

## *Dr Zbigniew Idziaszek*

*Opracowanie utworu pod tytułem:*

***"Kondensacja Bosego-Einsteina" w ramach kursu zaawansowanego, organizowanego dniach 31.08 – 25.09.09 będącego kontynuacją szkoleń z zakresu eksploatacji i zarządzania dużą infrastrukturą badawczą organizowanego przez Narodowe Laboratorium Technologii Kwantowych***



BOSE - EINSTEIN CONDENSATION IN IDEAL GASES

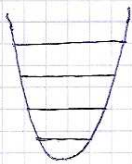
1

Ensembles in statistical physics

1) MICROCANONICAL ENSEMBLE

Partition function:  $\Gamma(N, E)$  = number of microstates with  $N$  particles and total energy  $E$

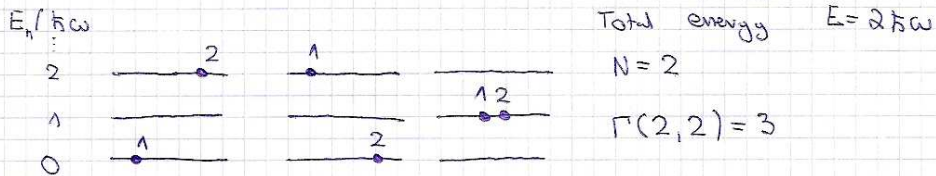
Example: Two particles in 1D harmonic oscillator potential



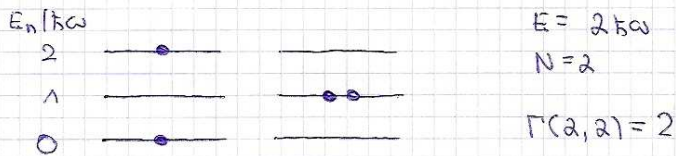
$E_n = \hbar\omega(n + \frac{1}{2})$

For simplicity we omit zero-point oscillation energy as the zero of energy is arbitrary

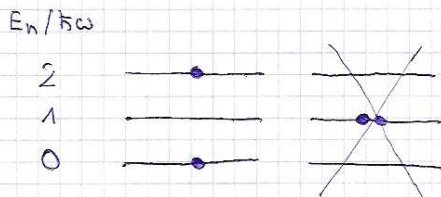
a) Partition function for distinguishable particles (Boltzmann statistics)



b) Partition function for bosons (Bose-Einstein statistics)



c) Partition function for fermions (Fermi-Dirac statistics)



Pauli exclusion principle prevents particles from occupying the same state



## 2) CANONICAL ENSEMBLE

(2)

Canonical partition function

$$Z(N, \beta) = \sum_E e^{-\beta E} \Gamma(N, E) \quad \beta = \frac{1}{k_B T}$$

Sum is taken over all eigenenergies of the many-body system

Control parameters:  $N$  - total number of particles  
 $T$  - temperature

## 3) GRAND CANONICAL ENSEMBLE

Partition function:

$$\Xi(z, \beta) = \sum_{N=0}^{\infty} z^N Z(N, \beta) = \sum_{N=0}^{\infty} \sum_E z^N e^{-\beta E} \Gamma(N, E)$$

Sum is taken over particle number and energies

Control parameters:  $z = e^{\beta \mu}$  - fugacity  
 $T$  - temperature

The grand canonical ensemble is most convenient for calculations since there are no constraints put on the total number of particles  $N$  and the total energy  $E$ . However, the experimental conditions (atoms in an isolated trap) favor microcanonical ( $N = \text{const}$ ,  $E = \text{const}$ ) and canonical ( $N = \text{const}$ ) ensembles.

Basic thermodynamic properties of the condensed system are not dependent on the statistical ensemble used, therefore most of our derivations will be performed in grand canonical ensemble. We will resort to the canonical and microcanonical ensemble, at the end of this lecture, when calculating fluctuations of the condensate.





GRAND CANONICAL PARTITION FUNCTION FOR AN IDEAL GAS ③

$$\begin{aligned} \Xi(z, \beta) &= \sum_{N=0}^{\infty} z^N \sum_E e^{-\beta E} \Gamma(N, E) = \sum_{N=0}^{\infty} z^{\sum_k n_k} \sum_E e^{-\beta \sum_k n_k E_k} \Gamma(N, E) \\ &= \sum_{n_0=0}^{\infty} \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \dots z^{\sum_k n_k} e^{-\beta \sum_k E_k n_k} \end{aligned}$$



Sum is taken over set  $\{n_k\}$  of occupation numbers of single-particle states with corresponding energies  $\{E_k\}$

$$\Xi(z, \beta) = \prod_{k=0}^{\infty} \left( \sum_{n_k=0}^{\infty} z^{n_k} e^{-\beta E_k n_k} \right) = \prod_{k=0}^{\infty} \frac{1}{1 - z e^{-\beta E_k}}$$

All the thermodynamic quantities can be calculated from

the grand canonical potential  $\Omega(z, \beta) = -k_B T \ln \Xi(z, \beta)$

Total number of particles in the system

$$\langle N \rangle = z \frac{\partial}{\partial z} \ln \Xi(z, \beta) = \sum_{k=0}^{\infty} \frac{z e^{-\beta E_k}}{1 - z e^{-\beta E_k}}$$

The equation above can be used to fix the value of  $z$ ,

when the total number of particles is used as control parameter

$$N = \langle N \rangle(\beta, z) = \sum_{k=0}^{\infty} \frac{z e^{-\beta E_k}}{1 - z e^{-\beta E_k}}$$

Total energy

$$\langle E \rangle = - \frac{\partial}{\partial \beta} \ln \Xi(z, \beta) = \sum_{k=0}^{\infty} E_k \frac{z e^{-\beta E_k}}{1 - z e^{-\beta E_k}}$$

Mean occupation of a single-particle state with energy  $E_k$

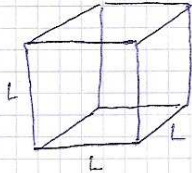
$$\langle n_k \rangle = - \frac{\partial}{\partial (\beta E_k)} \ln \Xi(z, \beta) = \frac{z e^{-\beta E_k}}{1 - z e^{-\beta E_k}}$$

$$\langle N \rangle = \sum_{k=0}^{\infty} \langle n_k \rangle$$



BOSE-EINSTEIN CONDENSATION IN A HOMOGENEOUS SYSTEM (4)

For simplicity we consider gas of  $N$  atoms in 3D box with periodic boundary conditions



Single particle wave functions

$$\Psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\vec{r}} \quad \vec{k} = \frac{2\pi}{L} (n_x, n_y, n_z)$$

$$\text{Energies } E_{\vec{k}} = \frac{\hbar^2 k^2}{2m} \quad V = L^3$$

In principle one can choose different boundary conditions, for instance Dirichlet b.c.:  $\Psi(0) = \Psi(L) = 0$ , corresponding to a quantum well. They should be, however, equivalent in the thermodynamic limit.

$$\ln \Xi(z, \beta) = - \sum_{\vec{k}} \ln(1 - z e^{-\beta E_{\vec{k}}}) = - \ln(1-z) + \sum_{j=1}^{\infty} \frac{z^j}{j} \sum_{\vec{k} \neq 0} e^{-\beta_j E_{\vec{k}}}$$

where we have used  $\ln(1-x) = - \sum_{n=1}^{\infty} \frac{x^n}{n}$

In the thermodynamic limit ( $N \rightarrow \infty, V \rightarrow \infty$ )

$$\sum_{\vec{k} \neq 0} e^{-\beta_j E_{\vec{k}}} = \sum_{\vec{k} \neq 0} e^{-\beta_j \frac{\hbar^2 k^2}{2m}} \rightarrow \frac{V}{(2\pi)^3} \int d^3k e^{-\beta_j \frac{\hbar^2 k^2}{2m}} = \frac{V}{\lambda^3 j^{3/2}}$$

We can replace summation by integration since separation between single particle energies becomes smaller and smaller as  $V$  increases.

$$\lambda = \sqrt{\frac{2\pi\hbar^2}{mk_B T}} \quad \text{thermal de Broglie wavelength}$$

$$\ln \Xi(z, \beta) = - \ln(1-z) + \sum_{j=1}^{\infty} \frac{z^j}{j} \frac{V}{\lambda^3 j^{3/2}} = - \ln(1-z) + \frac{V}{\lambda^3} g_{5/2}(z)$$

Here  $g_x(z) = \sum_{j=1}^{\infty} \frac{z^j}{j^x}$  is Bose function

Some properties:  $z \frac{d}{dz} g_x(z) = g_{x-1}(z)$

$$g_x(z) = \frac{1}{\Gamma(x)} \int_0^{\infty} dy \frac{y^{x-1}}{z^{-y} e^y - 1}; \quad g_x(1) = \zeta(x) \quad \text{where } \zeta(x) \text{ is Riemann zeta function}$$



