcal{H}}$ .

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📅 Date	@January 19, 2023
☑ Notes completed	☑
⚡ Status	Completed
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☑ Reviewed	<input type="checkbox"/>
🕒 Created	@January 19, 2023 8:54 AM

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## S-Particle Density

### One-particle density

The probability that at  $\vec{q}$   $\exists$  a particle with  $\vec{p}$  momentum.

We know  $\rho(\{\vec{p}_\alpha, \vec{q}_\alpha\}_\alpha^N)$ , the one-particle density is

$$f_1(\vec{p}, \vec{q}) = \left\langle \sum_\alpha \delta(\vec{p}_\alpha - \vec{p}, \vec{q}_\alpha - \vec{q}) \right\rangle$$

$$= N \int \prod_{\alpha=1}^N d^3 \vec{p}_\alpha d^3 \vec{q}_\alpha \rho \delta(\vec{p}_\alpha - \vec{p}, \vec{q}_\alpha - \vec{q})$$

### Two-particle density

Particles at  $\vec{q}, \vec{q}'$  with  $\vec{p}, \vec{p}'$ .

If the first particle is at  $\vec{q}, \vec{p}$  and the second at the primed, that probability is  $\int (\prod_{\alpha=3}^N d^3 \vec{p}_\alpha d^3 \vec{q}_\alpha) \rho(\vec{q}, \vec{p}, \vec{q}', \vec{p}', \{\vec{q}_\beta, \vec{p}_\beta\}_{\alpha=3}^N)$ . Now we can shuffle these two in  $2 \binom{N}{2}$  ways, because choosing two positions, and then also exchange with each other. Hence the total probability is

$$f_2(\vec{q}, \vec{p}, \vec{q}', \vec{p}') = N(N-1) \int \left( \prod_{\alpha=3}^N d^3 \vec{p}_\alpha d^3 \vec{q}_\alpha \right) \rho(\vec{q}, \vec{p}, \vec{q}', \vec{p}', \{\vec{q}_\beta, \vec{p}_\beta\}_{\alpha=3}^N)$$

### S-particle density

Similarly,

$$f_S(\{\vec{q}_i, \vec{p}_i\}_{i=1}^S) = \frac{N!}{(N-S)!} \int \left( \prod_{\alpha=S+1}^N d^3 \vec{p}_\alpha d^3 \vec{q}_\alpha \right) \rho(\{\vec{q}_i, \vec{p}_i\}_{i=1}^S, \{\vec{q}_\beta, \vec{p}_\beta\}_{\alpha=S+1}^N)$$

Note that  $f_S$  is not normalised to give 1 when integrated over  $\{\vec{q}_i, \vec{p}_i\}_{i=1}^S$ , but rather  $N!/(N-S)!$ . So we can divide by that to get  $\rho_S$ .

### So what's the point? (Spoiler : It's the BBGKY Heirarchy)

These densities will be useful in studying the evolution of systems. We look at a fairly general hamiltonian to illustrate this.

$$\mathcal{H} = \sum_{i=1}^N \left( \frac{p_i^2}{2m_i} + U(\vec{q}_i) \right) + \frac{1}{2} \sum_{\{i,j\}=1}^N V(\vec{q}_i - \vec{q}_j)$$

$\{i, j\} = 1$  indicates that  $i \neq j$ , and both start from 1.

By neglecting higher-order interactions, many hamiltonians can be written in this form.



We split the hamiltonian into three terms:

$$\begin{aligned}\mathcal{H}_s &= \sum_{i=1}^s \left( \frac{p_i^2}{2m_i} + U(\vec{q}_i) \right) + \frac{1}{2} \sum_{\{i,j\}=1}^s V(\vec{q}_i - \vec{q}_j) \\ \mathcal{H}_{N-s} &= \sum_{i=s+1}^N \left( \frac{p_i^2}{2m_i} + U(\vec{q}_i) \right) + \frac{1}{2} \sum_{\{i,j\}=s+1}^N V(\vec{q}_i - \vec{q}_j) \\ \mathcal{H}' &= \sum_{i=1}^s \sum_{j=s+1}^N V(\vec{q}_i - \vec{q}_j)\end{aligned}$$

Dividing the particles into two groups and separating their interaction terms.

First, we evaluate  $\frac{\partial \rho_1}{\partial t}$ . Later we may evaluate  $\frac{\partial \rho_s}{\partial t}$  as well.

$$\begin{aligned}\frac{\partial \rho_1}{\partial t} &= \int \left( \prod_{\alpha=2}^N d^3 \vec{p}_\alpha d^3 \vec{q}_\alpha \right) \frac{\partial \rho}{\partial t} \\ &= \int \left( \prod_{\alpha=2}^N d^3 \vec{p}_\alpha d^3 \vec{q}_\alpha \right) \{ \mathcal{H}, \rho \}\end{aligned}$$

Write the hamiltonian in three terms. Then the first one only depends on  $\vec{q}_1, \vec{p}_1$ , which we don't integrate over, so the derivatives in the Poisson bracket can be taken outside the integral, and we get  $\{ \mathcal{H}_1, \int \dots \rho \} = \{ \mathcal{H}_1, \rho_1 \}$ .

Similarly, one can show that the first term for  $\frac{\partial \rho_s}{\partial t}$  simplifies to  $\{ \mathcal{H}_s, \rho_s \}$ .

Second term:

$$\int \left( \prod_{\alpha=2}^N d^3 \vec{p}_\alpha d^3 \vec{q}_\alpha \right) \{ \mathcal{H}_{N-1}, \rho \} = \int \left( \prod_{\alpha=2}^N d^3 \vec{p}_\alpha d^3 \vec{q}_\alpha \right) \sum_{j=2}^N \left[ \frac{\vec{p}_j}{m} \frac{\partial \rho}{\partial \vec{q}_j} - \left( \nabla_{\vec{q}_i} U(\vec{q}_j) + \frac{1}{2} \sum_{k=2}^N \frac{\partial V(\vec{q}_j - \vec{q}_k)}{\partial \vec{q}_i} \right) \frac{\partial \rho}{\partial \vec{p}_j} \right]$$

The calculation is continued in the next class.

# Lecture 8 - 438

☰ Course	PH 438 - Stat Mech
📅 Date	@January 24, 2023
☑ Notes completed	☑
⚙ Status	Doubts
📎 Materials	
☑ Reviewed	☐
🕒 Created	@January 24, 2023 11:44 AM

Next:

## Continuing the calculation for $\frac{\partial \rho_1}{\partial t}$

**Second term:**

$$\int \left( \prod_{\alpha=2}^N d^3 \vec{p}_\alpha d^3 \vec{q}_\alpha \right) \{ \mathcal{H}_{N-1}, \rho \} = \int \left( \prod_{\alpha=2}^N d^3 \vec{p}_\alpha d^3 \vec{q}_\alpha \right) \sum_{j=2}^N \left[ \frac{\vec{p}_j}{m} \frac{\partial \rho}{\partial \vec{q}_j} - \left( \nabla_{\vec{q}_i} U(\vec{q}_j) + \frac{1}{2} \sum_{k=2}^N \frac{\partial V(\vec{q}_j - \vec{q}_k)}{\partial \vec{q}_i} \right) \frac{\partial \rho}{\partial \vec{p}_j} \right] \\ \int dq_j \frac{\partial \rho}{\partial q_j} \frac{p_j}{m} = (\rho p_j / m)_{\text{Surface terms}} - \int dq_j \rho \frac{\partial p_j}{\partial q_j} m$$

And similarly, since  $\frac{\partial U}{\partial q_j}$  and  $\frac{\partial V}{\partial q_j}$  are both independent of  $p_i$ , the same integration by parts means all the other terms go to zero as well. But the surface terms in each?

The surface terms in each of these are also zero because when you put in large limits of integration, since our system is finite  $\rho$  is 0 for large enough positions or momenta, the terms go to zero. And then the remaining integrals matter not.

**Third term:**

$$\int \left( \prod_{\alpha=2}^N d^3 \vec{p}_\alpha d^3 \vec{q}_\alpha \right) \{ \mathcal{H}', \rho \} \\ = \int \left( \prod_{\alpha=2}^N d^3 \vec{p}_\alpha d^3 \vec{q}_\alpha \right) \sum_{j=1}^N \frac{\partial \rho}{\partial p_j} \left( \sum_{k=2}^N \frac{\partial V(q_1 - q_k)}{\partial q_j} \right)$$

(since the  $\frac{\partial \mathcal{H}'}{\partial p_j}$  terms are 0)

$$= \int \left( \prod_{\alpha=2}^N d^3 \vec{p}_\alpha d^3 \vec{q}_\alpha \right) \sum_{j=2}^N \frac{\partial \rho}{\partial p_j} \frac{\partial V(q_1 - q_j)}{\partial q_j} + \sum_{k=2}^N \int \left( \prod_{\alpha=2}^N d^3 \vec{p}_\alpha d^3 \vec{q}_\alpha \right) \frac{\partial \rho}{\partial p_1} \frac{\partial V(q_1 - q_k)}{\partial q_1}$$

The first term is now susceptible to our integration by parts attack - we move the  $p_j$  derivative onto  $V$ , which gives 0, and the surface term then has  $\rho$ , which goes to 0 in large limits. And then the integral over the remaining variables doesn't matter.

Now we look at the second term:

$$\sum_{k=2}^N \int \left( \prod_{\alpha=2}^N d^3 \vec{p}_\alpha d^3 \vec{q}_\alpha \right) \frac{\partial \rho}{\partial p_1} \frac{\partial V(q_1 - q_k)}{\partial q_1} \\ = \sum_{k=2}^N \int d^3 q_k d^3 p_k \frac{\partial}{\partial p_1} \left( \int \prod_{\alpha=2, \neq k}^N d^3 \vec{p}_\alpha d^3 \vec{q}_\alpha \rho \right) \frac{\partial V(q_1 - q_k)}{\partial q_1}$$

Now Sir argued that  $k$  is merely a dummy index, and so long as our particles are all identical and so all the  $V$  terms are the same functionally, we can use symmetry to say that the result of the integral will be the same for all  $k$ , and write it as  $N - 1$

times the result for  $k = 2$ .

**doubt** - I'm not fully convinced of this symmetry - is  $\rho$  not going to cause an issue? Is it symmetric over all position coordinates? That seems unlikely.

This allows us to finally write, combining the three results,

$$\frac{\partial \rho_1}{\partial t} + \{\rho_1, \mathcal{H}_1\} = (N-1) \int d\Gamma_2 \frac{\partial \rho_2}{\partial p_1} \frac{\partial V(q_1 - q_2)}{\partial q_1}$$

And for a general  $s$ , the similar result is

$$\frac{\partial \rho_s}{\partial t} + \{\rho_s, \mathcal{H}_s\} = (N-s) \sum_{k=1}^s \int d\Gamma_{k+1} \frac{\partial \rho_{s+1}}{\partial p_k} \frac{\partial V(q_k - q_{s+1})}{\partial q_k}$$

Hence each  $\rho_s$  depends on higher order terms  $\rho_{s+1}$ , so this is known as the **BBGKY Heirarchy**.  $\rho_s$  is related to the probability of a collision of  $s$  particles, so we argue that higher-order terms are negligible in comparison, and terminate the heirarchy at some  $s$ , often at  $s = 2$  - so we neglect  $s = 3$  onwards and then have a system of two equations to solve for  $\rho_2$  and  $\rho_1$ .

Why do collisions relate to  $s$ -particle densities? The collision probability for two particles will be like  $f(p_1, q_1, p_2, q_1 + \delta q, t)$  - so it is subsumed by the two-particle density.

Overall, the RHS in the above expressions for time evolution occur because of the flux (into different regions in phase space) caused by interactions between particles, for example collisions.

Coming up next lecture : With the assumption of molecular chaos, we will eliminate some terms of the BBGKY heirarchy, destroy time reversibility, and obtain the Boltzmann equation.

# Lecture 9 - 438

☰ Course	PH 438 - Stat Mech
📅 Date	@January 30, 2023
☑ Notes completed	☑
⚙ Status	Extra material pending
📎 Materials	
☑ Reviewed	☐
🕒 Created	@January 30, 2023 10:42 AM

Next: [Lecture 10 - 438](#)

## Rate of Collisions

We want to find the rate of collisions for the purpose of evaluating the one-particle density by taking only 2-particle collisions into account. That is to say, we want to work out the RHS of  $\frac{\partial f_1}{\partial t} + \{f_1, \mathcal{H}_1\} = \frac{\partial f_{\text{coll}}}{\partial t}$ .

For a given  $\vec{q}, \vec{p}$  the rate of collisions with other particles is

$$\int d^3\vec{p}_2 d^3\vec{p}_1' d^3\vec{p}_2' \omega(\vec{p}, \vec{p}_2; \vec{p}_1', \vec{p}_2') f_2(\vec{q}, \vec{p}, \vec{q}, \vec{p}_2, t)$$

$\omega$  is the scattering cross-section, essentially representing the probability that a given collision produces certain momenta in the product. It contains all physical aspects of the collision itself, and can be evaluated for a particular model of interactions/collisions.

Why not take permutations into account? Because  $f_2$  already does that, it is unordered, unlike  $\rho_n$  which were ordered.

