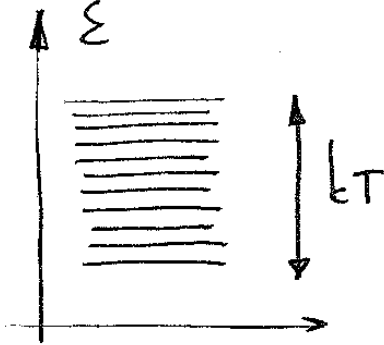


## Lecture#12

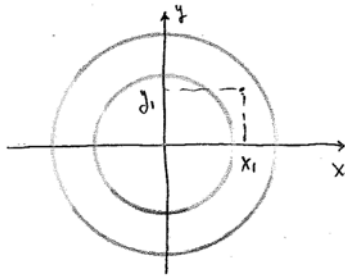
### Boltzmann Statistics

1) Thermal energy  $kT$  is much larger than energy difference between quantum levels.

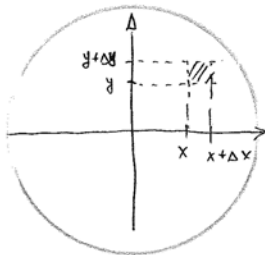


Probability to find a system with particular energy should be considered as continuous. To deal with continuously varying energy we have to introduce probability density  $\rho(\epsilon)$ .

Let consider simple example, you are throwing darts into target. Say you are good enough that each time you throw a dart you hit the target. We can say that the probability to hit the target in some undefined position is one. Let's now ask, another question, what is probability for a dart to hit a point with coordinates  $X_1 Y_1$ ? This question does not have any meaning, at least from mathematical standpoint.  $X_1 Y_1$  point is mathematical abstraction. There are infinitely many points on the target.



On the other hand the question what is probability to hit target in the area  $(x_1, y_1, x_1 + \Delta x, y_1 + \Delta y)$  is well legitimate. We need probability density to characterize this type of probability distributions.



Simple case Gaussian distribution density

$\rho(x, y) = \frac{1}{A} \cdot \exp\left(-\frac{x^2 + y^2}{2\delta^2}\right)$  - Probability density. A – normalization constant

$P(x, y) = \frac{1}{A} \cdot \exp\left(-\frac{x^2 + y^2}{2\delta^2}\right) dx dy$  - Probability for a dart to hit area

between  $x, y$  and  $x + dx, y + dy$ . Normalization constant A can be found from the condition that probability to hit target in some place is one. That is

$$P = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \frac{1}{A} \exp\left(-\frac{x^2 + y^2}{2\delta^2}\right) dx dy = 1 = \frac{1}{A} \int_{-\infty}^{+\infty} \exp\left(-\frac{x^2}{2\delta^2}\right) dx \int_{-\infty}^{+\infty} \exp\left(-\frac{y^2}{2\delta^2}\right) dy =$$

$$= \frac{1}{A} \cdot 2\pi\delta^2 = 1 \quad A = 2\pi\delta^2$$

Notice that  $\delta$  has dimension of length. Then the dimension of probability density  $\rho$  is inverse of area ( $1/m^2$ ). The dimension of probability density is example specific. For one-dimensional Gaussian  $1/m$ , for 3d it is  $1/m^3$ . We will also consider examples where  $\rho$  depends not on coordinate but on velocities or energy and so on.

Changing variables in distributions we use the same rule as for change variables in integration.

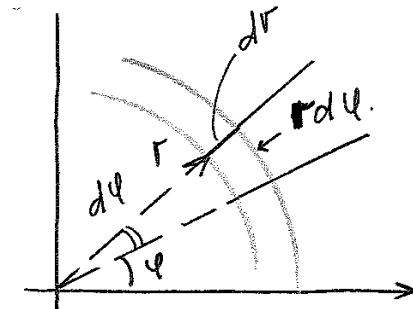
$$\iint_{R_{xy}} f(x, y) dx dy = \iint_{R_{uv}} f[x(u, v), y(u, v)] \left| \frac{\partial(x, y)}{\partial(u, v)} \right| du dv$$

Where  $J = \left| \frac{\partial(x, y)}{\partial(u, v)} \right| = \begin{vmatrix} \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} \end{vmatrix}$  is the Jacobian