We have singled out contribution from the ground state 5  
when calculating  $\ln \Xi(z, \beta)$  for the reason that will become  
obvious in a moment

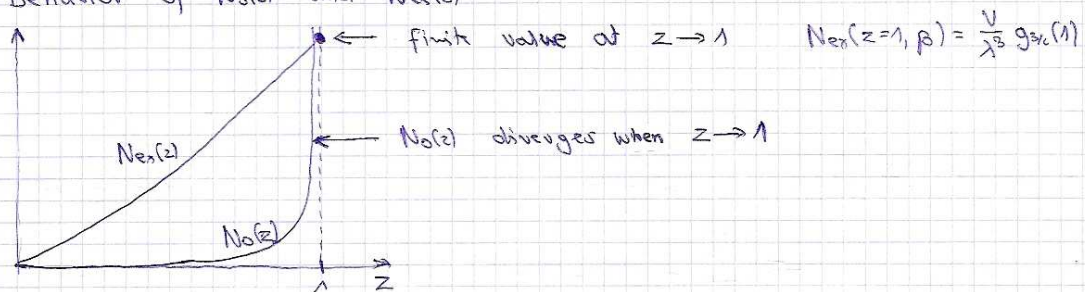
Total number of particles in a volume  $V$

$$N = \langle N \rangle(z, \beta) = z \frac{\partial}{\partial z} \ln \Xi(z, \beta) = \frac{z}{1-z} + \frac{V}{\lambda^3} g_{3/2}(z)$$

First term describes occupation of the ground state  $N_0(z) = \frac{z}{1-z}$

Second term gives number of particles in excited states  $N_{ex}(z, \beta) = \frac{V}{\lambda^3} g_{3/2}(z)$

Behavior of  $N_0(z)$  and  $N_{ex}(z)$



At high temperatures,  $z \ll 1$ , and  $N_{ex}(z) \sim V \sim N \gg 1$ . At the  
same time occupation of ground state is negligible  $N_0(z) \sim 1$ .

In this case finally  $z$  is fixed by the condition

$$N = \frac{V}{\lambda^3} g_{3/2}(z) = N_{ex}(z, T) \quad (*)$$

However, when temperature decreases ( $\lambda$  increases)  
at some point  $N_{ex}(z, T)$  is not sufficient to fulfill equation (\*)  
and in this case one has take into account occupation  
of the ground state, which becomes macroscopic.

In this case

$$N = \frac{z}{1-z} + \frac{V}{\lambda^3} g_{3/2}(z) \quad \text{as } z \approx 1$$

This is actual mechanism of Bose-Einstein condensation. The  
point when  $N_{ex}(z=1)$  becomes equal to the total number of  
particles defines the critical temperature





$$N = \frac{V}{\lambda_c^3} g_{3/2}(1) \Rightarrow k_B T_c = \frac{2\pi\hbar^2}{m} \left( \frac{n}{g_{3/2}(1)} \right)^{2/3} \quad n = N/V \quad (6)$$

$$g_{3/2}\left(\frac{3}{2}\right) = g_{3/2}(1)$$

Remarks

1) Critical temperature remains constant in the thermodynamic limit:  $N \rightarrow \infty$ ,  $V \rightarrow \infty$ ,  $\frac{N}{V} = n = \text{const}$ , since it depends on the density

2) Condition determining critical temperature:  $N = \frac{V}{\lambda_c^3} g_{3/2}(1)$  can be written as:  $\lambda \sim \left(\frac{V}{N}\right)^{1/3} = d$

Condensation happens when de Broglie wavelength becomes comparable to mean interparticle distance  $d$  - matter wave overlap

3) Bose-Einstein condensation occurs at high temperature with respect to single particle energy level spacing

$$k_B T_c = \frac{2\pi\hbar^2}{mL^2} \left( \frac{N}{g_{3/2}(1)} \right)^{2/3} \Rightarrow \frac{2\pi\hbar^2}{mL^2} = E_1 - E_0$$

$E_1 - E_0$  = energy difference between first excited ( $E_1$ ) and ground ( $E_0$ ) states

To appreciate this fact, let's calculate temperature when gas of  $N$  distinguishable particles "condense" to the ground state.

$$\langle N_0 \rangle = N \frac{e^{-\beta E_0}}{Z_1(\beta)} \quad Z_1(\beta) = \sum_{\nu} e^{-\beta E_{\nu}} - \text{classical partition function for single particle}$$

For 3D box with periodic boundary conditions it actually gives

$$\langle N_0 \rangle = N \frac{\lambda^3}{V} = \left( \frac{\lambda}{\lambda_c} \right)^3 g_{3/2}(1) = g_{3/2}(1) \left( \frac{T_c}{T} \right)^{3/2}$$

We note that at  $T = T_c$  occupation of ground state is still very small:  $\langle N_0 \rangle|_{T=T_c} = g_{3/2}(1) \sim 1$

In fact macroscopic occupation of ground state for distinguishable particles requires  $k_B T \ll E_1 - E_0$



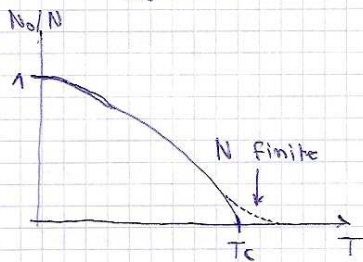


Number of condensed atoms versus temperature (7)

$$N_0(T) = N - N_{ex}(T) = N - \frac{V}{\lambda^3} g_{3/2}(1) = N \left(1 - \left(\frac{T_c}{T}\right)^3\right) = N \left(1 - \left(\frac{T}{T_c}\right)^{3/2}\right)$$

where we have used definition of critical temperature

$$N = \frac{V}{\lambda_c^3} g_{3/2}(1)$$

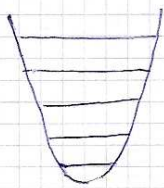


Mean number of condensed atoms has discontinuity at  $T = T_c$

Discontinuities are typical features of phase transitions

Remark: Actual condensates have large but finite ( $N \sim 10^6 - 10^9$ ) number of atoms. For them all the thermodynamic functions are smooth at  $T_c$ .

### IDEAL GAS IN 3D HARMONIC TRAP



For simplicity we consider spherically symmetric trap. All the result can be derived in similar manner also for anisotropic trap

$$E_{\vec{n}} = \hbar\omega (n_x + n_y + n_z) \quad \vec{n} = (n_x, n_y, n_z)$$

$E_0 = 0$  : zero of energy shifted to the ground state

We start by calculating logarithm of the grand canonical partition function

$$\begin{aligned} \ln \Xi(z, \beta) &= -\ln(1-z) + \sum_{j=1}^{\infty} \frac{z^j}{j} \sum_{\vec{n} \neq 0} e^{-\beta j E_{\vec{n}}} \\ \sum_{\vec{n} \neq 0} e^{-\beta j E_{\vec{n}}} &= \sum_{\vec{n} \neq 0} e^{-\beta j \hbar\omega (n_x + n_y + n_z)} = \left( \sum_{n=0}^{\infty} e^{-\beta j \hbar\omega n} \right)^3 - 1 = \\ &= \frac{1}{(1 - e^{-\beta j \hbar\omega})^3} - 1 \end{aligned}$$

$$\frac{1}{1 - e^{-x}} = 1 + \frac{e^{-x} h(x)}{x} \quad \text{where } h(x) = \frac{1}{2} + \frac{1}{24}x - \frac{1}{2880}x^3 + O(x^4)$$







Relatively accurate approximation is obtained when retaining 8

only the lowest order term in  $h(x)$

$$\frac{1}{1 - e^{-x}} \approx 1 + \frac{e^{-x/2}}{x}$$

Then

$$\frac{1}{(1 - e^{-\beta \hbar \omega})^3} - 1 = \left(1 + \frac{e^{-\beta \hbar \omega / 2}}{\beta \hbar \omega}\right)^3 - 1$$

$$\ln \Xi(z, \beta) = -\ln(1-z) + \tilde{T}^3 g_4\left(ze^{-\frac{3}{2}\frac{1}{\tilde{T}}}\right) + 3\tilde{T}^2 g_3\left(ze^{-\frac{1}{\tilde{T}}}\right) + 3\tilde{T} g_2\left(ze^{-\frac{1}{\tilde{T}}}\right)$$

where  $\tilde{T} = \frac{k_B T}{\hbar \omega}$  is temperature scaled in harmonic oscillator units

In the regime of macroscopic temperatures:  $k_B T \gg \hbar \omega$  ( $\tilde{T} \gg 1$ )

$$\ln \Xi(z, \beta) \approx -\ln(1-z) + \tilde{T}^3 g_4(z)$$

Mean number of particles in the system

$$\langle N \rangle = z \frac{\partial}{\partial z} \ln \Xi(z, \beta) = \underbrace{\frac{z}{1-z}}_{\text{condensate}} + \underbrace{\left(\frac{k_B T}{\hbar \omega}\right)^3 g_3(z)}_{\text{excited atoms (thermal part)}}$$