We further require momentum and energy conservation as

$$\begin{aligned}\vec{p} + \vec{p}_2 &= \vec{p}_1' + \vec{p}_2' \\ p^2 + p_2^2 &= p_1'^2 + p_2'^2\end{aligned}$$

There can be collisions which destroy  $\vec{p}$  and those which create  $\vec{p}$ . Taking both into account,

$$\frac{\partial f_{\text{coll}}}{\partial t} = \int d^3\vec{p}_2 d^3\vec{p}_1' d^3\vec{p}_2' \left[ \omega(\vec{p}_1', \vec{p}_2; \vec{p}, \vec{p}_2) f_2(\vec{q}, \vec{p}_1', \vec{q}, \vec{p}_2, t) - \omega(\vec{p}, \vec{p}_2; \vec{p}_1', \vec{p}_2') f_2(\vec{q}, \vec{p}, \vec{q}, \vec{p}_2, t) \right]$$

Since the underlying dynamics have time-reversal symmetry,  $\omega(\vec{p}, \vec{p}_2; \vec{p}_1', \vec{p}_2') = \omega(\vec{p}_1', \vec{p}_2; \vec{p}, \vec{p}_2)$ .

Then we use the **assumption of molecular chaos** :

$$f_2(\vec{q}, \vec{p}, \vec{q}, \vec{p}_2) = f_1(\vec{q}, \vec{p})f_1(\vec{q}, \vec{p}_2) \neq f_1(\vec{q}, \vec{p}_1)f_1(\vec{q}, \vec{p}_2)$$

This says that the momenta are uncorrelated prior to a collision (hence molecular chaos) but become correlated after a collision (as expected), and this is where we break time-reversal symmetry.

To do: **read in detail**

This gives us the Boltzmann equation, which is only in terms of  $f_1$ .

$$\frac{\partial f_{\text{coll}}}{\partial t} = \int d^3 \vec{p}_2 d^3 \vec{p}_1 d^3 \vec{p}_2' \omega(\vec{p}_1, \vec{p}_2'; \vec{p}, \vec{p}_2) \left[ f_1(\vec{q}, \vec{p}_1') f_1(\vec{q}, \vec{p}_2') - f_1(\vec{q}, \vec{p}) f_1(\vec{q}, \vec{p}_2) \right]$$

# Lecture 10 - 438

☰ Course	PH 438 - Stat Mech
📅 Date	@January 31, 2023
☑ Notes completed	☑
⚙ Status	Completed
📎 Materials	
☑ Reviewed	☐
🕒 Created	@January 31, 2023 11:37 AM

Next:

## Entropy of a Probability Distribution

$$S[p] = - \int dx p(x) \ln p(x) = \left\langle \ln \left( \frac{1}{p(x)} \right) \right\rangle$$

And this will come in handy defining the arrow of time. But where does this definition come from?

It's an extension of the discrete case, and can be motivated by trying to measure randomness or information - when the outcome is certain, for example, with  $p(x) = \delta(x - x_0)$ , or the discrete analog, there is no randomness (certain result), and so the entropy is 0.

The maximum entropy, or maximum disorder, is expected when all outcomes are equally likely, which this function also accomplishes. Discrete example :  $S[p] = - \sum_i p(x_i) \ln p(x_i)$ ,  $p(x_i) = \frac{1}{M} \implies S[p] = \ln M$ , which will be larger for a larger sample space, which is also a sensible requirement.

Something like  $\sum_i p(x_i)(1 - p(x_i))$  would also do the job, but the one we use by convention is nicer, so let's stick with that. It has the nice property that the surprisal - the function the entropy is an expectation value of - is additive for independent events.

## Boltzmann's H-Theorem

$$H(t) = \int d^3 \vec{q}_1 d^3 \vec{p}_1 f_1(\vec{q}_1, \vec{p}_1, t) \ln f_1(\vec{q}_1, \vec{p}_1, t)$$

Which should remind you strongly of the entropy function defined above, just missing a minus sign. We want to look at its time derivative.

$$\frac{dH}{dt} = \int d^3 \vec{q}_1 d^3 \vec{p}_1 (\ln f_1 + 1) \frac{\partial f_1}{\partial t}$$

Note that  $\frac{d}{dt} \int d^3 q_1 d^3 p_1 f_1(q_1, p_1, t) = \frac{dN}{dt} = 0 \implies \int d^3 q_1 d^3 p_1 \frac{\partial}{\partial t} f_1(q_1, p_1, t) = 0$ , so only the first term contributes,

And substitute  $\frac{\partial f_1}{\partial t} = \{\mathcal{H}_1, f_1\} + \frac{\partial f_{\text{coll}}}{\partial t}$ .

$$\begin{aligned} \{\mathcal{H}_1, f_1\} &= \frac{\partial \mathcal{H}_1}{\partial \vec{q}_1} \frac{\partial f_1}{\partial \vec{p}_1} - \frac{\partial f_1}{\partial \vec{q}_1} \frac{\partial \mathcal{H}_1}{\partial \vec{p}_1} = \frac{\partial U}{\partial \vec{q}_1} \frac{\partial f_1}{\partial \vec{p}_1} - \frac{p_1}{m} \frac{\partial f_1}{\partial \vec{q}} \\ \frac{dH}{dt} &= \int d^3 \vec{q} d^3 \vec{p}_1 \ln f_1 \left( \frac{\partial U}{\partial \vec{q}_1} \frac{\partial f_1}{\partial \vec{p}_1} - \frac{p_1}{m} \frac{\partial f_1}{\partial \vec{q}} + \frac{\partial f_{\text{coll}}}{\partial t} \right) \\ \text{Term 1 : } &\int d^3 \vec{q}_1 d^3 \vec{p}_1 \ln f_1 \frac{\partial U}{\partial \vec{q}_1} \frac{\partial f_1}{\partial \vec{p}_1} = \int d^3 q_1 \frac{\partial U}{\partial \vec{q}_1} \int d^3 p_1 \ln f_1 \frac{\partial f_1}{\partial \vec{p}} \\ &\int d^3 p \ln f_1 \frac{\partial f_1}{\partial \vec{p}_1} = f_1 \ln f_1|_{\text{boundary}} - \int d^3 p_1 \frac{\partial f_1}{\partial \vec{p}_1} = 0 \\ \text{Similarly, Term 2 : } &\int d^3 \vec{q}_1 d^3 \vec{p}_1 \ln f_1 \frac{p_1}{m} \frac{\partial f_1}{\partial \vec{q}_1} = \int d^3 p \frac{p}{m} (0) = 0 \\ \therefore \frac{dH}{dt} &= \int d^3 \vec{q}_1 d^3 \vec{p}_1 d^3 \vec{p}_2 d^3 \vec{p}'_1 d^3 \vec{p}'_2 \ln f_1 \cdot \omega(\vec{p}_1, \vec{p}_2; \vec{p}'_1, \vec{p}'_2) \left[ f_1(\vec{q}_1, \vec{p}'_1) f_1(\vec{q}_1, \vec{p}'_2) - f_1(\vec{q}_1, \vec{p}_1) f_1(\vec{q}_1, \vec{p}_2) \right] \end{aligned}$$

We could swap the momenta of the particles colliding and the results should be identical, so we do that, add the new expression to the old one and halve the whole thing - this should still be equal to  $\frac{dH}{dt}$ . So write

$$\frac{dH}{dt} = \frac{1}{2} \int \dots \ln(f_1(q, p) f_1(q, p_2)) \dots$$

And then we use time reversal symmetry in the integrand to exchange the primed and unprimed coordinates. This is another new term, which we again add to the term we already have and halve the total, taking care of the primes and unprimes and sign changes because the  $f_1(\vec{q}_1, \vec{p}_1') f_1(\vec{q}_1, \vec{p}_2') - f_1(\vec{q}_1, \vec{p}_1) f_1(\vec{q}, \vec{p}_2)$  term is antisymmetric with respect to prime exchange,

$$\frac{dH}{dt} = -\frac{1}{4} \int d^3 \vec{q}_1 d^3 \vec{p}_1 d^3 \vec{p}_2 d^3 \vec{p}_1' d^3 \vec{p}_2' \omega(\vec{p}_1, \vec{p}_2; \vec{p}_1', \vec{p}_2') \left[ f_1(\vec{q}_1, \vec{p}_1') f_1(\vec{q}_1, \vec{p}_2') - f_1(\vec{q}_1, \vec{p}_1) f_1(\vec{q}, \vec{p}_2) \right] (\ln f_1(p_1') f_1(p_2'))$$

Now note that for the two cases:

- $f_1(p_1') f_1(p_2') > f_1(p_1) f_1(p_2)$ , then both the difference and  $\ln$  terms are positive, so  $\frac{dH}{dt}$  is negative.
- $f_1(p_1') f_1(p_2') < f_1(p_1) f_1(p_2)$ , then both the difference and  $\ln$  terms are negative, so  $\frac{dH}{dt}$  is negative.

Hence Boltzmann showed that  $H$  always decreases with time - hence an arrow of time is defined.

And this is the end of Kinetic theory. The quiz will be on probability plus kinetic theory. Next lecture, we start with equilibrium.

To do

- ☐ CMP Presentation
- ☐ Get cycle
- ☐ Lunch
- ☐ Bathe
- ☐ Astro ideas
- ☐

# Lecture 11 - 438

☰ Course	PH 438 - Stat Mech
📅 Date	@February 2, 2023
☑ Notes completed	☑
⚡ Status	Completed
📎 Materials	
☑ Reviewed	<input type="checkbox"/>
🕒 Created	@February 2, 2023 8:41 AM

Next: [Lecture 12 - 438](#)

## Equilibrium Statistical Mechanics

### ▼ Recap

- $\rho$  (phase space density) evolves with its poisson bracket with the hamiltonian
- Equilibrium is defined as the phase space density not changing with time, because that means the macroscopic observables don't change.
- The equilibrium condition is satisfied by all  $\rho_{eq} \equiv \rho_{eq}(\mathcal{H}(\vec{p}, \vec{q}))$ , because then  $\{\rho_{eq}, \mathcal{H}\} = 0$ . Sufficient but not necessary.
- Approach to equilibrium - we saw last lecture that there exists an arrow of time, the boltzmann H function will decrease until it reaches a minima, and that will be an equilibrium.
  - What if there is no minima? Analysis of the definition of H should show that that would indicate unphysical systems, such as ones which do not obey energy conservation, though we have not discussed this in class.

### Ergodic Hypothesis

The ensemble average for a macroscopic observable is an average over measurements from a set - ensemble - of identical systems,  $\langle \Theta \rangle = \int d\Gamma \rho(\vec{p}, \vec{q}) \Theta(\vec{p}, \vec{q})$ .

The time average is an average over multiple measurements of the same system over time,  $\bar{\Theta} = \frac{1}{T} \int_0^T dt \Theta(\vec{p}, \vec{q})$ .



The Ergodic hypothesis states that for a system at equilibrium, these two averages will be the same.

There is no general proof of this, though the idea seems sensible. There are special systems where it can be proven, and others where it is violated, but for most everyday systems this experimentally seems to hold. So we take it on faith until we see a violation.

There are other phrasings of the same idea, it's interesting to look up other ways of stating the Ergodic hypothesis and linking them.

## Micro-canonical Ensembles

Take a box of gas, the macrostate would be characterised by macroscopic variables energy, volume, mols ( $E, V, N$ ). The corresponding microstates are confined to a region of energy  $E$  in phase space.

For a microstate  $\mu(\vec{p}, \vec{q})$ , the energy thus must be  $\mathcal{H}(\mu) = E$ . Assuming we are at equilibrium with  $\rho_{eq} \equiv \rho_{eq}(\mathcal{H}(\vec{p}, \vec{q}))$ , this means all microstates have the same phase space density, the same probability of occurrence. This is referred to as *All allowed microstates are equally probable - Equal a-priori probability*.

$$p(\mu) = \begin{cases} 0 & \mathcal{H}(\mu) \neq E \\ \frac{1}{\Omega(E, V, N)} & \mathcal{H}(\mu) = E \end{cases}$$

Where  $\Omega(E, V, N)$  is the number of allowed microstates : want  $\int p(\mu) d\Gamma = 1$

Then the entropy (written in a discrete sense here, but it makes little difference to the qualitative results)

$$S = -k_B \sum_{\mu=1}^{\Omega} p(\mu) \ln p(\mu) = k_B \ln \Omega$$

Notice the new constant  $k_B$  we've put in front of the entropy expression - Boltzmann wanted to move on from an information idea of entropy, which was dimensionless, to thermodynamic entropy, with units of joules per kelvin.  $k_B = 1.38 * 10^{-6} \text{ J/K}$ .

## The ~~Four~~ Three Laws of Thermodynamics

We won't discuss the third law (which talks of absolute zero) because a proper discussion on that requires quantum stat mech, and we shall limit ourselves to classical in this course, hold your commutators.

## Zeroth Law

If two systems with different temperatures are brought into contact, heat flows from the warmer to the colder system until a thermal equilibrium is reached - then they are said to be at the same temperature.

What this seemingly obvious statement does for us is define temperature itself, as the macroscopic variable which decides the direction of heat flow, like a heat potential.

For the purpose of the definition, we assume a thermally isolated pair of systems, so the total energy remains constant,  $E = E_1^0 + E_2^0 = E_1 + E_2$  (sum of initial and final energies is this total). (Note that only energy, and not volume or number of particles is allowed to be changed.)