Polar coordinate

$$x, y \rightarrow r, \varphi, \quad x = r \cos \varphi, y = r \sin \varphi$$

$$J = \left| \frac{\partial(x, y)}{\partial(r, \varphi)} \right| = \begin{vmatrix} \cos \varphi & -r \sin \varphi \\ \sin \varphi & r \cos \varphi \end{vmatrix} = r$$



The probability density in polar coordinate is

$$\rho(r, \varphi) = \frac{1}{2\pi\delta^2} \exp\left(-\frac{r^2}{2\delta^2}\right)$$

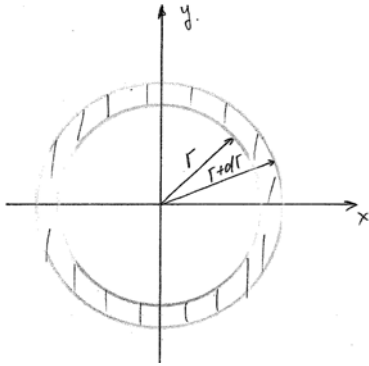
The probability to find a dart in the area  $(r, \varphi \rightarrow r + dr, \varphi + d\varphi)$

$$P(r, \varphi) = \frac{1}{2\pi\delta^2} \exp\left(-\frac{r^2}{2\delta^2}\right) r d\varphi dr$$

We can perform some manipulations with  $\rho$  and find some other probabilities of interest.

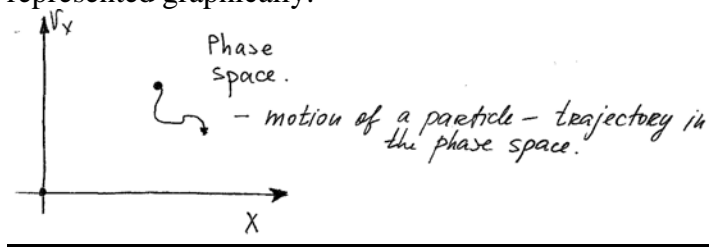
For example, if we want to know the probability to find a dart in the ring between  $r$  and  $r + dr$  we perform integration over polar angle.

$$P(r) = \int_0^{2\pi} d\varphi dr \rho(r, \varphi) = \frac{2\pi}{2\pi\delta^2} \cdot \exp\left(-\frac{r^2}{2\delta^2}\right) r dr$$



### Boltzmann Statistics for classical system. Maxwell distribution.

Consider a molecule of mass  $m$  in dilute gas. Let us denote the position of the center of mass of this molecule as  $\vec{r}$  and the velocity of the molecule as  $\vec{v}$ . The Translational degree of freedom can be treated classically to an excellent approximation if the gas is dilute and the temperature is not too low. The state of the molecule can be described by specifying that the position of the center of mass of the molecule lie in the range  $(\vec{r}, d\vec{r})$ , i.e. in a volume element of magnitude  $d^3\vec{r} = dx dy dz$  near position  $\vec{r}$  and that the velocity lies in the range  $(\vec{v}, d\vec{v})$  i.e. within velocity space volume  $d^3\vec{v} = dv_x dv_y dv_z$  near the velocity  $\vec{v}$ . For a molecule living in one-dimensional space the state of a molecule can be represented graphically.



For a molecule in 3 dimensional spaces, the state of the molecule is determined by position in 6-dimensional phase space (state space).

Other assumptions (approximations)

- 1) Gas is dilute – interaction between molecules is negligible, molecules are distinguishable – the need for this approximation will be described in the end of the course.
- 2) The molecule is in thermal contact with heat reservoir at temperature T. and therefore obeys the Boltzmann distribution.

The probability to find a molecule in the range  $(\vec{r}, d\vec{r})$  and  $(\vec{v}, d\vec{v})$  is

$$P(\vec{r}, \vec{v}) = P(r_x, r_y, r_z, v_x, v_y, v_z) = \rho(\vec{r}, \vec{v}) d^3\vec{v} d^3\vec{r} = A \exp[-\beta E(v, r)] d^3\vec{v} d^3\vec{r}$$

Where  $\left(\beta = \frac{1}{kT}\right)$  and A is a normalization constant that can be found from integration.