In analogy to the previous scenario in a box, Bose-Einstein condensation takes place when

$$N = \left(\frac{k_B T_c}{\hbar \omega}\right)^3 g_3(1) \quad g_3(1) = \zeta(3) \approx 1.202$$

$$\text{Critical temperature} \quad T_c = \frac{\hbar \omega}{k_B} \left(\frac{N}{\zeta(3)}\right)^{1/3}$$

Remarks

1) For  $N \gg 1 \Rightarrow k_B T_c \gg \hbar \omega$ , which is consistent with our previous assumption

2) Thermodynamic limit in the trap is defined in the following way:

$$N \rightarrow \infty$$

$$\omega \rightarrow 0$$

$$N \omega^3 = \text{const}$$

With this choice  $T_c$  remains constant in the thermodynamic limit





Number of condensed atoms in a trap

9

$$N_0(T) = N - N_{ex}(T) = N - \left(\frac{k_B T}{\hbar \omega}\right)^3 g_3(z) \leftarrow \text{below } T_c \text{ we put } z \approx 1$$

$$N_0(T) = N - \left(\frac{T}{T_c}\right)^3 N = N \left[1 - \left(\frac{T}{T_c}\right)^3\right]$$

Similar discontinuity as in 3D box at  $T = T_c$

Mean energy and specific heat

$$\langle E \rangle = - \frac{\partial}{\partial \beta} \ln \Xi(z, \beta) = 3 \hbar \omega \left(\frac{k_B T}{\hbar \omega}\right)^4 g_4(z)$$

Below  $T_c$ , we can put  $z \approx 1$  and

$$\langle E \rangle = 3 \left(\frac{k_B T}{\hbar \omega}\right)^4 g_4(1) \hbar \omega = 3 N k_B T \frac{g_4(1)}{g_3(1)} \left(\frac{T}{T_c}\right)^3 \quad g_4(1) = \frac{\pi^4}{90} \approx 1.08$$

$$\text{At } T = T_c \quad \langle E \rangle|_{T_c} = 3 N k_B T \frac{g_4(1)}{g_3(1)} \quad \frac{g_4(1)}{g_3(1)} \approx 0.9$$

We can compare this result with high energy (classical) limit,

when equipartition principle holds and  $\langle E \rangle_d = 3 N k_B T$

for harmonic oscillator

Specific heat at constant volume (constant  $\omega$  in the case of trap)

$$C = \frac{\partial E}{\partial T}$$

$$\text{Below } T_c: \quad C = \frac{\partial E}{\partial T} = \frac{\partial}{\partial T} \left( 3 \left(\frac{k_B T}{\hbar \omega}\right)^3 g_4(z) \hbar \omega \right) = 12 \left(\frac{k_B T}{\hbar \omega}\right)^3 g_4(z) k_B$$

$$C = 12 N k_B \left(\frac{T}{T_c}\right)^3 \frac{\xi(4)}{\xi(3)}$$

Above  $T_c$ : We have to take into account temperature

dependence of the fugacity  $z$  when differentiating with

respect to  $T$

$$C = \frac{\partial E}{\partial T} = 12 k_B \left(\frac{k_B T}{\hbar \omega}\right)^3 g_4(z) + 3 \left(\frac{k_B T}{\hbar \omega}\right)^4 g_3(z) \hbar \omega \frac{\partial z}{\partial T}$$





How to calculate  $\frac{\partial Z}{\partial T}$  above  $T_c$ ? We take condition for total number of particles

10

$$N = N_0(T) + N_{ex}(T) = \frac{N}{1-z} + \left(\frac{k_B T}{\hbar \omega}\right)^3 g_3(z)$$

Above  $T_c$  population of ground state is negligible

$$N = \left(\frac{k_B T}{\hbar \omega}\right)^3 g_3(z)$$

Differentiating with respect to  $T$  yields

$$0 = \frac{\partial N}{\partial T} = 3 \frac{k_B}{\hbar \omega} \left(\frac{k_B T}{\hbar \omega}\right)^2 g_3(z) + \left(\frac{k_B T}{\hbar \omega}\right)^3 g_2(z) \frac{\partial z}{\partial T}$$

$$\text{Then } \frac{\partial z}{\partial T} = -\frac{3}{T} \frac{g_3(z)}{g_2(z)}$$

And specific heat

$$C = 3 k_B \left(\frac{k_B T}{\hbar \omega}\right)^3 \left(4 g_4(z) - 3 \frac{g_3(z)^2}{g_2(z)}\right) \quad T > T_c$$

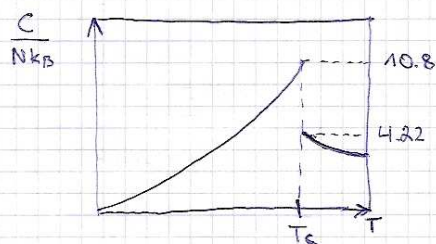
Let's calculate how specific heat behaves across  $T_c$ .

Close to critical temperature we can put  $z \approx 1$

$$C(T_c^-) = 12 N k_B \frac{g(4)}{g(3)} \approx 10.8 N k_B \quad \text{just below } T_c$$

$$C(T_c^+) = 3 k_B \frac{N}{g_3(1)} \left(4 g_4(1) - 3 \frac{g_3(1)^2}{g_2(1)}\right) = 3 N k_B \left(4 \frac{g(4)}{g(3)} - 3 \frac{g(3)}{g(2)}\right) \approx 4.22 N k_B \quad \text{just above } T_c$$

Specific heat is discontinuous across  $T_c$ . This is yet another signature of a phase transition



For comparison, in a homogeneous system the specific heat is continuous across  $T_c$  but it has discontinuous derivative





FLUCTUATIONS OF THE NUMBER OF CONDENSED ATOMS

11

So far we have calculated all the properties of an ideal Bose gas using grand canonical ensemble. Not all the quantities can be found this way. Let's consider fluctuations of the number of condensed atoms

$$\langle \delta^2 N_0 \rangle = \langle N_0^2 \rangle - \langle N_0 \rangle^2$$

In the grand canonical ensemble

$$\langle \delta^2 N_0 \rangle = \langle N_0 \rangle (\langle N_0 \rangle + 1)$$

This relation holds in fact for arbitrary single-particle state

$$\langle \delta^2 n_\nu \rangle = \langle n_\nu \rangle (\langle n_\nu \rangle + 1) = \frac{z e^{-\beta E_\nu}}{(1 - z e^{-\beta E_\nu})^2} = \frac{\partial}{\partial (\beta \epsilon_\nu)^2} \ln \Xi(z, \beta)$$

At  $T \rightarrow 0$  we obtain for condensate fluctuations

$$\langle \delta^2 N_0 \rangle = \langle N_0 \rangle (\langle N_0 \rangle + 1) \xrightarrow{T \rightarrow 0} N(N+1),$$

which is incorrect since at  $T \rightarrow 0$  we expect all the particles to condense in the ground state and there will be no fluctuations. Therefore fluctuations have to be calculated in the microcanonical or canonical ensemble.

For further considerations it is convenient to split the system into two parts: condensate (0) and excited states (E).

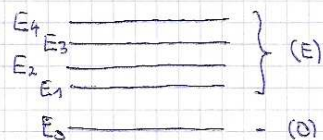
Their statistics is related:

$$\langle N_0 \rangle = N - \langle N_E \rangle$$

$$\langle \delta^2 N_0 \rangle = \langle \delta^2 N_E \rangle \quad (N = \text{const})$$

Microcanonical partition function can be represented as a product of partition functions for two subsystem

$$\Gamma(N, E) = \sum_{N_E=0}^N \sum_{E'} \Gamma_0(N - N_E, E - E') \Gamma_E(N_E, E')$$



Since ground state is not degenerate

$$\Gamma_0(N - N_E, E - E') = \delta_{E, E'} \quad (\text{assuming } E_0 = 0)$$

and

$$\Gamma(N, E) = \sum_{N_E=0}^N \Gamma_E(N - N_E, E)$$





Then probability of finding  $N_e$  particles in excited subsystem is 12

$$p_{HC}(N_e | N, E) = \frac{\Gamma_e(N_e, E)}{\Gamma(N, E)} \quad \sum_{N_e=0}^N p_{HC}(N_e | N, E) = 1$$

From the probability distribution we can calculate all the statistical properties of interest

$$\langle N_e \rangle_{HC} = \sum_{N_e=0}^N p_{HC}(N_e | N, E) N_e$$

$$\langle \delta^2 N_e \rangle_{HC} = \sum_{N_e=0}^N (N_e - \langle N_e \rangle_{HC})^2 p_{HC}(N_e | N, E)$$

In basically similar manner we can decompose canonical partition function into partition functions for excited subsystems  $Z_e(N_e, \beta)$

$$Z(N, \beta) = \sum_{N_e=0}^N Z_e(N_e, \beta) \quad p_{HC}(N_e | N, \beta) = \frac{Z_e(N_e, \beta)}{Z(N, \beta)}$$

While the number of particles fluctuates between condensate and thermal part, there is no exchange of energy. This observation leads us to the idea of Fourth Statistical

Ensemble (sometimes we like to call it Maxwell Demon ensemble: MD)

In MD ensemble there is an exchange of particles with the reservoir, which is, however, not associated with an exchange of the energy. The role of the reservoir is played by condensate of large (infinite) number of particles.