What is the size of the allowed phase space now?

$$\Omega(E) = \int_0^E dE_1 \Omega_1(E_1) \Omega_2(E - E_1)$$

Use different  $\Omega_i$  because the volumes and mols change too, and substitute  $E_2 = E - E_1$ .

Now recall that  $\Omega = e^{S/k_B}$ , so

$$\Omega(E) = \int_0^E dE_1 e^{(S_1(E_1) + S_2(E - E_1)) \frac{1}{k_B}}$$

Now recall the Saddle Point Approximation, an integral of the form  $\int e^{N\phi(x)} dx$  goes as  $\propto e^{N\phi(x_{\max})}$ ,  $x_{\max}$  being the point of maxima, when  $N \rightarrow \infty$ .

Entropy is an extensive quantity, so is of the form  $N\phi(E)$ , and thus for macroscopic systems (large N) a very large contribution to  $\Omega(E)$  is from  $\exp(\frac{1}{k_B}(S_1(E_1^{\max}) + S_2(E - E_1^{\max})))$ . What is  $E_1^{\max}$ ? Look for the extrema,

$$\begin{aligned} \frac{dS_1(E_1)}{dE_1} + \frac{dS_2(E - E_1)}{dE_1} &= 0 \\ \implies \frac{dS_1}{dE_1} &= \frac{dS_2}{dE_2} \end{aligned}$$

And we have defined that the equilibrium condition is of temperature equality, so  $\frac{dS_i}{dE_i}$  must be a function of the temperature of the system, so that both these constraints become equivalent. Later, we'll see that it behaves as  $1/T$ .

▼ Sidenote on the validity of some assumptions we made

We assumed  $\Omega_1 \times \Omega_2 \approx \Omega \Leftrightarrow S \approx S_1 + S_2$ , which is valid for weakly interacting systems. The same final results can be derived for strongly interacting systems, using correction terms in  $\Omega$  or  $S$ , or perhaps some other method, but it is much more mathematically challenging.

# Lecture 12 - 438

☰ Course	PH 438 - Stat Mech
📅 Date	@February 7, 2023
☑ Notes completed	☑
⚙ Status	Completed
📎 Materials	
☑ Reviewed	<input type="checkbox"/>
🕒 Created	@February 7, 2023 11:38 AM

Next:

## Microcanonical Ensemble

A system where  $N, V$  are fixed but  $E$  is not. Assuming  $\rho_{eq}(\mathcal{H})$ , say we have  $\Omega$  microstates with the energy  $E$ , then all of them are equally likely.

$$p(\mu(\{\vec{q}_i, \vec{p}_i\}_i^N)) = \begin{cases} 0 & \mathcal{H}(\mu) \neq E \\ \frac{1}{\Omega(E, V, N)} & \mathcal{H}(\mu) = E \end{cases}$$

Note that Lagrange multipliers seem to be often-used in this course to impose constraints, it would be wise to brush up on them.

We can also derive the same by maximising entropy.

Assuming we take microstates from the above system and assign them probabilities  $p_i$ ,

$$S' = - \sum_i^{\Omega} p_i \ln p_i - \lambda \left( \sum_i^{\Omega} p_i - 1 \right)$$
$$\frac{\partial S'}{\partial \lambda} = 0, \frac{\partial S'}{\partial p_i} = 0 \implies p_i = \frac{1}{\Omega} \forall i$$

Recall how we determined when entropy is maximised for a composite system, for certain energies of each system (In relation with the Zeroth law). We saw that the number of microstates of a particular energy increased exponentially around this point (refer to the previous lecture), and hence even if all microstates are equally

likely, there is a certain macroscopic configuration which allows for the most microstates, and hence is more likely to happen - this is the equilibrium point we reached.

## First Law of Thermodynamics

Say you have a system with one side a piston, you apply force  $\vec{J}$  to push it in by  $\delta\vec{x}$ , doing work on the system and increasing its energy but decreasing its volume.

Assuming initially at equilibrium, this tells us:

$$\begin{aligned} 0 = dS &= S(E + \vec{J} \cdot \delta\vec{x}, A(x - \delta x), N) - S(E, Ax, N) \\ &= \frac{\partial S}{\partial E} \vec{J} \cdot \delta\vec{x} + \frac{\partial S}{\partial x} \delta x \\ \implies \left( \frac{J}{T} + \frac{\partial S}{\partial x} \right) \delta x &= 0 \implies \left. \frac{\partial S}{\partial x} \right|_{N,E} = -\frac{J}{T} \end{aligned}$$

Hence we can identify another variable which must be equal for systems to be in composite equilibrium, this time when they are connected by a movable piston - can apply force on one another. We can write this in terms of pressure, taking the convention that  $P = -J/A$  for inwards  $J$ :  $\frac{\partial S}{\partial V} = \frac{P}{T}$

Now we can (in more general situations too) write the infinitesimal of entropy as  $dS = \frac{1}{T}dE - \frac{P}{T}dV$ , hence  $dE = TdS + PdV$ . We have also identified  $PdV$  with the work  $dW$ , so  $TdS$  has to be identified as the heat energy  $dQ$ .

## Two-Level System

A ground and an excited state at a difference  $\varepsilon$ ,  $N$  particles and energy  $E$ , hence there must be  $n_1 = E/\varepsilon$  particles in the excited state. This is the macrostate, the number of microstates consistent with this is  $\binom{N}{n_1}$  ( $N$  choose  $n_1$ ). Write entropy using Stirling's approximation,

$$\begin{aligned} S &= k_B \ln \Omega = k_B \ln \frac{N!}{n_1!(N - n_1)!} \\ &= k_B (N \ln N - \cancel{N} - n_1 \ln n_1 + \cancel{n_1} - (N - n_1) \ln(N - n_1) + \cancel{N} - \cancel{n_1}) \\ &= -Nk_b \left( \frac{n_1}{N} \ln \frac{n_1}{N} + \frac{N - n_1}{N} \ln \frac{N - n_1}{N} \right) \end{aligned}$$

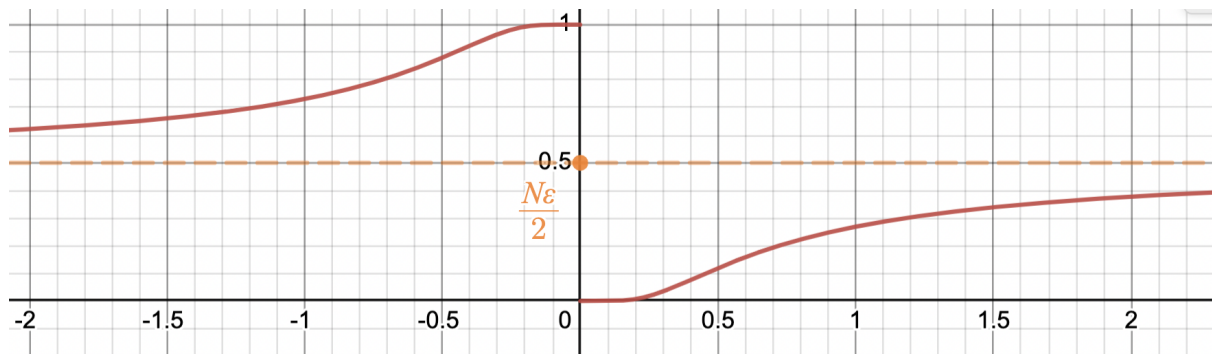
Then substitute  $n_1 = E/\varepsilon$  and write  $\frac{1}{T} = \frac{\partial S}{\partial E}$ :

$$\frac{1}{T} = -\frac{k_B}{\varepsilon} \ln \frac{N_{\varepsilon} - E}{N_{\varepsilon}}$$

$$\implies E = \frac{N_{\varepsilon}}{\exp \frac{\varepsilon}{k_B T} + 1}$$

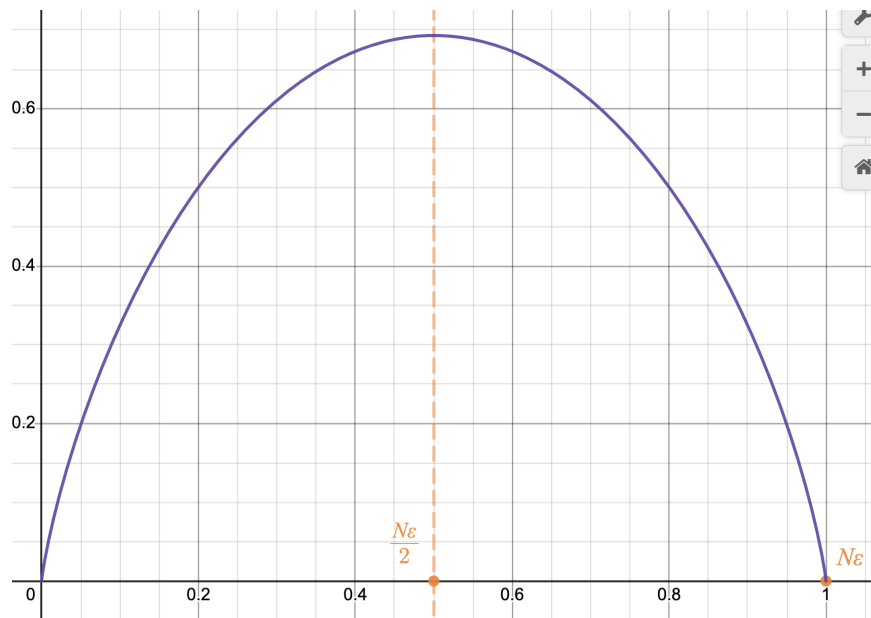
We can plot this to understand the behaviour of the system.

## Energy vs Temperature



0 at 0, increases asymptotically to  $\frac{N_{\varepsilon}}{2}$  as  $T \rightarrow \infty$ .

## Entropy vs Energy



At both  $E = 0$  and  $E = N_{\varepsilon}$ , the entropy should be 0, and it peaks at  $E = N_{\varepsilon}/2$ . But note a couple of related issues:

1. The energy can't be above  $\frac{N_{\varepsilon}}{2}$  for positive temperature, according to the E vs T graph.

- The entropy decreases with increasing energy after  $\frac{N\varepsilon}{2}$ , which identifies with negative temperature.

The answer is that the remaining energies are in fact associated with negative temperature - all the maths is consistent, but it messes with our interpretation of temperature.

The issue is that in practical systems, other behaviours of the system we have not accounted for here come into play (such as particles having positions and momenta and vibrational modes), and  $dS/dE$  is always positive, leading to our temperature identification remaining sensible.

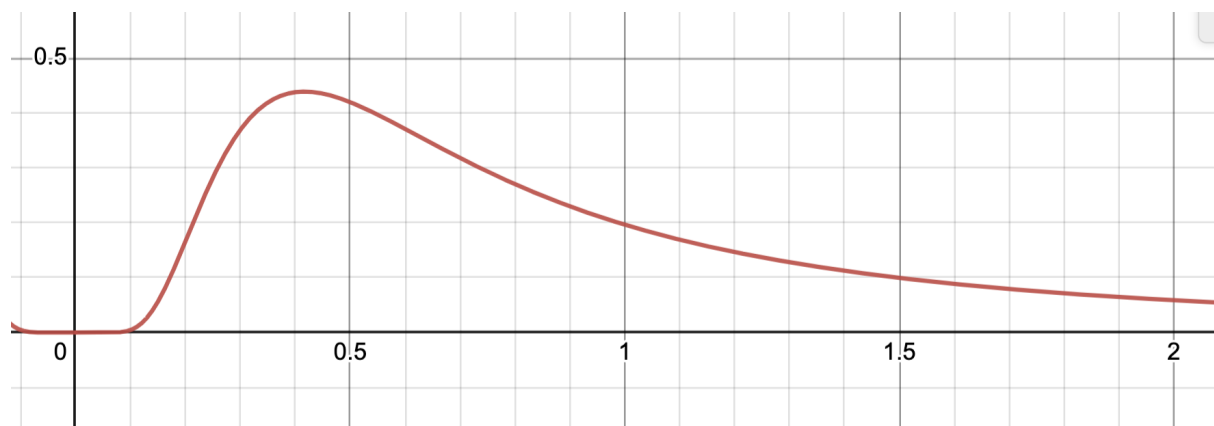
For hypothetical systems such as this, and for some weird systems modelled by hypothetical systems such as this, it actually makes more sense to interpret temperature as increasing as follows:

$$0^+ \rightarrow +\infty \rightarrow -\infty \rightarrow 0^-$$

$$\text{Cold} \rightarrow \text{Hot}$$

## Heat Capacity

$$C = \frac{dE}{dT} = \frac{Nk_B \left( \frac{\varepsilon}{k_B T} \right)^2 e^{\varepsilon/k_B T}}{(e^{\varepsilon/k_B T} + 1)^2}$$



# Lecture 13 - 438

☰ Course	PH 438 - Stat Mech
📅 Date	@February 9, 2023
☑ Notes completed	☑
⚙ Status	Completed
📎 Materials	
☑ Reviewed	<input type="checkbox"/>
🕒 Created	@February 9, 2023 8:41 AM

Next: Lecture 14 - 438

## Microcanonical Ensemble, continued

Ideal gas:

- No interactions
- No external potential (Other than a potential well to enforce finite volume)

Working in the limited volume  $V$ , we modify our probability slightly:

$$p(\mu) = \begin{cases} \frac{1}{\Omega(E, V, N)} & q_i \in V_{\text{box}}, \sum_i \frac{p_i^2}{2m} = E \\ 0 & \text{otherwise} \end{cases}$$

Then

$$\int_V \frac{1}{\Omega} \delta \left( E - \sum_i \frac{p_i^2}{2m} \right) d\Gamma = 1$$

For each particle,  $\int d^3 q_i = V$ , hence (N particles)

$$\Omega = V^N \oint_{\sum_i p_i^2 = 2mE} \prod_i d^3 p_i$$

Where the integral is over the surface of a  $3N$ -dim hypersphere, so it is the area of such a hypersphere.