Let's define the partition function for MD ensemble

$$Y(\lambda, E) = \sum_{N_e=0}^{\infty} e^{\lambda N_e} \Gamma_e(N_e, E) \quad \lambda - \text{control parameter}$$

The sum is well defined for all values of  $\lambda$ . This can be seen from the following property

$$\Gamma_e(N_e, E) = 0 \quad \text{for } N_e E_1 > E$$

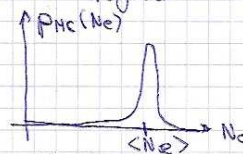
Moreover, in the case of  $\lambda = 1$

$$Y(\lambda=1, E) = \sum_{N_e=0}^{\infty} \Gamma_e(N_e, E) = \Gamma(N, E) \left( \sum_{N_e=0}^N p_{HC}(N_e | N, E) + \sum_{N_e=N+1}^{\infty} \frac{\Gamma_e(N_e, E)}{\Gamma(N, E)} \right)$$



Below  $T_c$  the probability distribution is well peaked around mean value  $\langle N_e \rangle$ . Therefore we can neglect contribution from the second term, and

$$Y(\lambda=1, \epsilon) \approx \Gamma(N_e, \epsilon),$$



which becomes exact in the thermodynamic limit.

Using this property we can calculate mean occupation and fluctuations in the microcanonical ensemble, directly from  $Y(\lambda, \epsilon)$

$$\langle N_e \rangle_{N_e}^{\infty} = \frac{\partial}{\partial \lambda} \ln Y(\lambda, \epsilon) \Big|_{\lambda=0}$$

$$\langle \delta N_e \rangle_{N_e}^{\infty} = \frac{\partial^2}{\partial \lambda^2} \ln Y(\lambda, \epsilon) \Big|_{\lambda=0}$$

The upper index " $\infty$ " denotes the fact that formulas become exact as  $N \rightarrow \infty$

In order to determine  $Y(\lambda, \epsilon)$  we can introduce the following generating function

$$\Xi_e(\lambda, \beta) = \sum_{\epsilon} e^{-\beta \epsilon} Y(\lambda, \epsilon)$$

One can show that  $\Xi_e(\lambda, \beta)$  is in fact grand-canonical partition function of excited subsystem

$$\Xi_e(\lambda, \beta) = \sum_{\epsilon} e^{-\beta \epsilon} \sum_{N_e=0}^{\infty} e^{\lambda N_e} \Gamma_e(N_e, \epsilon)$$

where fugacity  $z = e^{\lambda}$ . For an ideal gas  $\Xi_e(\lambda, \beta)$  is known analytically

$$\Xi_e(\lambda, \beta) = \prod_{k=1}^{\infty} \frac{1}{1 - e^{\lambda - \beta \epsilon_k}}$$

In comparison to  $\Xi(\lambda, \beta)$  for the whole system, in the formula  $\Xi_e(\lambda, \beta)$  we omit ground state contribution ( $k=0$  term)



We can relate  $\Xi_e(\lambda, \beta)$  to the canonical partition function of the excited subsystem (14)

$$\Xi_e(\lambda, \beta) = \sum_{N_e=0}^{\infty} e^{\lambda N_e} Z_e(N_e, \beta)$$

Using the fact that probability distribution  $p_{CN}(N_e|N, \beta)$  of number of atoms in excited subsystem is well peaked around mean value  $\langle N_e \rangle$  when  $T < T_c$ , we can relate

$\Xi_e(\lambda=0, \beta)$  to  $Z(N, \beta)$ :

$$\begin{aligned} \Xi_e(\lambda=0, \beta) &= \sum_{N_e=0}^{\infty} Z_e(N_e, \beta) = Z(N, \beta) \left[ \sum_{N_e=0}^N \frac{Z_e(N_e, \beta)}{Z(N, \beta)} + \sum_{N_e=N+1}^{\infty} \frac{Z_e(N_e, \beta)}{Z(N, \beta)} \right] \\ &= Z(N, \beta) \left[ \sum_{N_e=0}^N p_{CN}(N_e|N, \beta) + \underbrace{\sum_{N_e=N+1}^{\infty} \frac{Z_e(N_e, \beta)}{Z(N, \beta)}}_{\text{this contribution is negligible below } T_c} \right] \end{aligned}$$

Then  $\Xi_e(\lambda=0, \beta) \approx Z(N, \beta)$ .

This becomes exact in the thermodynamic limit.

The statistics of the condensate in the canonical ensemble can be calculated from the grand canonical partition function of excited subsystem.

$$\langle N_e \rangle_{CN}^{\infty} = \frac{\partial}{\partial \lambda} \ln \Xi_e(\lambda, \beta) \Big|_{\lambda=0}$$

$$\langle \delta^2 N_e \rangle_{CN}^{\infty} = \frac{\partial^2}{\partial \lambda^2} \ln \Xi_e(\lambda, \beta) \Big|_{\lambda=0}$$

Let's verify how it works

$$\begin{aligned} \langle N_e \rangle_{CN}^{\infty} &= \frac{\partial}{\partial \lambda} \ln \Xi_e(\lambda, \beta) \Big|_{\lambda=0} = \frac{1}{\Xi_e(\lambda=0, \beta)} \frac{\partial}{\partial \lambda} \Xi_e(\lambda, \beta) \Big|_{\lambda=0} \\ &= \frac{1}{\Xi_e(\lambda=0, \beta)} \sum_{N_e=0}^{\infty} N_e Z_e(N_e, \beta) \approx \sum_{N_e=0}^N N_e \frac{Z_e(N_e, \beta)}{Z(N, \beta)} + \\ &+ \sum_{N_e=N+1}^{\infty} N_e \frac{Z_e(N_e, \beta)}{Z(N, \beta)} \approx \sum_{N_e=0}^N p_{CN}(N_e|N, \beta) N_e = \langle N_e \rangle_{CN} \end{aligned}$$





15

Mean occupation and fluctuations for condensate in a trap

$$\ln \Xi_e(\lambda, \beta) = \left(\frac{k_B T}{\hbar \omega}\right)^3 g_4(e^\lambda)$$

In comparison to equation for  $\ln \Xi(z, \beta)$  we have omitted contribution from ground state and we substituted  $z \rightarrow e^\lambda$

$$\langle N_e \rangle_{CN} = \frac{\partial}{\partial \lambda} \ln \Xi_e(\lambda, \beta) \Big|_{\lambda=0} = \left(\frac{k_B T}{\hbar \omega}\right)^3 g_3(e^\lambda) \Big|_{\lambda=0} = \left(\frac{k_B T}{\hbar \omega}\right)^3 \frac{3}{\zeta(3)}$$

$$\langle \delta^2 N_e \rangle_{CN} = \frac{\partial^2}{\partial \lambda^2} \ln \Xi_e(\lambda, \beta) \Big|_{\lambda=0} = \left(\frac{k_B T}{\hbar \omega}\right)^3 g_2(e^\lambda) \Big|_{\lambda=0} = \left(\frac{k_B T}{\hbar \omega}\right)^3 \frac{2}{\zeta(2)}$$

We can rewrite these formulas using definition of the critical temperature

$$\langle N_e \rangle_{CN} = N \left(\frac{T}{T_c}\right)^3 \quad T < T_c$$

$$\langle \delta^2 N_e \rangle_{CN} = N \frac{\zeta(2)}{\zeta(3)} \left(\frac{T}{T_c}\right)^3 \quad T < T_c$$

Now scaling with the system size is clearly visible. Average number of condensed atoms in canonical ensemble is the same as in the grand canonical one - statistical ensembles are equivalent with respect to mean values.

$$\langle N_0 \rangle_{CN} = \langle N_0 \rangle_{GC} = N \left(1 - \left(\frac{T}{T_c}\right)^3\right)$$

Fluctuations scale normally with the number of particles - they are proportional to  $N$ . This feature is very common in statistical mechanics, however, this is not a general property

Example Fluctuations in a homogeneous system

$$\ln \Xi_e(\lambda, \beta) = \frac{V}{\lambda^3} g_{5/2}(e^\lambda)$$

Using naively the formula for  $\langle \delta^2 N_e \rangle_{CN}$  we would obtain

$$\langle \delta^2 N_e \rangle_{CN} = \frac{\partial^2}{\partial \lambda^2} \ln \Xi_e(\lambda, \beta) \Big|_{\lambda=0} = \frac{V}{\lambda^3} g_{3/2}(e^\lambda) \Big|_{\lambda=0}$$

But  $g_{1/2}(z)$  diverges as  $z \rightarrow 1$ :  $g_{1/2}(z) = \sum_{n=1}^{\infty} \frac{z^n}{\sqrt{n}}$







This means that we have to calculate  $\ln \Xi_e(\lambda, \beta)$  more carefully.

16

$$\ln \Xi_e(\lambda, \beta) = - \sum_{\vec{k} \neq 0} \ln(1 - e^{\lambda} e^{-\beta E_{\vec{k}}})$$

$$\frac{\partial}{\partial \lambda} \ln \Xi_e(\lambda, \beta) = \sum_{\vec{k} \neq 0} \frac{e^{\lambda} e^{-\beta E_{\vec{k}}}}{1 - e^{\lambda} e^{-\beta E_{\vec{k}}}}$$

$$\frac{\partial^2}{\partial \lambda^2} \ln \Xi_e(\lambda, \beta) = \sum_{\vec{k} \neq 0} \left( \frac{e^{\lambda} e^{-\beta E_{\vec{k}}}}{1 - e^{\lambda} e^{-\beta E_{\vec{k}}}} \right)^2 + \sum_{\vec{k} \neq 0} \frac{e^{\lambda} e^{-\beta E_{\vec{k}}}}{1 - e^{\lambda} e^{-\beta E_{\vec{k}}}}$$

$$= \sum_{\vec{k} \neq 0} \frac{e^{\lambda} e^{-\beta E_{\vec{k}}}}{(1 - e^{\lambda} e^{-\beta E_{\vec{k}}})^2}$$

$$\frac{\partial^2}{\partial \lambda^2} \ln \Xi_e(\lambda, \beta) \Big|_{\lambda=0} = \langle \delta^2 N_e \rangle_{CN} = \sum_{\vec{k} \neq 0} \frac{e^{-\beta E_{\vec{k}}}}{(1 - e^{-\beta E_{\vec{k}}})^2} = \frac{1}{4} \sum_{\vec{k} \neq 0} \frac{1}{\sinh^2 \frac{\beta E_{\vec{k}}}{2}}$$

$$\beta E_{\vec{k}} = \frac{1}{k_B T} \frac{\hbar^2}{2m} \left( \frac{2\pi}{L} \right)^2 (n_x^2 + n_y^2 + n_z^2) = \frac{E_1}{k_B T} (n_x^2 + n_y^2 + n_z^2) \ll 1 \quad \text{when } n_x, n_y, n_z \text{ are not too large}$$

$$\langle \delta^2 N_e \rangle_{CN} \approx \frac{1}{\beta^2} \sum_{\vec{k} \neq 0} \frac{1}{E_{\vec{k}}^2} = \left( \frac{2m k_B T}{\hbar^2} \right)^2 \sum_{\vec{k} \neq 0} \frac{1}{|\vec{k}|^4} \quad E_1 = \frac{2\pi^2 \hbar^2}{mL^2}$$

This is in fact source of problems in the previous approach.

If we replace summation by integration in the thermodynamic limit, we will obtain divergent integral

$$\sum_{\vec{k} \neq 0} \frac{1}{|\vec{k}|^4} \xrightarrow{V \rightarrow \infty} \frac{V}{(2\pi)^3} \int_0^\infty k \frac{1}{k^4} = \infty$$

The integral is infrared divergent, which means that contribution of low momentum modes is most important

$$\langle \delta^2 N_e \rangle_{CN} = \frac{1}{\beta^2} \sum_{\vec{k} \neq 0} \frac{1}{E_{\vec{k}}^2} = \left( \frac{k_B T}{E_1} \right)^2 \sum_{\vec{n} \neq 0} \frac{1}{|\vec{n}|^4}$$

and finally using definition of  $T_c$

$$\langle \delta^2 N_e \rangle_{CN} = \frac{1}{\pi^2} \left( \frac{N}{g(3/2)} \right)^{4/3} \left( \frac{T}{T_c} \right)^2 c_1 \quad \text{where } c_1 = \sum_{\vec{n} \neq 0} \frac{1}{|\vec{n}|^4} = 16.53$$

Fluctuations are anomalous (not proportional to  $N$  in thermodynamic limit)





17

## FLOCTUATIONS IN THE MICROCANONICAL ENSEMBLE

For an ideal gas the following relation holds

$$\langle \delta N_e \rangle_{MC} = \langle \delta N_e \rangle_{CN} - \frac{[\langle \delta N_e \delta E \rangle_{CN}]^2}{\langle \delta E \rangle_{CN}}$$

Microcanonical fluctuations are always smaller than the canonical ones. This relation allows to calculate fluctuations in the microcanonical ensemble solely from quantities given in the canonical ensemble, which is simpler for analytical treatment

Particle - energy correlations:

$$\langle \delta N_e \delta E \rangle_{CN} = \langle N_e E \rangle_{CN} - \langle N_e \rangle_{CN} \langle E \rangle_{CN} = \frac{\partial}{\partial \lambda} \left( - \frac{\partial}{\partial \beta} \right) \ln \Xi_e(\lambda, \beta) \Big|_{\lambda=0}$$

Energy fluctuations:

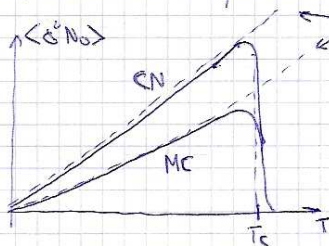
$$\langle \delta E \rangle_{CN} = \frac{\partial}{\partial \beta} \ln \Xi_e(\lambda, \beta) \Big|_{\lambda=0}$$

In the case of 3D harmonic trap  $\ln \Xi_e(\lambda, \beta) = \left( \frac{k_B T}{\hbar \omega} \right)^3 g_4(e^{-\lambda})$

After some algebra we get

$$\langle \delta N_e \rangle_{MC} = N \left( \frac{\zeta(2)}{\zeta(3)} - \frac{3 \zeta(3)}{4 \zeta(4)} \right) \left( \frac{T}{T_c} \right)^3$$

Microcanonical fluctuations are also normal in the trap



Maxwell-Demon ensemble predictions

For actual finite size systems, fluctuations drops smoothly to values of order 1 above  $T_c$





Equation of state for a homogeneous Bose gas below  $T_c$

(18)

$$-pV = \Omega(z, \beta) = -k_B T \ln \Xi(z, \beta)$$

see e.g. K Huang,  
Statistical mechanics

$$\ln \Xi(z, \beta) = -\ln(1-z) + \frac{V}{\lambda^3} g_{5/2}(z)$$

$$\frac{V}{\lambda^3} g_{5/2}(z) \approx \frac{V}{\lambda^3} g_{5/2}(1) \sim N \quad \text{for } T < T_c$$

$$\frac{z}{1-z} = N_0 \Rightarrow z = \frac{N_0}{1+N_0}$$

$$\text{Then: } -\ln(1-z) = -\ln\left(1 - \frac{N_0}{1+N_0}\right) = -\ln\left(\frac{1}{1+N_0}\right) = \ln(1+N_0) \sim \ln N$$

We can neglect logarithmic contribution from the ground state

$$pV = k_B T \frac{V}{\lambda^3} g_{5/2}(1)$$

$$p = \frac{k_B T}{\lambda^3} g_{5/2}(1)$$

We observe that pressure does not depend on volume, which means that ideal gas has infinite compressibility below  $T_c$ .

$$\frac{\partial V}{\partial p} = \infty$$

This pathology is removed when one includes two-body interactions





19

Appendix : Derivation of relation between fluctuations in microcanonical and canonical ensemble

We consider excited subsystem with the fugacity  $z$  and energy  $E$  as basic variables

$$N_{ex} = N_{ex}(z, E)$$

Taking total differential of  $N_{ex}$

$$dN_{ex} = \left( \frac{\partial N_{ex}}{\partial z} \right)_E dz + \left( \frac{\partial N_{ex}}{\partial E} \right)_z dE$$

Then

$$z \left( \frac{\partial N_{ex}}{\partial z} \right)_T = z \left( \frac{\partial N_{ex}}{\partial z} \right)_E + z \left( \frac{\partial N_{ex}}{\partial E} \right)_z \left( \frac{\partial E}{\partial z} \right)_T$$