▼ Surface area of  $d$ -dim hypersphere

Obviously, for radius  $R$ ,  $A_d = S_d R^{d-1}$ . (A circumference goes as  $R$ , a sphere's surface area is  $4\pi R^2$ , and so on.)

Now we'll do some trickery, start with a  $d$ -dim gaussian, the integral of which we know, and obtain  $S_d$  from it.

$$\left[ \int_{\mathbb{R}} e^{-x^2} dx \right]^d = \sqrt{\pi}^d$$

$$\left[ \int_{\mathbb{R}} e^{-x^2} dx \right]^d = \int e^{-\sum_i x_i^2} \prod_i dx_i$$

$\sum_i x_i^2 = r^2$  and  $\prod_i dx_i$ , the unit volume, can be written as  $A_d dr$  because of radial symmetry.  $y = r^2$ , then

$$\sqrt{\pi}^d = S_d \int r^{d-1} e^{-r^2} dr$$

$$= \frac{1}{2} S_d \int y^{\frac{d}{2}-1} e^{-y} dy = \frac{1}{2} S_d \Gamma\left(\frac{d}{2}\right)$$

Using that result,

$$\Omega(E, V, N) = V^N A_{3N}^{R=\sqrt{2mE}} = V^N S_{3N} (2mE)^{\frac{3N-1}{2}}$$

$$= V^N \frac{2\pi^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}\right)} (2mE)^{\frac{3N-1}{2}}$$

(Note for revision : This formula turns out to be wrong by a factor. Refer to next lecture.)

Now we can also evaluate the entropy,

$$\begin{aligned}
S(E, V, N) &= k_B \ln \Omega \\
&= k_B \left[ N \ln V + \ln 2 + \frac{3N}{2} \ln \pi + \frac{3N-1}{2} \ln(2mE) \right. \\
&\quad \left. - \left( \frac{3N}{2} - 1 \right) \ln \left( \frac{3N}{2} - 1 \right) + \left( \frac{3N}{2} - 1 \right) \right] \\
&\stackrel{\text{Large } N}{\approx} k_B \left[ N \ln V + \frac{3N}{2} \ln \pi + \frac{3N}{2} \ln(2mE) \right. \\
&\quad \left. - \left( \frac{3N}{2} \right) \ln \left( \frac{3N}{2} \right) + \left( \frac{3N}{2} \right) \ln e \right] = Nk_B \ln \left[ V \left( \frac{4\pi emE}{3N} \right)^{3/2} \right]
\end{aligned}$$

And then we can do something truly spectacular - start off by using this to evaluate temperature,

$$\begin{aligned}
\frac{\partial S}{\partial E} &=: \frac{1}{T} \\
\Rightarrow \frac{3Nk_B}{2E} &= \frac{1}{T} \Rightarrow E = \frac{3}{2} Nk_B T
\end{aligned}$$

This is the famous **equipartition theorem**!

There was a doubt raised as to why we got a finite  $\Omega$  - that is because we have swept under the rug a binning we have done, treating  $q_i$  as if there is a maximum resolution, as if they belong to a discrete set. This can also be noticed by seeing that if  $\Omega$  is just an amount and  $p(\mu)$  the probability and not the probability density, then we need to divide  $d\Gamma$  by the small volume we're discretising to for dimensional consistency.

Of course, if  $\Omega$  is not an amount, and  $p(\mu)$  is the probability density instead, then it's all good, because there's no argument for  $\Omega$  being infinite - but then it's not entirely accurate to call it the number of microstates.

# Lecture 16 - 438

☰ Course	PH 438 - Stat Mech
📅 Date	@February 16, 2023
☑ Notes completed	☑
⚙ Status	Completed
📎 Materials	
☑ Reviewed	<input type="checkbox"/>
🕒 Created	@February 16, 2023 8:41 AM

Next:

## Classical Harmonic Oscillators

At  $E, V, N$ ,

$$\mathcal{H}(q, p) = \sum_{i=1}^N \frac{p_i^2}{2m} + \frac{1}{2} m \omega^2 q_i^2$$
$$\Omega(E, V, N) = \int d\Gamma \delta(E - \mathcal{H})$$
$$\mathcal{H} = \frac{\omega}{2} \sum_i p_i'^2 + q_i'^2 = E$$

Thus to calculate  $\Omega$  we need to evaluate the surface area of a sphere in  $2N$  dimensional space, along with factors of  $\sqrt{m\omega}$  due to the rescaled coordinates and hence rescaled  $d\Gamma$ .

Then, similarly to previous lectures, we can derive the one-particle probability  $p(\vec{p}_1)$  as

$$p(\vec{q}_1, \vec{p}_1) = \frac{\Omega(E - \frac{p_1^2}{2m} - \frac{1}{2} m \omega^2 q_1^2, N - 1)}{\Omega(E, N)}$$
$$\sim \exp \left( -\beta \left( \frac{p_1^2}{2m} + \frac{1}{2} m \omega^2 q_1^2 \right) \right)$$

And we should obtain, on calculating the expectation values of the potential and kinetic energies, results as per the equipartition theorem:

$$\int \frac{p^2}{2m} \cdot p(q, p) dq dp = \left\langle \frac{p^2}{2m} \right\rangle = \frac{1}{2} k_B T$$

$$\int \frac{1}{2} m \omega^2 q^2 \cdot p(q, p) dq dp = \left\langle \frac{1}{2} m \omega^2 q^2 \right\rangle = \frac{1}{2} k_B T$$

The quantum harmonic oscillator should give the same results as the classical in the limit of high temperature.

## Quantum Harmonic Oscillator

The hamiltonian, in terms of quantum numbers:

$$\mathcal{H}(\{n_i\}) = \sum_i \hbar \omega \left( n_i + \frac{1}{2} \right)$$

$$\frac{E}{\hbar \omega} = \sum_i n_i + \frac{N}{2}$$

And hence we have a constraint for the microcanonical ensemble. It is merely a combinatorics problem then to see how to divide  $M = \frac{E}{\hbar \omega} - \frac{N}{2}$  of something into  $N$  groups, which is identical to choosing  $N - 1$  dividers to place when the  $M$  things are placed in a row, or from another perspective, ordering  $M + N - 1$  things when  $M$  and  $N - 1$  are identical.

$$\Omega(E, N) = \frac{(M + N - 1)!}{M!(N - 1)!}$$

While the algebra is left to us, the heat capacity is

$$C = N k_B \left( \frac{\hbar \omega}{k_B T} \right)^2 \frac{e^{\frac{\hbar \omega}{k_B T}}}{\left( e^{\frac{\hbar \omega}{k_B T}} - 1 \right)^2}$$

Classically,  $C = N k_B$ . When we let  $T \rightarrow \infty$  (or  $\hbar \rightarrow 0$ ), we obtain

$$C \approx Nk_B \left( \frac{\hbar\omega}{k_B T} \right)^2 \left( \frac{1 + \frac{\hbar\omega}{k_B T}}{\left( \frac{\hbar\omega}{k_B T} \right)^2} \right)$$

$$= Nk_B \left( 1 + \frac{\hbar\omega}{k_B T} \right)$$

Which tends to the correct answer, but also gives us a correction term at intermediate temperatures.

Anytime there's a gap  $\Delta E$  between the ground and first excited states in a system, should have the heat capacity behave like  $\sim e^{-\Delta E/kT}$  at low temperature.

We can of course calculate the one-particle probability and will obtain the Boltzmann distribution and equipartition theorem again.

# Lecture 17 - 438

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📅 Date	@February 27, 2023
☑ Notes completed	☑
⚡ Status	Completed
📎 Materials	
☑ Reviewed	<input type="checkbox"/>
🕒 Created	@February 27, 2023 10:41 AM

Next:

## Canonical Ensemble

In contrast to the isolated system that gave rise to the microcanonical ensemble, here the system can exchange energy with the surroundings, but the temperature of the system is fixed at  $T$ , in equilibrium with the surroundings.

We label the microstates with  $(N, V, T)$ , energy has a PDF  $P_\epsilon(\epsilon)$ . We'll try to find the probability density of microstates, knowing that the form  $\rho(\mathcal{H})$  will automatically satisfy equilibrium conditions.

We call the surroundings a *reservoir* (for a different-lettered subscript), and note that system + reservoir is an isolated system hence having the microcanonical ensemble and total fixed energy  $E_T$ . Assuming  $E_T \gg \mathcal{H}_s(\mu_s)$ , we'll calculate  $p(\mu_s)$ .

$$p(\mu_s \otimes \mu_r) = \frac{1}{\Omega_T(E_T)} \quad (\text{For } \mathcal{H}_s(\mu_s) + \mathcal{H}_r(\mu_r) = E_T)$$
$$p(\mu_s) = \sum_{\mu_r} p(\mu_s \otimes \mu_r) = \frac{\Omega_R(E_T - \mathcal{H}_r(\mu_r))}{\Omega_T(E_T)}$$

(Technically should have  $V_T, N_T$  and  $V_T - V_s, N_T - N_s$  as parameters above, but since we don't allow number or force exchange, these are constants, and the qualitatively

$$\begin{aligned}
\mathcal{H}_T &= \mathcal{H}_s + \mathcal{H}_r + \cancel{\mathcal{H}_{\text{int}}} \\
\mu_T &= \mu_s \otimes \mu_r \\
\Omega_T &= \Omega_s \times \Omega_r \\
S_T &= S_s + S_r + \cancel{S_{\text{corr}}}
\end{aligned}$$

▼ What followed was a long discussion on the validity of this model, where we discussed doubts such as

- What if the system is moving in the reservoir? Does this account for those situations, since mathematically we seem to not be taking the position of the system into account.
  - I don't know the answer to this, intuitively I feel like the results will be the same, but I have no idea how to justify that right now.
  - As a followup, should we be counting the number of possible locations of the system as well?
    - This I think is answered no, because we're looking at a specific subset of states which follow the rule that some particles stay in a particular region. We're not looking at what if these particles were confined anywhere, the system is a well-defined and fixed subregion of the universe.
- Is it still valid to use the microcanonical ensemble when we're limiting the possible microstates and hence some are not equally probable?
  - Yes, we are starting with a microcanonical and then looking at how a certain subset of those states is distributed using conditional probability and information about the rest of the system. It's a valid derivation, in my opinion.
- How is energy getting exchanged without an interaction hamiltonian?
  - Constraints, boundary conditions, the energy being a variable parameter, whatever you want to call it, but we can model behaviours in more ways than only modifying the hamiltonian.

$$\begin{aligned}
\langle \mathcal{H}_s(\mu_s) \rangle &= E \\
\langle \mathcal{H}_r(\mu_r) \rangle &= E_T - E \\
S_r(E_T - \mathcal{H}_s(\mu_s)) &= S_r(E_T - E) + (E - \mathcal{H}_s(\mu_s)) \frac{\partial S_r}{\partial E_r} + \dots
\end{aligned}$$

This taylor expansion allows us to simplify the expression for  $p(\mu_s)$  in terms of  $\Omega_s$ :

$$\begin{aligned}
p(\mu_s) &= \frac{\Omega_R(E_T - \mathcal{H}_r(\mu_r))}{\Omega_T(E_T)} = \frac{\exp(\frac{1}{k_B} S_r(E_T - E) + \frac{1}{k_B T} (E - \mathcal{H}_s(\mu_s)))}{\exp(\frac{1}{k_B} S_r(E_T - E) + \frac{T}{k_B T} S(E))} \\
&= \exp\left(\frac{E - TS(E) - \mathcal{H}_s(\mu_s)}{k_B T}\right) \\
&\implies p(\mu_s) \propto e^{-\beta \mathcal{H}}
\end{aligned}$$



# Lecture 18 - 438

☰ Course	PH 438 - Stat Mech
📅 Date	@February 28, 2023
☑ Notes completed	☑
⚙ Status	Completed
📎 Materials	
☑ Reviewed	<input type="checkbox"/>
🕒 Created	@February 28, 2023 11:44 AM

Next: Lecture 19 - 438

Recall some major results we derived in the previous lecture about the

## Canonical Ensemble

$$S_T(E_T) = S_r(E_T - E) + S_s(E)$$
$$p(\mu_s) \propto e^{-\beta \mathcal{H}_s(\mu_s)}$$

Then we define

$$\text{The Partition Function : } Z := \sum_{\{\mu_s\}} e^{-\beta \mathcal{H}_s(\mu_s)}$$

$$\text{s.t. } p(\mu_s) = \frac{1}{Z} e^{-\beta \mathcal{H}_s(\mu_s)}$$

$$\ln Z = -(E - TS)/k_B T$$

$$\text{Helmholtz Free Energy : } F(E) := E - TS(E)$$

$$\therefore F = -k_B T \ln Z$$

## Probability Distribution of Energy

$$\begin{aligned}
p(\varepsilon) &= \sum_{\{\mu_s\}} p(\mu_s) \delta(\mathcal{H}_s(\mu_s) - \varepsilon) = \frac{1}{Z} e^{-\beta \varepsilon} \sum_{\{\mu_s\}} \delta(\mathcal{H}_s(\mu_s) - \varepsilon) \\
&= \frac{1}{Z} e^{-\beta \varepsilon} \Omega(\varepsilon) = \frac{1}{Z} e^{-\beta \varepsilon} e^{\frac{TS(\varepsilon)}{k_B T}} \quad (\text{Using } S(\varepsilon) = k_B \ln \Omega(\varepsilon)) \\
&= \frac{e^{-\beta F(\varepsilon)}}{Z}
\end{aligned}$$

Since  $F(\varepsilon) \propto N$  (is an extensive quantity), in the limit of large  $N$  the saddle-point approximation can be applied, which will pick out the energy when  $F(\varepsilon)$  is **minimised** - this is **equilibrium** in the canonical ensemble.