Taking  $z=1$  we obtain

$$\langle \delta^2 N_{ex} \rangle_{CN} = \langle \delta^2 N_{ex} \rangle_{MC} + \left( \frac{\partial N_{ex}}{\partial E} \right)_z \left( \frac{\partial E}{\partial z} \right)_T \Big|_{z=1}$$

$$\langle \delta^2 N_{ex} \rangle_{CN} = z \left( \frac{\partial N_{ex}}{\partial z} \right)_T \Big|_{z=1} = \left( \frac{\partial}{\partial \lambda} N_{ex} \right)_T \Big|_{\lambda=0} \quad - \text{fluctuations in the canonical ensemble}$$

$$\langle \delta^2 N_{ex} \rangle_{MC} = z \left( \frac{\partial N_{ex}}{\partial z} \right)_E \Big|_{z=1} = \left( \frac{\partial N_{ex}}{\partial \lambda} \right)_T \Big|_{\lambda=0} \quad - \text{fluctuations in the microcanonical ensemble}$$

$$z \left( \frac{\partial N_{ex}}{\partial E} \right)_z \left( \frac{\partial E}{\partial z} \right)_T \Big|_{z=1} = \frac{k_B T^2 \left( \frac{\partial N_{ex}}{\partial T} \right)_z z \left( \frac{\partial E}{\partial z} \right)_T}{k_B T^2 \left( \frac{\partial E}{\partial T} \right)_z}$$

$$k_B T^2 \left( \frac{\partial E}{\partial T} \right)_z \Big|_{z=1} = - \left( \frac{\partial E}{\partial \beta} \right)_z \Big|_{z=1} = \frac{\partial}{\partial \beta} \ln \Xi_e(z, \beta) \Big|_{z=1} = \langle \delta^2 E \rangle_{CN}$$

$$k_B T^2 \left( \frac{\partial N_{ex}}{\partial T} \right)_z \Big|_{z=1} = - \left( \frac{\partial N_{ex}}{\partial \beta} \right)_z \Big|_{z=1} = \left( - \frac{\partial}{\partial \beta} \right) z \frac{\partial}{\partial z} \ln \Xi_e(z, \beta) \Big|_{z=1} = \langle \delta N_{ex} \delta E \rangle_{CN}$$

$$z \left( \frac{\partial E}{\partial z} \right)_T \Big|_{z=1} = \left( - \frac{\partial}{\partial \beta} \right) \left( z \frac{\partial}{\partial z} \right) \ln \Xi_e(z, \beta) \Big|_{z=1} = \langle \delta N_{ex} \delta E \rangle_{CN}$$

Finally

$$\langle \delta^2 N_{ex} \rangle_{CN} = \langle \delta^2 N_{ex} \rangle_{MC} + \frac{[\langle \delta N_{ex} \delta E \rangle_{CN}]^2}{\langle \delta^2 E \rangle_{CN}} \quad \square$$





## Collisions of ultracold atoms

Scattering of two atoms interacting via isotropic potential  $U(r)$ . In the relative coordinate

$$\left[ -\frac{\hbar^2}{2\mu} \Delta + U(r) \right] \Psi(\vec{r}) = E \Psi(\vec{r}) \quad E = \frac{\hbar^2 k^2}{2\mu} \quad \frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B}$$

We assume that  $U(r)$  is a short range potential

$U(r) = 0$  for  $r > r_0$ ,  $r_0$  - range of potential

Expansion in partial waves

$$\Psi(\vec{r}) = \sum_{lm} \psi_l(r) Y_{lm}(\hat{r}) \quad \hat{r} = \frac{\vec{r}}{r}$$

Radial Schrödinger equation

$$\left[ -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\hbar^2}{2\mu} \frac{l(l+1)}{r^2} + U(r) \right] \psi_l(r) = E \psi_l(r)$$

At  $r > r_0$  and at  $E > 0$

$$\left[ -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\hbar^2}{2\mu} \frac{l(l+1)}{r^2} \right] \psi_l(r) = \frac{\hbar^2 k^2}{2\mu} \psi_l(r)$$





Solution is given in terms of spherical Bessel functions

$$\Psi_l(r, E) = C_l(E) (j_l(kr) - \tan \delta_l(k) n_l(kr))$$

Coefficients  $C_l(E)$  depend on the boundary conditions at  $r \rightarrow \infty$ , whereas phase shifts are determined by the potential  $U(r)$

Asymptotic behavior at large  $r$

$$j_l(kr) \xrightarrow{r \rightarrow \infty} \frac{1}{kr} \sin(kr - l\frac{\pi}{2})$$

$$n_l(kr) \xrightarrow{r \rightarrow \infty} -\frac{1}{kr} \cos(kr - l\frac{\pi}{2})$$

$$\text{Then } \Psi_l(r, E) \xrightarrow{r \rightarrow \infty} \frac{C_l(E)}{\cos \delta_l} \sin(kr - l\frac{\pi}{2} + \delta_l(k))$$

Let's consider radial Schrödinger equation at  $E=0$ , and at  $r > r_0$

$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] R_l(r, E=0) = 0 \quad \text{where } \Psi_l(r) = \frac{R_l(r)}{r}$$

The trivial solution is  $R_l(r) = A r^{l+1} + B r^{-l}$

$$\Psi_l(r, E=0) = A r^l + B \frac{1}{r^{l+1}}$$





We can compare this result with the behavior of the wave function at large, but finite  $r$ , in the limit  $k \rightarrow 0$

$$\Psi_c(r, E) = C_c(k) (j_c(kr) - \tan \delta_c(k) n_c(kr))$$

$$j_c(x) \xrightarrow{x \rightarrow 0} \frac{x^c}{(2l+1)!!}$$

$$n_c(x) \xrightarrow{x \rightarrow 0} -\frac{(2l-1)!!}{x^{l+1}}$$

$$\begin{aligned} \Psi_c(r, E) &\xrightarrow{k \rightarrow 0} C_c(k) \left( \frac{(kr)^c}{(2l+1)!!} + \tan \delta_c(k) \frac{(2l-1)!!}{(kr)^{l+1}} \right) \\ &= C_c(k) \frac{k^c}{(2l+1)!!} \left( r^c + \frac{(2l-1)!!}{(2l+1)!!} \frac{\tan \delta_c(k)}{k^{2l+1}} \frac{1}{r^{l+1}} \right) \end{aligned}$$

Comparing with solution at  $E=0$

$$\Psi_c(r, E=0) = A r^c + B \frac{1}{r^{l+1}} = A \left( r^c + \frac{B}{A} \frac{1}{r^{l+1}} \right)$$

We observe that

$$\frac{B}{A} = \frac{1}{(2l+1)!!} \frac{\tan \delta_c(k)}{k^{2l+1}} \Rightarrow \tan \delta_c(k) \sim k^{2l+1}$$

This property of the phase shifts near threshold ( $E=0$ ) is called in the literature Wigner threshold law.

Our derivation is valid as long as the potential is finite range. However, realistic interaction potentials exhibit power-law behavior, for instance interaction of atoms in electronic ground state is given by van der Waals interaction  $U(r) \xrightarrow{r \rightarrow \infty} -\frac{C_6}{r^6}$ . In such cases





threshold behavior changes above some angular momentum quantum number  $l$ .

Using first order Born approximation one can show that contribution to the phase shift scale as  $\delta_l \sim k^{n-2}$  from the long range potential  $\frac{1}{r^n}$ . Therefore in the case of long range potentials

$$\tan \delta_l \sim k^{2l+1} \quad \text{for } 2l < n-3$$

$$U(r) \underset{r \rightarrow \infty}{\sim} -\frac{C_0}{r^n}$$

$$\tan \delta_l \sim k^{n-2} \quad \text{for } 2l > n-3$$

In the case of s-wave scattering ( $l=0$ )

$$\psi_0(r) = A + B \frac{1}{r} = A \frac{r+B/A}{r} \sim \frac{r-a}{r} \quad E=0$$

where  $a$  is the scattering length, defined in the limit of zero energy

$$\frac{B}{A} = -a = \lim_{k \rightarrow 0} \frac{\tan \delta_0(k)}{k}$$

$$a = -\lim_{k \rightarrow 0} \frac{\tan \delta_0(k)}{k}$$





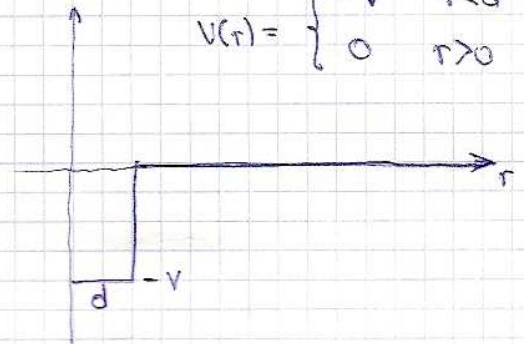


Since total cross section is  $\sigma_{\text{tot}} = \frac{4\pi}{k^2} \sum_l (2l+1) \sin^2 \delta_l$ , then according to the threshold law, the only contribution at low energies is due to s-wave scattering. The total cross section is  $\sigma = 4\pi a^2$

( $\sigma = 8\pi a^2$  in the case of indistinguishable particles)

Example Square well potential

$$V(r) = \begin{cases} -V & r < d \\ 0 & r > d \end{cases}$$



$$\left( -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + V(r) \right) \psi(r) = E \psi(r)$$

Solution at  $r < d$   $\psi(r) = A \sin kr$

where  $\frac{\hbar^2 k^2}{2m} = E + V = \frac{\hbar^2 k^2}{2m} + \frac{\hbar^2 \xi^2}{2m}$

Solution at  $r > d$ :  $\psi(r) = B \sin(kr + \delta_0)$  for  $E > 0$

$$\psi(r) = B e^{-\xi r}$$

for  $E < 0$

$$\frac{\hbar^2 k^2}{2m} = E$$

$$-\frac{\hbar^2 \xi^2}{2m} = E$$

Comparing logarithmic derivatives at  $r=d$

$$\frac{\psi'(d^-)}{\psi(d^-)} = \frac{\psi'(d^+)}{\psi(d^+)}$$





$$E > 0 \quad \frac{A q \cos qd}{A \sin qd} = \frac{B k \cos(kd + \delta_0)}{B \sin(kd + \delta_0)}$$

After straightforward algebra we obtain

$$k \cot \delta_0(k) = - \frac{k^2 + q \cot qd}{q \cot qd - k \cot kd} \quad q = \sqrt{k^2 + s^2}$$

$$k \cot \delta_0(k) = - \frac{s \cot(sd)}{sd \cot(sd) - 1} + O(k^2)$$

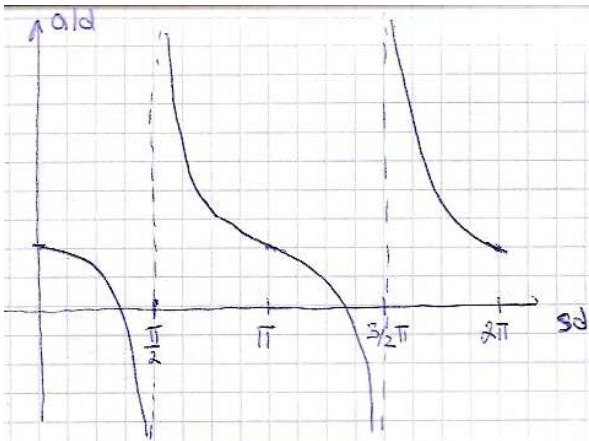
By definition, the lowest order term is given by  $-\frac{1}{a}$

$$a = d - \frac{1}{s} \tan sd$$

The next order term, proportional to  $k^2$  is called effective range

$$k \cot \delta_0(k) = -\frac{1}{a} + \frac{1}{2} R_{\text{eff}} k^2 \quad R_{\text{eff}} - \text{effective range of potential}$$





The scattering length diverges each time the bound state enters the potential well:

Comparing logarithmic derivatives  $\frac{Aq \cos qd}{A \sin qd} = \frac{-B \kappa e^{-\kappa d}}{B e^{-\kappa d}}$

$$q \cot qd = -\kappa \quad |E| \rightarrow 0 \quad \Rightarrow \quad s \cot sd = -\kappa = \frac{1}{d-a}$$

$$E = -\frac{\hbar^2 \kappa^2}{2\mu} = -\frac{\hbar^2}{2\mu} \frac{1}{(d-a)^2}$$

Weakly bound state exists for a positive and large

$$E \approx -\frac{\hbar^2}{2\mu a^2} \quad \text{For } a \rightarrow \infty \quad E \rightarrow 0^-$$

Formula  $E = -\frac{\hbar^2}{2\mu a^2}$  for the energy of weakly bound state is universal and holds for potentials different than square well





Similar result can be obtained using Fermi pseudopotential

$$U(r) = \frac{2\pi\hbar^2 g}{m} \delta(\vec{r}) \frac{\partial}{\partial r} r$$

$$\left( -\frac{\hbar^2}{2m} \Delta + \frac{2\pi\hbar^2 g}{m} \delta(\vec{r}) \frac{\partial}{\partial r} r \right) \psi(r) = E \psi(r)$$

Bound state wave function at  $r > 0$   $\psi(r) = \frac{A}{r} e^{-\lambda r}$   $E = -\frac{\hbar^2 \lambda^2}{2m}$

$$\Delta \frac{A}{r} e^{-\lambda r} = -4\pi \delta(\vec{r}) e^{-\lambda r} A + \frac{A}{r} \lambda^2 e^{-\lambda r}$$

Substituting into Schrödinger equation

$$-\frac{\hbar^2}{2m} \left( -4\pi \delta(\vec{r}) A e^{-\lambda r} + \frac{A \lambda^2}{r} e^{-\lambda r} \right) + \frac{2\pi\hbar^2 g}{m} \delta(\vec{r}) \left( \frac{\partial}{\partial r} r \frac{A}{r} e^{-\lambda r} \right)_{r=0} = -\frac{\hbar^2 \lambda^2}{2m} e^{-\lambda r} \frac{A}{r}$$

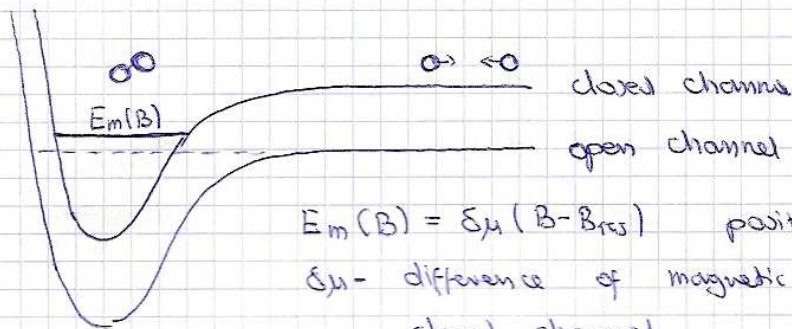
we obtain  $\lambda = \frac{1}{a}$ , and

$$E = -\frac{\hbar^2}{2m a^2}$$





### Magnetic Feshbach resonances



$$E_m(B) = \delta\mu (B - B_{res}) \quad \text{position of bound state}$$

$\delta\mu$  - difference of magnetic moments between open and closed channel

$B_{res}$  - value of magnetic field when the bound state crosses the dissociation threshold of the open channel

Magnetic Feshbach resonances allow to effectively tune interactions of ultracold atoms. Open and closed channels correspond to different internal states of atoms (typically hyperfine states). Close to the resonance the scattering length is given by

$$a(B) = a_{bg} \left( 1 - \frac{\Delta B}{B - B_0} \right)$$

$a_{bg}$  - background scattering length

(scattering length of the open channel in the absence of interchannel coupling)

$\Delta B$  - resonance width

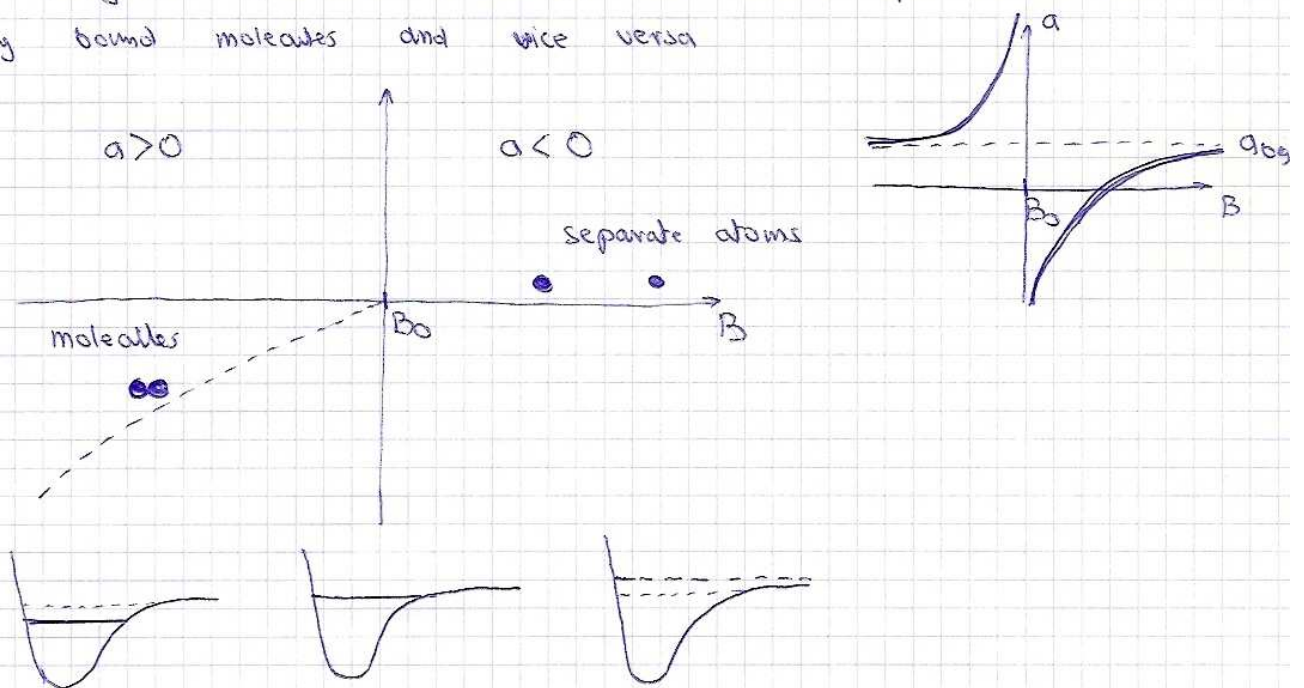
$B_0$  - position of resonance





Position of resonance ( $B_0$ ) is different from  $B_{res}$  because of the coupling between channels: energies of dressed states (open + closed channel) are slightly different from energies of bare states