#### ▼ Sidenote

Reet had an interesting suggestion that we could perhaps define a new information-based function for the PDF of the energy like how entropy is for the microstates and use that directly.

## Average Energy

$$\begin{aligned}
E = \langle \mathcal{H}_s(\mu_s) \rangle &= \sum_{\{\mu_s\}} \frac{e^{-\beta \mathcal{H}_s(\mu_s)}}{Z} \mathcal{H}_s(\mu_s) \\
&= \frac{1}{Z} \frac{-\partial}{\partial \beta} \sum_{\{\mu_s\}} e^{-\beta \mathcal{H}_s(\mu_s)} = \frac{1}{Z} \frac{-\partial Z}{\partial \beta} \\
&= \frac{-\partial}{\partial \beta} (\ln Z)
\end{aligned}$$

## Variance of Energy Distribution

$$\begin{aligned}
\sigma_E^2 &= \langle \mathcal{H}_s(\mu_s)^2 \rangle - \langle \mathcal{H}_s(\mu_s) \rangle^2 \\
&= \sum \mathcal{H}^2 \frac{e^{-\beta \mathcal{H}}}{Z} - \frac{1}{Z^2} \left( \sum \mathcal{H} e^{-\beta \mathcal{H}} \right)^2 \\
&= \frac{\partial^2 Z}{\partial \beta^2} = -\frac{\partial}{\partial \beta} \langle \mathcal{H} \rangle = k_B T^2 \frac{\partial \langle \mathcal{H} \rangle}{\partial T} \\
&= k_B T^2 C
\end{aligned}$$

The partition function encodes all the information about the system - it is a kind of moment-generating function, and all higher moments and cumulants can be generated from it.

## Two-level system (under canonical ensemble)

Each particle  $i$  is in the  $n_i$ th state,  $n_i \in \{0, 1\}$ , excited state has energy  $\varepsilon$  and total system has  $E, N$ .

$$\begin{aligned}
 \mathcal{H} &= \sum_i n_i \varepsilon, \\
 Z &= \sum_{\{\mu_s\}} e^{-\beta \sum_i n_i \varepsilon} = \sum_{\mu_s} \prod_i e^{-\beta n_i \varepsilon} \\
 &= \prod_i (1 + e^{-\beta \varepsilon}) = (1 + e^{-\beta \varepsilon})^N \\
 \therefore E &= -\frac{\partial \ln Z}{\partial \beta} = \frac{N \varepsilon}{e^{\beta \varepsilon} + 1} \\
 p(\mu) &= \frac{1}{Z} e^{-\beta \varepsilon \sum_i n_i} = \frac{1}{Z} \prod_i e^{-\beta \varepsilon n_i} = \prod_i p_i \\
 \therefore p_i &:= \frac{e^{-\beta \varepsilon n_i}}{1 + e^{-\beta \varepsilon}}
 \end{aligned}$$

# Lecture 19 - 438

☰ Course	PH 438 - Stat Mech
📅 Date	@March 2, 2023
☑ Notes completed	☑
⚡ Status	Completed
📎 Materials	
☑ Reviewed	<input type="checkbox"/>
🕒 Created	@March 2, 2023 8:56 AM

Next:

## Ideal Gas - Canonical Ensemble

$$\begin{aligned}
 \mathcal{H}(\mu_s) &= \sum_{i=1}^N \frac{p_i^2}{2m} \\
 Z &= \sum_{\{\mu_s\}} e^{-\beta \sum_{i=1}^N \frac{p_i^2}{2m}} \\
 &= \frac{1}{N!} \int \prod_i \frac{d^3 q_i d^3 p_i}{h^6} e^{-\beta \sum_{i=1}^N \frac{p_i^2}{2m}} \\
 &= \frac{V^N}{h^{3N} N!} \left( \int dp e^{-\beta \frac{p^2}{2m}} \right)^{3N} = \frac{V^N}{h^{3N} N!} \left( \sqrt{\frac{2\pi m}{\beta}} \right)^{3N} \\
 &= \frac{V^N}{N!} \left( \underbrace{\frac{2\pi m k_B T}{h^2}}_{1/\lambda(T)^2} \right)^{3N/2}
 \end{aligned}$$

$$\text{Thermal Wavelength : } \lambda(T) = \frac{h}{\sqrt{2\pi m k_B T}}$$

$$Z(E, V, N) = \frac{V^N}{N! \lambda(T)^{3N}}$$

Average energy is  $\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = \frac{3}{2} N k_B T$ , the free energy is  $F(E) = -k_B T \ln Z = -N k_B T \left( \ln \left( \frac{eV}{N} \right) + \frac{3}{2} \ln(2\pi m k_B T) \right)$ .

Then we can derive some state variables from  $F$  using  $F := E - TS \implies dF = dE - TdS - SdT$ , and the

**First Law of Thermodynamics**  $\rightarrow dE = TdS + \vec{J} \cdot d\vec{x}$

$$\begin{aligned}\vec{J} &= \frac{\partial F}{\partial \vec{x}} \\ S &= -\frac{\partial F}{\partial T} \\ -P &= \frac{\partial F}{\partial V} - \frac{Nk_B T}{V} \\ \mu &= \frac{\partial F}{\partial N} = k_B T \ln \left( \frac{N\lambda^3}{V} \right)\end{aligned}$$

## Gibbs Canonical Ensemble

Have movable pistons/some other form of flexible volume such that the system and surroundings can do mechanical work on each other. The macrostate is characterised by  $N, P, T$  now. Then a very similar approach to that of the canonical ensemble leads to the probability of a microstate.

$\chi$  is some state variable working analogously to volume - could be volume itself too.

$$\begin{aligned}p(\mu_s) &= \frac{\Omega_r(E_T - \mathcal{H}_s(\mu_s), \chi_T - \chi(\mu_s))}{\Omega_T(E_T, V_T)} \\ S_r &= S_r(E_T - E, V_T - V) + (E - \mathcal{H}_s(\mu_s)) \frac{\partial S_r}{\partial E_r} + (\vec{x} - \vec{x}_s) \frac{\partial S}{\partial \vec{x}} \frac{V^N}{N!} + \dots \\ p(\mu_s, \vec{x}_s) &= e^{\beta \mathcal{G}} e^{-\beta \mathcal{H}_s(\mu_s) + \beta \vec{J} \cdot \vec{x}} \\ -k_B T \ln Z &= \mathcal{G} = E - TS - \vec{J} \cdot \vec{x}\end{aligned}$$

The final expression is the **Gibbs' Free Energy**. A free energy can always be defined like this, given a partition function.

We can also get the volume and other state variables from the Gibbs free energy:

$$\vec{x} = -\frac{\partial \mathcal{G}}{\partial \vec{J}}$$

Now we can obtain the partition function explicitly,

$$\begin{aligned}
 p(\mu_s, V) &= \frac{1}{Z} e^{-\beta \sum_i \frac{p_i^2}{2m}} e^{-\beta PV} \\
 Z &= \frac{1}{N!} \int_0^\infty dV e^{-\beta PV} \int \prod_i \frac{d^3 q_i d^3 p_i}{h^6} e^{-\beta \sum_{i=1}^N \frac{p_i^2}{2m}} \\
 &= \frac{1}{N! \lambda^{3N}} \int_0^\infty dV e^{-\beta PV} V^N = \frac{1}{N! (\beta P)^{3N}}
 \end{aligned}$$

And then obtain state variables,

$$V = \frac{\partial G}{\partial P} = \frac{Nk_B T}{P}$$

When we take the derivative wrt  $\beta$ , we'll not get the average energy, but average of  $\mathcal{H} + PV$  (refer to the probability distribution). We call this the **enthalpy**.

$$\langle \mathcal{H} + PV \rangle = -\frac{\partial \ln Z}{\partial \beta} = \frac{5}{2} Nk_B T$$

# Lecture 20 - 438

☰ Course	PH 438 - Stat Mech
📅 Date	@March 6, 2023
☑ Notes completed	<input type="checkbox"/>
⚡ Status	In progress
📎 Materials	
☑ Reviewed	<input type="checkbox"/>
🕒 Created	@March 6, 2023 5:51 PM

Next: [Lecture 21 - 438](#)

## Grand Canonical Ensemble

Allowing number exchange with the surroundings, so the equilibrium condition becomes equality of chemical potential  $\mu$ .

For notational clarity, we will now refer to system macrostates with  $M = (\mu, V, T)$  and microstates with  $\omega = [\{(\vec{p}_i, \vec{q}_i)\}_{i=1}^N, N]$ .

We could also allow mechanical work à la Gibbs Canonical Ensemble, though we skip that in class.

$$\begin{aligned} p(\omega_s) &= \sum_{\{\omega_R\}} p(\omega_T) = \frac{\Omega_R(E_T - \mathcal{H}_s(\omega_s), N_T - N(\omega_s))}{\Omega_T(E_T, N_T)} \\ &= \frac{\exp(\frac{1}{k_B T} S_R(E_T - \mathcal{H}_s(\omega_s), N_T - N(\omega_s)))}{\exp(\frac{1}{k_B T} S_T(E_T, N_T))} \end{aligned}$$

Writing  $\langle \mathcal{H}_s(\omega_s) \rangle = E$ ,  $\langle N(\omega_s) \rangle = N$ , we expand  $S_R$  around these mean values.

$$\begin{aligned} S_T(E_T, N_T) &= S(E, N) + S_R(E_T - E, N_T - N) \\ &\quad S_R(E_T - \mathcal{H}_s(\omega_s), N_T - N(\omega_s)) \\ &\approx S_R(E_T - E, N_T - N) + (E - \mathcal{H}_s(\omega_s)) \frac{\partial S_R}{\partial E_R} + (N - N(\omega_s)) \frac{\partial S_R}{\partial N_R} \\ &= S_R(E_T - E, N_T - N) + \frac{1}{T} (E - \mathcal{H}_s(\omega_s)) - \frac{\mu}{T} (N - N(\omega_s)) \end{aligned}$$

Hence we can write

$$\begin{aligned}
 p(\omega_s) &= e^{\beta(E-TS-\mu N)} e^{-\beta \mathcal{H}_s(\omega_s) + \beta \mu u N(\omega_s)} \\
 \xRightarrow{\text{Grand Canonical Partition}} Q(\mu, V, T) &= \sum_{\omega_s} e^{-\beta \mathcal{H}_s(\omega_s) + \beta \mu u N(\omega_s)} \\
 &= \sum_{N=0}^{N_T} e^{\beta \mu N} \sum_{\omega_s | N} e^{-\beta \mathcal{H}_s(\omega_s | N)} = \sum_{N=0}^{N_T} e^{\beta \mu N} Z_c(N, V, T)
 \end{aligned}$$

Where  $Z_c$  is the canonical partition function. Often, we take  $N_T \rightarrow \infty$  here.

In the GC ensemble, the Grand Potential  $\mathcal{G} = -k_B T \ln Q = E - TS - \mu N$  is minimised.

We can write a probability distribution for  $N$ ,

$$p(N_s) = \frac{e^{\beta \mu N_s} Z_c(N_s, V, T)}{Q(\mu, V, T)}$$

$\langle N \rangle =$



# Lecture 21 - 438

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📅 Date	@March 13, 2023
☑ Notes completed	☑
⚙ Status	Completed
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☑ Reviewed	<input type="checkbox"/>
🕒 Created	@March 13, 2023 10:37 AM

Next: Lecture 22 - 438

We'll work out a couple more classical cases before moving on to quantum.