Using magnetic Feshbach resonances one convert free atoms into weakly bound molecules and vice versa





Simple Model of a magnetic Feshbach resonance

$$-\frac{\hbar^2}{2m} \Delta \Psi + W \Psi = E \Psi \quad \Psi(r) = \begin{pmatrix} \psi_o(r) \\ \psi_c(r) \end{pmatrix}$$

$$W = \begin{pmatrix} -V_o & \frac{2\pi\hbar^2 b}{m} \delta(r) \frac{\partial}{\partial r} \\ \frac{2\pi\hbar^2 b}{m} \delta(r) \frac{\partial}{\partial r} & -V_c \end{pmatrix} \quad r < d$$

$$W(r) = \begin{pmatrix} \infty & 0 \\ 0 & 0 \end{pmatrix} \quad r > d$$

Off diagonal elements of the interaction matrix, modeled by Fermi pseudopotential are responsible for coupling of the open and closed channel.

First, solution without coupling ( $b=0$ )

Open channel:

(for simplicity we assume  $E=0$ )

$$\psi_o(r) = \begin{cases} A \sin \frac{q_o r}{r} & r < d \\ B \frac{r - a_b q_o}{r} & r > d \end{cases}$$

$$V_o = \frac{\hbar^2 q_o^2}{2m}$$

$$V_c = \frac{\hbar^2 a_c^2}{2m}$$





Comparing logarithmic derivatives at  $r=d$

$$\frac{R_0'(d^-)}{R_0(d^-)} = \frac{q_0 \cos q_0 d}{\sin q_0 d}$$

$$\frac{R_0'(d^+)}{R_0'(d^+)} = \frac{1}{d - a_{0g}}$$

we obtain  $a_{0g} = d - \frac{\tan q_0 d}{q_0}$

Closed channel:

Here we cannot put  $E=0$

Radial equation for  $R_c(r) = r \psi_c(r)$ :

$$\left( -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} - V_c \right) R_c(r) = \Delta R_c(r)$$

$$\Delta + V_c = \frac{\hbar^2 q^2}{2m}$$

$$\Delta = \frac{\hbar^2 \delta^2}{2m}$$

$$R_c(r) = \begin{cases} A \sin(qr) & r < d \\ 0 & r > d \end{cases}$$

$$\delta^2 + q_c^2 = q^2$$

Wave function must vanish at  $r=d$

$$R_c(d) = 0 \Rightarrow \sin(qd) = 0 \Rightarrow qd = n\pi$$

We consider first bound state ( $n=1$ ) that causes resonance

$$q^2 = \frac{\pi^2}{d^2} = \delta^2 + q_c^2$$







Now, full solution ( $b \neq 0$ ), at energy  $E=0$

$$\psi_0(r) = \begin{cases} \frac{A}{r} \sin(q_0 r + \eta_0) & r < d \\ \frac{r-a}{r} & r > d \end{cases} \quad \psi_c(r) = \begin{cases} \frac{B}{r} \sin(q_c r + \eta_c) & r < d \\ 0 & r > d \end{cases}$$

Substituting into Schrödinger equation

$$-\frac{\hbar^2}{2m} \Delta \psi_0 - V_0 \psi_0 + \frac{2\pi \hbar^2 b}{m} \delta(\vec{r}) \left( \frac{\partial}{\partial r} r \psi_c \right)_{r=0} = 0$$

$$-\frac{\hbar^2}{2m} \Delta \psi_c - V_c \psi_c + \frac{2\pi \hbar^2 b}{m} \delta(\vec{r}) \left( \frac{\partial}{\partial r} r \psi_0 \right)_{r=0} = 0$$

At  $r < d$

$$\Delta \psi_0 = -4\pi A \sin \eta_0 \delta(\vec{r}) - \frac{A}{r} q_0^2 \sin(q_0 r + \eta_0)$$

$$\Delta \psi_c = -4\pi B \sin \eta_c \delta(\vec{r}) - \frac{B}{r} q_c^2 \sin(q_c r + \eta_c)$$

$$\left( \frac{\partial}{\partial r} r \psi_0 \right)_{r=0} = A q_0 \cos \eta_0$$

$$\left( \frac{\partial}{\partial r} r \psi_c \right)_{r=0} = B q_c \cos \eta_c$$

Comparing terms with Dirac delta function

$$A \sin \eta_0 - b B q_c \cos \eta_c = 0 \quad \Rightarrow \quad A = B \frac{b q_c \cos \eta_c}{\sin \eta_0}$$

$$B \sin \eta_c - b A q_0 \cos \eta_0 = 0$$

$$B \sin \eta_c = b q_0 \cos \eta_0 \quad B \frac{b q_c \cos \eta_c}{\sin \eta_0} \quad \Rightarrow \quad \tan \eta_c \tan \eta_0 = b^2 q_0 q_c$$





Now we connect solutions at  $r=d$

Closed channel:  $\sin(q_c d + \eta_c) = 0 \Rightarrow \underline{\tan(q_c d) + \tan \eta_c = 0}$

Open channel:

$$R_o(d^-) = B \sin(q_o d + \eta_o)$$

$$R_o(d^+) = d - a$$

$$\frac{R_o'(d^-)}{R_o(d^-)} = \frac{q_o \cos(q_o d + \eta_o)}{\sin(q_o d + \eta_o)} = \frac{R_o'(d^+)}{R_o(d^+)} = \frac{1}{d-a} \Rightarrow \underline{d-a = \frac{1}{q_o} \tan(q_o d + \eta_o)}$$

Combining all the underlined equations we obtain

$$d-a = \frac{(d-a_{b_0}) \frac{q_o}{\tan \eta_o} + 1}{\frac{q_o}{\tan \eta_o} - q_o^2 (d-a_{b_0})}$$

$$E^* = \frac{\hbar^2}{m d^2}$$

close to resonance

$$\frac{q_o}{\tan \eta_o} = - \frac{\tan q_c d}{b^2 q_c} = - \frac{\tan \left[ \pi - \frac{\delta d^2}{2\pi} \right]}{b^2 q_c} \stackrel{\downarrow}{\approx} - \frac{1}{b^2 q_c} \tan \left( \pi - \frac{\delta d^2}{2\pi} \right) = \frac{1}{b^2 a_c} \frac{\Delta}{E^*}$$





$$\frac{d-a}{d-a_{0g}} = \frac{\Delta + E^* \frac{b q_c}{d-a_{0g}}}{\Delta - E^* b^2 q_c q_0^2 (d-a_{0g})}$$

Assuming that position of band state changes aJ for magnetic Feshbach resonance

$$\Delta = \delta\mu (B - B_{res})$$

we obtain

$$\frac{a-d}{a_{0g}-d} = \frac{B - B_{res} + \frac{E^*}{\delta\mu} \epsilon}{B - B_{res} - \frac{E^*}{\delta\mu} [q_0(a_{0g}-d)]^2 \epsilon} \quad \epsilon = \frac{b^2 q_c}{d-a_{0g}} \text{ - proportional to coupling}$$

Comparing with the formula for magnetic Feshbach resonance

$$\frac{a}{a_{0g}} = 1 - \frac{\Delta B}{B - B_0} = \frac{B - B_0 - \Delta B}{B - B_0}$$

we determine position of the resonance ( $B_0$ ) and its width ( $\Delta B$ )

$$B_0 = B_{res} + \frac{E^*}{\delta\mu} \epsilon (q_0(a_{0g}-d))^2 \leftarrow \text{shifted from } B_{res} \text{ by coupling}$$

$$\Delta B = - \frac{E^* \epsilon}{\delta\mu} (1 + q_0^2 (a_{0g}-d)^2)$$