## Harmonic Oscillator (Canonical and Grand Canonical)

$N$  distinct (and distinguishable) oscillators,

$$\mathcal{H} = \sum_i \frac{p_i^2}{2m} + \frac{1}{2}m\omega^2 q_i^2$$

$Z_N(N, V, T) = \sum_{\{\omega_s\}} e^{-\beta \mathcal{H}(\omega_s)}$  is the canonical partition function,

$$\begin{aligned} Z(N, V, T) &= \int \cdots \int \prod_i^N dp_i dq_i e^{-\beta p_i^2/2m} e^{-\beta m\omega^2 q_i^2/2} \\ &= \sqrt{\frac{2\pi m}{\beta}}^N \sqrt{\frac{2\pi}{\beta m\omega^2}}^N = \left(\frac{2\pi}{\beta\omega}\right)^N \end{aligned}$$

Using this, we can derive the partition function for the grand canonical ensemble,

$$\begin{aligned} Q(\mu, V, T) &= \sum_{N=0}^{\infty} e^{\beta\mu N} \left(\frac{2\pi}{\beta\omega}\right)^N \\ &= \frac{1}{1 - \frac{2\pi}{\beta\omega} e^{\beta\mu}} \end{aligned}$$

Since the partition function must exist, be normalisable and hence positive,

$$e^{\beta\mu} < \frac{\beta\omega}{2\pi}$$

Generally, for distinguishable particles  $Z_N = Z_1^N$ , whereas for indistinguishable  $Z_N = \frac{1}{N!} Z_1^N$ , which give the grand canonical partition functions  $1/(1 - e^{\beta\mu} Z_1)$  and  $\exp(e^{\beta\mu} Z_1)$  respectively.

Note, we took  $N$  to be unbounded here, but in practical problems we tend to have constraints forcing a limit on  $N$  - we will have a question on this in the assignment.

## Euler Equation (for Extensive Systems)

If we scale all our extensive macroscopic variables by some  $\lambda$ , the energy scales by  $\lambda$  as well :  $E(\lambda S, \lambda V, \lambda N) = \lambda E(S, V, N)$ . This is what defines an extensive system.

**doubt** - do all the vars need to be extensive for the system to be so?

Take the derivative of this wrt  $\lambda$ :

$$E = \frac{\partial E}{\partial(\lambda S)} S + \frac{\partial E}{\partial(\lambda V)} V + \frac{\partial E}{\partial(\lambda N)} N$$

This should hold for all values of  $\lambda$ , so put  $\lambda = 1$  (we've already differentiated wrt  $\lambda$  wherever needed, so can do).

$$\begin{aligned} \therefore E &= \frac{\partial E}{\partial S} S + \frac{\partial E}{\partial S} \frac{\partial S}{\partial V} V + \frac{\partial E}{\partial S} \frac{\partial S}{\partial N} N \\ \therefore E &= TS - PV + \mu N \end{aligned}$$

Which is the **Euler equation**.

Put in the differential form and eliminate  $dE = TdS + \mu dN - PdV$  from both sides, then we get the **Gibbs-Duhem relation**,

$$SdT - VdP + Nd\mu = 0$$

The Euler equation also tells us that the grand canonical potential per particle becomes the chemical potential,  $\mu = \mathcal{G}/N$ .

# Lecture 22 - 438

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📅 Date	@March 14, 2023
☑ Notes completed	☑
⚙ Status	Doubts
📎 Materials	
☑ Reviewed	☐
🕒 Created	@March 14, 2023 11:39 AM

Next:

Logistics:

Assignment 3 is up, get it done. Discussion day yet to be decided.

Quiz 2: 21st Mar, Canonical + Grand Canonical, 1 pg handwritten formula sheet.

## Quantum Statistical Mechanics

Classically, our volume element is written as  $d\Gamma = \frac{1}{a^{3N} N!} \prod_{i=1}^N d^3\vec{p} d^3\vec{q}$ , where  $a$  is some scaling corresponding to the coarse graining. Trusting the validity of the quantum mechanical picture and that it should limit to the classical picture in some regimes,  $a = h$  seems appropriate.

Classically, the value of  $a$  is an ad-hoc choice as long as its dimensionally correct. Quantum mechanically, due to  $dp dq > h$  (uncertainty principle),  $h$  seems an appropriate choice.

### Validity of Classical Picture

For an example, consider the canonical partition function,

$$Z(N, V, T) = \frac{V^N}{N! \lambda^{3N}},$$
$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

Quantum effects become significant when  $\lambda \approx \text{avg interparticle spacing} \implies \frac{1}{\sqrt{T}} \approx (V/N)^{1/3}$ , so at low temperatures or high densities. The classical regime is  $\lambda \gg \text{spacing?}$  **doubt** - Not satisfied with how we've argued this.

## Revision : Quantum

Mostly too trivial to note down. Microstates become quantum states.

## Observables, operators and averages

It is worth noting that two kinds of averages occur in QSM: The first being the calculation of an expectation value is a kind of average,  $\langle \hat{O} \rangle = \langle \psi | \hat{O} | \psi \rangle$ , and the second being the averages over the ensemble of states, written as  $\bar{O}$ . Classically,

$$\bar{O}(t) = \int \prod_i d^3 p_i d^3 q_i O(\{p_i, q_i\}, t) \rho(\{p_i, q_i\}, t)$$

We want to write a similar quantum mechanical expression.

$$\begin{aligned} \overline{\langle \hat{O} \rangle} &= \sum_{\alpha} p_{\alpha} \langle \psi_{\alpha} | \hat{O} | \psi_{\alpha} \rangle \\ &= \sum_{\alpha, n, m} p_{\alpha} \langle \psi_{\alpha} | n \rangle \langle n | \hat{O} | m \rangle \langle m | \psi_{\alpha} \rangle \\ &= \sum_{n, m} \langle n | \hat{O} | m \rangle \langle m | \underbrace{\left( \sum_{\alpha} p_{\alpha} | \psi_{\alpha} \rangle \langle \psi_{\alpha} | \right)}_{\rho} | n \rangle \\ &= \text{Tr}(\rho \hat{O}) \end{aligned}$$

Where  $\rho$  is the density matrix, a pure state is one where  $\rho = |\psi\rangle\langle\psi|$  can be written, mixed states are others which can only be written as  $\rho = \sum_{\alpha} p_{\alpha} |\psi_{\alpha}\rangle\langle\psi_{\alpha}|$ . That happens when the states are not quantum mechanically superimposed but simply form an ensemble of possible states with classical probabilities of one of the ensemble being the true state.

## Density Matrices

- $\text{Tr}(\rho) = 1$ , always, because the coefficients for unit normalised states denote probabilities.
- Want real numbers for operator expectation values, so  $\rho^{\dagger} = \rho$ .
- Positivity:  $\langle \phi | \rho | \phi \rangle \geq 0 \forall |\phi\rangle$ .

These three properties are simple to derive from the definition of a density matrix.

Recall classically  $\frac{\partial \rho}{\partial t} = \{\mathcal{H}, \rho\}$ . We can quite easily derive the quantum mechanical counterpart,

$$i\hbar \frac{\partial \rho}{\partial t} = [\mathcal{H}, \rho]$$

Which we'll show is (as in classical) satisfied by  $\rho \equiv \rho(\mathcal{H})$ .

This was followed by a discussion on whether the probabilities could be time-dependent, identities of quantum states, etc. Nothing conclusive to note.

# Lecture 23 - 438

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📅 Date	@March 16, 2023
☑ Notes completed	☑
⚙ Status	Completed
📎 Materials	
☑ Reviewed	<input type="checkbox"/>
🕒 Created	@March 16, 2023 8:49 AM

Next:

## Quantum Stat Mech - Ensembles

### Microcanonical

We don't use the microcanonical ensemble often in QSM, because

- If we have two microcanonical systems connected, there is no guarantee the energy exchange will still give energy eigenstates. **Why is this such a problem? Why consider two systems at all?**

$$\langle n | \rho | m \rangle = \begin{cases} \frac{1}{\Omega(N, V, E)} & n = m, \varepsilon_n = E \\ 0 & \text{otherwise} \end{cases}$$
$$S = k_B \ln \Omega$$

### Canonical

probability  $p(\text{micro-can has energy } E_\nu) \propto e^{-\beta E_\nu}$

In the energy eigenbasis,

$$\begin{aligned}\rho_{nm} &= \rho_n \delta_{nm}, \quad \rho_n = \frac{1}{Z_N} e^{-\beta E_n} \\ Z_N(\beta) &= \sum_n e^{-\beta E_n} = \text{Tr}(e^{-\beta \mathcal{H}}) \\ \therefore \rho &= \frac{e^{-\beta \mathcal{H}}}{\text{Tr}(e^{-\beta \mathcal{H}})} \\ \overline{\langle \hat{O} \rangle}_N &= \text{Tr}(\rho \hat{O}) = \frac{\text{Tr}(\hat{O} e^{-\beta \mathcal{H}})}{\text{Tr}(e^{-\beta \mathcal{H}})}\end{aligned}$$

## Grand-Canonical

Since  $N$  isn't fixed any longer, our density matrix is now in Fock space.

$$\begin{aligned}\hat{\rho} &= \frac{\exp(-\beta(\mathcal{H} - \mu \hat{N}))}{Q(\mu, V, T)} \\ Q(\mu, V, T) &= \text{Tr}(e^{-\beta(\mathcal{H} - \mu \hat{N})}) \\ &= \sum_{N=0}^{\infty} e^{\beta \mu \hat{N}}\end{aligned}$$

Let's do an example problem with the canonical ensemble:

## Free Particle with Born von Karman boundary conditions (Periodic box)

$\phi(x + aL, y + bL, z + cL) = \phi(x, y, z)$  and so on.  $\mathcal{H} = \frac{\hat{p}^2}{2m}$ . Solution:

$$\begin{aligned}\phi_E(\vec{r}) &= \frac{e^{i\vec{k} \cdot \vec{r}}}{L^{3/2}} \\ E &= \frac{\hbar^2 k^2}{2m}, \quad \vec{k} = \frac{2\pi \vec{n}}{L}\end{aligned}$$

Density matrix in coordinate basis:

$$\begin{aligned}
\hat{\rho} &= \frac{\langle \vec{r} | e^{-\beta \mathcal{H}} | \vec{r}' \rangle}{\text{Tr}(e^{-\beta \mathcal{H}})} \\
\langle \vec{r} | e^{-\beta \mathcal{H}} | \vec{r}' \rangle &= \sum_{E, E'} \langle \vec{r} | E \rangle \langle E | e^{-\beta \mathcal{H}} | E' \rangle \langle E' | \vec{r}' \rangle \\
&= \sum_E \langle \vec{r} | E \rangle e^{-\beta E} \langle E | \vec{r}' \rangle = \sum_E e^{-\beta E} \phi_E(\vec{r}) \phi_E^*(\vec{r}') \\
&= \frac{1}{L^3} \sum_{\vec{k}} e^{-\beta \frac{\hbar^2 k^2}{2m}} e^{i\vec{k} \cdot (\vec{r} - \vec{r}')} \\
&\rightarrow \frac{1}{L^3} \frac{L^3}{(2\pi)^3} \int d^3 \vec{k} \exp\left(-\beta \frac{\hbar^2 k^2}{2m} + i\vec{k} \cdot (\vec{r} - \vec{r}')\right) \\
&= \left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2} \exp\left(-\frac{m}{2\beta\hbar^2} |\vec{r} - \vec{r}'|^2\right) \\
\text{Tr}(e^{-\beta \mathcal{H}}) &= \left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2} \int d^3 \vec{r} 1 \\
&= V \left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2} = \frac{V}{\lambda^3}
\end{aligned}$$

Thus

$$\hat{\rho}(\vec{r}, \vec{r}') = \frac{1}{V} \exp\left(-\frac{m}{2\beta\hbar^2} |\vec{r} - \vec{r}'|^2\right)$$

## Average Energy

$$\begin{aligned}
\langle \mathcal{H} \rangle &= \text{Tr}(\rho \mathcal{H}) \\
&= -\frac{\hbar^2}{2mV} \int d^3 \vec{r} \nabla^2 \exp\left(-\frac{m}{2\beta\hbar^2} |\vec{r} - \vec{r}'|^2\right) \\
&= \frac{1}{2\beta V} \int d^3 \vec{r} \exp\left(-\frac{m}{2\beta\hbar^2} |\vec{r} - \vec{r}'|^2\right) \left(3 - \frac{m}{\beta\hbar^2} |\vec{r} - \vec{r}'|^2\right)_{\vec{r}=\vec{r}'} \\
&= \frac{3}{2} k_B T
\end{aligned}$$



# Lecture 24 - 438

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📅 Date	@March 20, 2023
☑ Notes completed	☑
⚙ Status	Completed
📎 Materials	
☑ Reviewed	<input type="checkbox"/>
🕒 Created	@March 20, 2023 10:39 AM

Next: Lecture 25 - 438

We want to extend the quantum stat mech ideas we discussed last time to multi-particle systems with indistinguishability. This will lead us to quantum ideal gases.

## Quantum Multi-Particle Systems

### Indistinguishability

$$|\psi(x_1, x_2)|^2 = |\psi(x_2, x_1)|^2 \\ \implies E|\psi(1, 2)\rangle = |\psi(2, 1)\rangle = e^{i\phi}|\psi(1, 2)\rangle$$

For real particles, two exchanges should be identity, so  $\phi = 0, \pi$

$$|\psi(2, 1)\rangle = \begin{cases} |\psi(1, 2)\rangle & \text{Bosons} \\ -|\psi(1, 2)\rangle & \text{Fermions} \end{cases}$$

People do work with particles with  $\phi \neq 0, \pi$  — these are called *anyons*, since any angle is allowed.

A permutation  $P$  has an even or odd parity based on the number of exchanges required to accomplish the permutation ( $P$ ). The parity is  $(-1)^P$ .

Under  $P$ , fermionic states are eigenstates with eigenvalue  $(-1)^P$ , whereas bosonic states have eigenvalue  $+1$ . We denote them by a minus and a plus in the subscript respectively.

### N Particles

$$\mathcal{H} = \sum_{\alpha=1}^N \mathcal{H}_{\alpha},$$

$$\mathcal{H}_{\alpha} |k_{\alpha}\rangle = \frac{\hbar^2 k^2}{2m} |k_{\alpha}\rangle$$

General eigenstate :  $|k_1\rangle \dots |k_N\rangle$

$$\langle x_1 \dots x_N | k_1 \dots k_N \rangle = \frac{1}{V} e^{i \sum_{\alpha} x_{\alpha} k_{\alpha}}$$

But this product state does not represent a boson or fermion. For those, we have to symmetrise and antisymmetrise.

## Antisymmetrisation

$$|k_1 \dots k_N\rangle_- = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P |k_1 \dots k_N\rangle$$

Note that for this state, having any two  $k_i$  equal leads to the wavefunction vanishing - trivial for a fully antisymmetric state, but can also understand this by noting how every permutation which exchanges those two  $k_i$  can be paired with one which doesn't exchange them and has one less exchange, so those two terms cancel.

This is what gives us Pauli's Exclusion Principle for fermions.

## Symmetrisation

$$|k_1 \dots k_N\rangle_+ = \frac{1}{\sqrt{N_+}} \sum_P P |k_1 \dots k_N\rangle$$

$N_+$  here is  $N! \prod_k n_k!$ , multiplying over every distinct  $k$  with degeneracy  $n_k$ . This is easy to prove:

$$\begin{aligned} {}_+ \langle k_1 \dots k_N | k_1 \dots k_N \rangle_+ &= \frac{1}{N_+} \sum_{P, P'} \langle \dots P | | P' \dots \rangle \\ &= \frac{N!}{N_+} \sum_{P'} \langle \dots 1 | P' | \dots \rangle \end{aligned}$$

The inner product will only be non-zero when  $\dots 1 = \dots' (= P' \dots)$ , which leaves the freedom to have all permutations in all degenerate subsets of sizes  $n_k$ , hence giving a factor of  $n_k!$  for each, hence  $\frac{N! \prod_k n_k!}{N_+} = 1$ .



# Lecture 25 - 438

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📅 Date	@March 23, 2023
☑ Notes completed	<input type="checkbox"/>
⚡ Status	In progress
📎 Materials	
☑ Reviewed	<input type="checkbox"/>
🕒 Created	@March 27, 2023 10:43 AM

Next: [Lecture 26 - 438](#)

## Ideal Quantum Gas

Consider the grand canonical partition function for a quantum multi-particle system as we discussed last lecture, with discretised energy levels given by  $\varepsilon(k)$  and degeneracies  $n_k$ :

$$\begin{aligned} Q(\mu, V, T) &= \sum_{N=0}^{\infty} e^{\beta\mu N} Z_N(\beta) \\ &= \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_{\{n_k\}, \sum_k n_k = N} e^{-\beta \sum_k \varepsilon(k) n_k} \\ &= \sum_{\{n_k\}} e^{\beta\mu \sum_k n_k} e^{-\beta \sum_k \varepsilon(k) n_k} \\ &= \sum_{\{n_k\}} \prod_k e^{\beta(\mu - \varepsilon(k)) n_k} \end{aligned}$$

For fermions,  $n_k \in \{0, 1\}$ , so this simplifies to

$$Q_-(\mu, V, T) = \prod_k (1 + e^{-\beta(\varepsilon(k) - \mu)})$$

For bosons,  $n_k \in \mathbb{N}$ , so the sum becomes a geometric series and hence

$$Q_+(\mu, V, T) = \prod_k \frac{1}{1 - e^{-\beta(\varepsilon(k) - \mu)}}$$

Written concisely,

$$Q_\eta(\mu, V, T) = \prod_k (1 - \eta e^{-\beta(\varepsilon(k) - \mu)})^{-\eta}$$

Recall from the Euler equation,

$$\begin{aligned} -k_B T \ln Q &= \mathcal{G} = E - TS - \mu N = -PV \\ \therefore \frac{PV}{k_B T} &= \ln Q_\eta \end{aligned}$$

### Statistics - FD and EB:

$$\begin{aligned} N &= \frac{\partial \ln Q_\eta}{\partial \beta \mu} = -\eta \frac{\partial}{\partial \beta \mu} \sum_k \ln(1 - \eta e^{-\beta(\varepsilon(k) - \mu)}) \\ &= -\eta \sum_k \frac{-\eta e^{-\beta(\varepsilon(k) - \mu)}}{1 - \eta e^{-\beta(\varepsilon(k) - \mu)}} = \sum_k \frac{\eta^2 (=1)}{e^{\beta(\varepsilon(k) - \mu)} - \eta} \\ N &= \sum_k \langle n_k \rangle, \text{ so } \langle n_k \rangle = \frac{1}{e^{\beta(\varepsilon(k) - \mu)} - \eta} \end{aligned}$$

### Considering Degenerate states

For  $g$  degenerate states per energy level, we get a power of  $g$  for each energy level (since these are separate states, each with occupation or no occupation):

$$\begin{aligned} Q_-(\mu, V, T) &= \prod_k \left(1 + e^{\beta(\mu - \varepsilon(k))}\right)^g \\ \implies \frac{PV}{k_B T} &= g \sum_k \ln \left(1 + z e^{\beta \varepsilon(k)}\right) \end{aligned}$$

# Lecture 26 - 438

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📅 Date	@March 27, 2023
☑ Notes completed	☑
⚙ Status	Completed
📎 Materials	
☑ Reviewed	<input type="checkbox"/>
🕒 Created	@March 27, 2023 10:47 AM

Next: Lecture 27 - 438

## Ideal Fermi Gas

$$Q(\mu, V, T) = \prod_k (1 + ze^{-\beta\epsilon(k)})^g$$

$$z = e^{\beta\mu}, \epsilon(k) = \frac{\hbar^2 k^2}{2m}, \lambda = \frac{h}{\sqrt{2\pi m k_b T}}$$

$$\frac{P}{k_b T} = \frac{g}{\lambda^3} f_{5/2}(z)$$

$$\frac{N}{V} = \frac{g}{\lambda^3} f_{3/2}(z)$$

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

$$\text{Fermi Dirac Integral : } f_\nu(z) = \frac{1}{\Gamma(\nu)} \int_0^\infty dx \frac{x^{\nu-1}}{e^{x/z} + 1}$$

## Fermi Dirac Integral, $z \rightarrow 0$ limit

$$\begin{aligned}
f_\nu(z) &= \frac{1}{\Gamma(\nu)} \int_0^\infty dx \, z x^{\nu-1} e^{-x} (1 + z e^{-x})^{-1} \\
&= -\frac{1}{\Gamma(\nu)} \int_0^\infty dx \, x^{\nu-1} \sum_{\alpha=1}^{\infty} (-z e^{-x})^\alpha \\
&= -\sum_{\alpha=1}^{\infty} \frac{(-z)^\alpha}{\Gamma(\nu)} \int_0^\infty dx \, x^{\nu-1} e^{-\alpha x} \\
&\stackrel{y=\alpha x}{=} -\sum_{\alpha=1}^{\infty} \frac{(-z)^\alpha}{\Gamma(\nu)} \frac{\Gamma(\nu)}{\alpha^\nu} = \sum_{\alpha=1}^{\infty} (-1)^{\alpha+1} \frac{z^\alpha}{\alpha^\nu}
\end{aligned}$$

Then, for small  $z$ , we can truncate this series where we want.

## Compute Macro Variables

$$\begin{aligned}
\frac{P\lambda^3}{gk_B T} &= z - \frac{z^2}{2^{5/2}} + \frac{z^3}{3^{5/2}} + \dots \approx z \\
\frac{N\lambda^3}{gV} &= z - \frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} + \dots \approx z
\end{aligned}$$

For  $z \rightarrow 0$ ,  $N\lambda^3/V$  is small, which (as we discussed in a past lecture) is the classical limit. So in the classical limit, we equate the pressure-temperature and number-volume ratios and get the classical ideal gas equation,

$$PV = Nk_B T$$

Now if we work in slightly larger  $z$ , we can use these two expressions to add correction terms from one to the other.

$$\begin{aligned}
z &= \frac{N\lambda^3}{gV} + \frac{z^2}{2^{3/2}} + \dots \\
&\approx \frac{N\lambda^3}{gV} + \left(\frac{N\lambda^3}{gV}\right)^2 \frac{1}{2^{3/2}} \\
\frac{P\lambda^3}{gk_B T} &\approx z - \frac{z^2}{2^{5/2}} \\
&\approx \frac{N\lambda^3}{gV} + \left(\frac{N\lambda^3}{gV}\right)^2 \frac{1}{2^{3/2}} - \frac{1}{2^{5/2}} \left(\frac{N\lambda^3}{gV} + \left(\frac{N\lambda^3}{gV}\right)^2 \frac{1}{2^{3/2}}\right)^2 \\
&\approx \frac{N\lambda^3}{gV} + \left(\frac{N\lambda^3}{gV}\right)^2 \left(\frac{1}{2^{3/2}} - \frac{1}{2^{5/2}}\right) \\
&\approx \frac{N\lambda^3}{gV} + \left(\frac{N\lambda^3}{gV}\right)^2 \frac{1}{2^{3/2}}
\end{aligned}$$

This increased pressure (as compared to the classical, non-degenerate limit) can be understood as the manifestation of the sort-of repulsion of fermions since they can't occupy the same state - think the degeneracy pressure in neutron stars.



# Lecture 27 - 438

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📅 Date	@March 28, 2023
☑ Notes completed	☑
⚙ Status	Completed
📎 Materials	
☑ Reviewed	<input type="checkbox"/>
🕒 Created	@March 28, 2023 11:43 AM

Next: [Lecture 28 - 438](#)

**Quantum Limit,**  $\frac{N\lambda^3}{Vg} \rightarrow \infty \Leftrightarrow T \rightarrow 0$

$$\langle n_k \rangle = \frac{1}{e^{\beta(\varepsilon(k) - \mu)} + 1} \rightarrow \begin{cases} 1 & \varepsilon(k) < \mu(T=0) \\ 0 & \varepsilon(k) > \mu(T=0) \end{cases}$$

Thus we get  $\langle n_k \rangle = \Theta(\varepsilon_F - \varepsilon(k))$ , where  $\varepsilon_F = \mu(T=0)$  is the fermi energy.

For non-zero temperatures, we see the familiar shape of the Fermi-Dirac distribution.

Back at  $T \rightarrow 0$ ,  $k_F := \sqrt{2m\varepsilon_F}/\hbar$ , then (for degeneracy  $g$  for every energy level),

$$\begin{aligned} N &= \sum_k g \langle n_k \rangle = \sum_{k < k_F} g \\ &\xrightarrow[N, V \rightarrow \infty, N/V=n]{\text{Thermodynamic limit}} g \frac{V}{(2\pi)^3} \int_0^{k_F} d^3k \\ &= \frac{gV k_F^3}{6\pi^2} \\ &\Rightarrow k_F = \sqrt[3]{\frac{6\pi^2 N}{gV}}, \\ \mu(T=0) = \varepsilon_F &= \frac{\hbar^2}{2m} \left( \frac{6\pi^2 n}{g} \right)^{2/3} \end{aligned}$$

Note that there are two levels of limits here - the thermodynamic limit, which is always working in the background in this course, that  $N, V \rightarrow \infty$  but their ratio is some finite  $n$ . And then again, for the quantum limit, we need  $n\lambda^3/g \rightarrow \infty$ . It may seem useless to separate these limits, but it's very necessary for rigour.

## Finite temperature corrections (Using perturbation)

First, we need to write the fermi integral in a more useful form for this regime,

$$\begin{aligned}
 f_\nu(z) &= \frac{1}{\Gamma(\nu)} \int_0^\infty dx \frac{x^{\nu-1}}{e^{x/z} + 1} \\
 &= \frac{1}{\Gamma(\nu)} \left[ \cancel{\frac{1}{\nu} \frac{x^\nu}{e^{x/z} + 1} \Big|_0^\infty} - \int_0^\infty dx \frac{x^\nu}{\nu} \frac{d}{dx} \left( \frac{1}{e^{x/z} + 1} \right) \right] \\
 &\quad \text{Sub } x = \ln z + t \\
 f_\nu(z) &= \frac{1}{\Gamma(\nu+1)} \int_0^\infty dx x^\nu \frac{d}{dx} \left( \frac{-1}{e^{x/z} + 1} \right) \\
 &= \frac{1}{\Gamma(\nu+1)} \int_{-\ln z}^\infty dt (\ln z + t)^\nu \frac{d}{dt} \left( \frac{-1}{e^t + 1} \right)
 \end{aligned}$$

Now the  $\frac{d}{dt} \left( \frac{-1}{e^t + 1} \right)$  is the derivative of the Fermi-Dirac distribution, so it peaks around  $t = 0$  and tends to 0 everywhere else quite quickly. So we can approximate this integral by one with the same integrand but limits  $-\infty \leq t \leq \infty$  - the additional region we're integrating over is barely going to contribute, but makes computation easier.

$$f_\nu(z) = \frac{1}{\Gamma(\nu+1)} \sum_{\alpha} \binom{\nu}{\alpha} (\ln z)^{\nu-\alpha} \int_{-\infty}^{\infty} dt t^\alpha \frac{d}{dt} \left( \frac{-1}{e^t + 1} \right)$$

Now note that  $t^\alpha \frac{d}{dt} \left( \frac{-1}{e^t + 1} \right)$  is (slightly non-trivially) an odd function for odd  $\alpha$ , so the integral is 0. For even  $\alpha$ , we can evaluate it as double the fermi function:

$$\int_{-\infty}^{\infty} dt t^\alpha \frac{d}{dt} \left( \frac{-1}{e^t + 1} \right) = \begin{cases} 0 & \text{odd } \alpha \\ 2f_\alpha(1)\Gamma(\alpha+1) & \text{even } \alpha \end{cases}$$

Thus

$$f_\nu(z) = \frac{(\ln z)^\nu}{\Gamma(\nu+1)} \sum_{\alpha=0}^{\infty} 2f_{2\alpha}(1) \frac{\Gamma(\nu+1)}{\Gamma(\nu-2\alpha+1)} (\ln z)^{-2\alpha}$$

Some standard values of  $f_\nu(1)$ :

$$\begin{aligned}f_0(1) &= \frac{1}{2} \\f_1(1) &= \frac{\pi^2}{12} \\f_2(1) &= \frac{7\pi^4}{720}\end{aligned}$$

Thus we get the Sommerfeld expansion:

$$f_\nu(z) = \frac{(\ln z)^\nu}{\Gamma(\nu + 1)} \left[ 1 + \frac{\pi^2}{6} \frac{\nu(\nu - 1)}{(\ln z)^2} + \frac{7\pi^4}{360} \frac{\nu(\nu - 1)(\nu - 2)(\nu - 3)}{(\ln z)^4} + \dots \right]$$

Using the first term of this expansion, we can obtain the fermi energy from  $N\lambda^3/gV = f_{3/2}(e^{\beta\varepsilon_F})$ .

# Lecture 28 - 438

☰ Course	PH 438 - Stat Mech
📅 Date	@April 3, 2023
☑ Notes completed	☑
⚡ Status	Doubts
📎 Materials	
☑ Reviewed	☐
🕒 Created	@April 3, 2023 10:44 AM

Next: Lecture 29 - 438

## Ideal Bose Gas

$$n_k \in \mathbb{N} \cup \{0\},$$

$$\begin{aligned} Q_+(\mu, V, T) &= \prod_k \sum_{n_k} e^{\beta(\mu - \varepsilon(k))n_k} \\ &= \prod_k \frac{1}{1 - ze^{-\beta\varepsilon(k)}} \text{ when } z < e^{\beta\varepsilon(k)} \forall k \\ &\quad \therefore z < \min\{e^{\beta\varepsilon(k)}\} = 1 \\ &\quad \therefore 0 < z < 1 \implies \mu < 0 \end{aligned}$$

*what does this mean, though?*

$$\begin{aligned} \frac{PV}{k_B T} &= \ln Q_+(\mu, V, T) \\ &= -g \sum_k \ln(1 - ze^{-\beta\varepsilon(k)}) \\ N &= \sum_k \langle n_k \rangle = g \sum_k \frac{1}{e^{\beta\varepsilon(k)}/z - 1} \\ \sum_k &\rightarrow \frac{V}{(2\pi)^3} \int d^3k \end{aligned}$$

It is important that we separate the  $k = 0$  state from the rest before we sum, because the continuum limit gives the wrong answer in that case - in systems like

the Bose-Einstein condensate, we know that the ground state has a large contribution, but the integral has  $d^3k \propto k^2 dk$  terms which remove the ground state contribution. So

$$\begin{aligned}\frac{P}{k_B T} &= -g \int_0^\infty \frac{4\pi k^2}{(2\pi)^3} dk \ln(1 - ze^{-\beta\varepsilon(k)}) - \frac{g}{V} \ln(1 - z) \\ \frac{N}{V} &= g \int_0^\infty \frac{4\pi k^2}{(2\pi)^3} dk \frac{1}{e^{\beta\varepsilon(k)}/z - 1} + \frac{g}{V} \frac{z}{z - 1}\end{aligned}$$

In the  $z \rightarrow 0$  classical limit, the extra term has no contribution, but in the  $z \rightarrow 1$  quantum limit, it has some significant contribution - let it be  $\frac{z}{z-1} \rightarrow N_0 = \mathcal{O}(N)$ . Since this is the  $k = 0$  contribution term,  $N_0$  is the number of ground state particles (for each of the  $g$  degenerate ground states).

$$\begin{aligned}z &= N_0/(N_0 + 1), \\ \frac{\ln(1 - z)}{V} &= \frac{1}{V} \ln\left(\frac{1}{N_0 + 1}\right) \\ &\sim \Theta\left(\frac{\ln N}{N}\right) \xrightarrow{z \rightarrow 1} 0\end{aligned}$$

Thus  $P/k_B T$  does not change in the quantum limit.

Using the substitution  $x = \beta \frac{\hbar^2 k^2}{2m}$ , we obtain

$$\begin{aligned}\frac{P}{k_B T} &= \frac{g}{\lambda^3} \frac{4}{3\sqrt{\pi}} \int_0^\infty dx \frac{x^{3/2}}{e^{x/z} - 1} \\ \frac{N}{V} &= \frac{g}{\lambda^3} \frac{2}{\sqrt{\pi}} \int_0^\infty dx \frac{x^{1/2}}{e^{x/z} - 1} + \frac{N_0}{V}\end{aligned}$$

Notice the similar integrals in both expressions. These are called **Bose-Einstein functions**:

$$\begin{aligned}g_\nu(z) &= \frac{1}{\Gamma(\nu)} \int_0^\infty dx \frac{x^{\nu-1}}{e^{x/z} - 1} \\ \frac{P}{k_B T} &= \frac{g}{\lambda^3} g_{5/2}(z) \\ \frac{N - N_0}{V} &= \frac{g}{\lambda^3} g_{3/2}(z)\end{aligned}$$

▼ Sidenote - Average energy

$$\begin{aligned}
 E &= -\frac{\partial \ln Q_+}{\partial \beta} = \sum_k \varepsilon(k) n(k) \\
 &= \frac{3}{2} PV????
 \end{aligned}$$

## Evaluating the Bose-Einstein functions

$$\begin{aligned}
 g_\nu(z) &= \frac{1}{\Gamma(\nu)} \int_0^\infty dx \frac{x^{\nu-1}}{e^x/z - 1} \\
 &= \frac{1}{\Gamma(\nu)} \int_0^\infty dx \, z e^{-x} x^{\nu-1} \left( \sum_{\alpha=0}^\infty (z e^{-x})^\alpha \right) \\
 &= \sum_{\alpha=1}^\infty \frac{z^\alpha}{\Gamma(\nu)} \int_0^\infty dx e^{-\alpha x} x^{\nu-1} \\
 &= \sum_{\alpha=1}^\infty \frac{1}{\Gamma(\nu)} \frac{z^\alpha}{\alpha^\nu} \int_0^\infty e^{-y} y^{\nu-1} dy \\
 &= \sum_{\alpha=1}^\infty \frac{z^\alpha}{\alpha^\nu}
 \end{aligned}$$

And thus we can express  $P/k_B T, N/V$  as series in  $z$ .

$$\begin{aligned}
 \frac{P\lambda^3}{gk_B T} &= g_{5/2}(z) = z + \frac{z^2}{2^{5/2}} + \frac{z^3}{3^{5/2}} + \dots \\
 \frac{(N - N_0)\lambda^3}{gV} &= g_{3/2}(z) = z + \frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} + \dots
 \end{aligned}$$

# Lecture 29 - 438

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📅 Date	@April 6, 2023
☑ Notes completed	☑
⚙ Status	Completed
📎 Materials	
☑ Reviewed	<input type="checkbox"/>
🕒 Created	@April 6, 2023 8:43 AM

Next:

## Classical Limit : $z \rightarrow 0$

$$z = \frac{N\lambda^3}{gV} - \frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} + \dots$$
$$\approx \frac{N\lambda^3}{gV} - \frac{1}{2^{3/2}} \left( \frac{N\lambda^3}{gV} \right)^2 + \dots$$

Because when  $z$  is small,  $z^2$  can be neglected in the expression for  $z$ , so we can put  $z = N\lambda^3/gV$  in the RHS for correction terms.

$$\frac{P\lambda^3}{gk_B T} = z + \frac{z^2}{2^{5/2}} + \frac{z^3}{3^{5/2}} + \dots$$
$$\implies PV \approx Nk_B T ()$$

As opposed to the Fermi gas, the correction terms here come with a negative sign - effective attraction.

## Quantum Limit : $z \rightarrow 1$

$$\begin{aligned}
\frac{N}{V} &= \frac{g}{\lambda^3} g_{3/2}(z) + \frac{N_0}{V} \\
\Rightarrow \frac{(N - N_0) N_e}{V} &= \frac{g}{\lambda^3} g_{3/2}(z) \\
&\leq \frac{g}{\lambda^3} g_{3/2}(1) \\
g_{3/2}(1) &= 1 + \frac{1}{2^{3/2}} + \frac{1}{3^{3/2}} + \dots \\
&= \zeta(3/2) = 2.612\dots \text{ (Riemann-Zeta, standard result)} \\
\therefore \frac{N_e}{V} &\leq \frac{g}{\lambda^3} 2.612\dots
\end{aligned}$$

Thus, there is an effective limit on the number of particles the excited states can hold, given a volume and temperature.

## Bose-Einstein Condensate

If we try to have more than that, all of them go to the ground state, becoming a bose-einstein condensate where a macroscopic number of particles enter the ground state - this is a momentum-space condensation, since all particle condense to the same energy-momentum state.

This occurs because the solution of our system is where the  $N_e$  we want and  $g_{3/2}(z)$  (scaled by other things appropriately) become equal. If  $g_{3/2}(z)$  was asymptotic for  $z \rightarrow 1$  (since it is clearly an increasing function of  $z$ ), every  $N_e$  would be a possible solution, but for  $\nu > 1$ ,  $g_\nu(z \rightarrow 1)$  converges to some finite value, hence  $N_e$  is bounded (though  $N$  is not, the rest goes into  $N_0$ ).

$\nu \leq 1$  would not have this hold. For other-dimensional gases, or for relativistic gases, etc, you get different  $\nu$  - 2D gives  $\nu = 1$ , which diverges. There are some questions in the assignment about this.

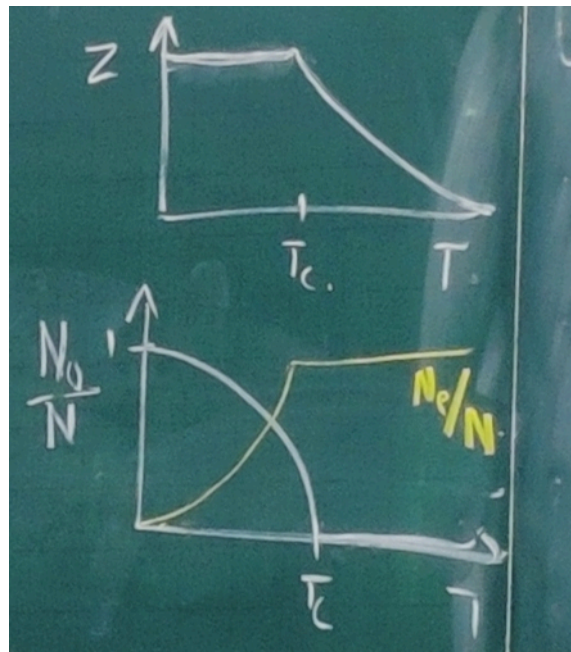
Thus, the bose-einstein condensation condition (in terms of temperature) can be derived.

$$\begin{aligned}
\frac{N}{V} &\geq \frac{g}{\lambda^3} \zeta(3/2) \\
\Rightarrow T &\leq T_c = \frac{h^2}{2\pi m k_B} \left( \frac{N}{V \zeta(3/2)} \right)^{2/3}
\end{aligned}$$

Since  $z = 1 - \frac{1}{N_0}$ , we can plot  $N_e/N$ ,  $N_0/N$  and  $z$  vs  $T$ , and for  $T \leq T_c$  you have BEC behaviour so  $N_0/N$  is a large fraction and  $z$  stays very close to 1,



whereas  $N_e/N$  is a small fraction which increases with temperature. After  $T > T_c$ , we see normal behaviour -  $z$  decreases,  $N_0/N$  is almost 0,  $N_e/N$  is almost 1.



Also, for  $T \leq T_c$ , the pressure gains  $T^{5/2}$  behaviour:

$$P = \frac{g k_B T}{\lambda^3} g_{5/2}(1) \sim 1.3 T^{5/2}$$

And since we're adding particles to the ground state which has no momentum and no pressure contribution, we have infinite compressibility (as in  $\frac{\partial P}{\partial V}$  is infinite, not that you can actually compress it infinitely, because then the macroscopic definition of compressibility and other steps in our calculations, like the continuum limit, breaks down).