$\iint \rho(\vec{r}, \vec{v}) d^3\vec{r} d^3\vec{v} = 1$ . The integration is in our molecule with all possible velocities from  $-\infty$  to  $+\infty$  and with all possible position in the container volume V.

If we make a comparison with the Boltzmann equation for discrete quantum system with degeneracy

$$\frac{P(E_1)}{P(E_2)} = \frac{g_1 \exp\left(-\frac{E_1}{kT}\right)}{g_2 \exp\left(-\frac{E_2}{kT}\right)}$$

We find that our description of classical probability implies that we have the same number of quantum states in volume  $d^3\vec{r} d^3\vec{v}$  irrespectively where in the phase space we take this volume. This can be proven with quantum mechanics if we consider wave nature of particles.

If one multiplies the probability by the total number of molecule under consideration one obtains the mean number of molecules in this position and velocity range.

$$f(\vec{r}, \vec{v}) = N \rho(\vec{v}, \vec{r})$$

$$f(\vec{r}, \vec{v}) d^3\vec{r} d^3\vec{v} \equiv \text{the mean number of molecules with position between } \vec{r} \text{ and } \vec{r} + d\vec{r}$$

and velocity between  $\vec{v}$  and  $\vec{v} + d\vec{v}$

$$f(\vec{r}, \vec{v}) d^3\vec{r} d^3\vec{v} = A N \exp(-\beta E) d^3\vec{r} d^3\vec{v}$$

### **Example 1 Isothermal atmosphere**

Let us consider a system of non-interacting particles in gravitational field (we may use similar arguments for electrical field and other more complicated geometries)

Then the energy of particle is a sum of potential and kinetic energies:

$$E = mgz + m \frac{v^2}{2}$$

We also assume that temperature is the same in all parts of the system. Then the probability to find a particle in the range  $(\vec{r}, d\vec{r})$  and  $(\vec{v}, d\vec{v})$  is a product of two terms. One depends only on velocity the other only on coordinate of the particle

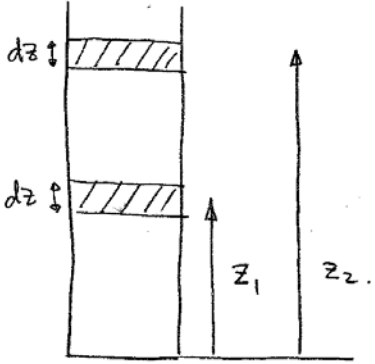
$$P(\vec{r}, \vec{v}) = P(r_x, r_y, r_z, v_x, v_y, v_z) = \rho(\vec{r}, \vec{v}) d^3 \vec{v} d^3 \vec{r} = A \exp\left[-\beta m \frac{v^2}{2}\right] d^3 \vec{v} \exp[-\beta mgz] d^3 \vec{r}$$

If we are not interested (at the moment) in the velocity distribution we may integrate over all possible velocities of the particle and obtain a probability to find a particle in with position between  $\vec{r}$  and  $\vec{r} + d\vec{r}$

$$P_1(\vec{r}) = P_1(r_x, r_y, r_z) = \rho_1(\vec{r}) d^3 \vec{r} = A \exp[-\beta mgz] d^3 \vec{r} \iiint \exp\left[-\beta m \frac{v^2}{2}\right] d^3 \vec{v} = B \exp[-\beta mgz] d^3 \vec{r}$$

Where integration is from  $-\infty$  to  $+\infty$  for each component of the velocity and B is the normalization constant that depends on mass of the particle and temperature. Since potential energy in our isothermal atmosphere does not depend on x and y coordinates we can write that

$$\frac{\text{probability to find a molecule in volume } Sdz \text{ at } z=z_1}{\text{Probability to find a molecule in volume } Sdz \text{ at } z=z_2} = \frac{\rho(E_1) dz}{\rho(E_2) dz} = \frac{\exp\left(-\frac{mgz_1}{kT}\right)}{\exp\left(-\frac{mgz_2}{kT}\right)}$$



After setting  $z_2=0$  we have

$$\rho(z) = \frac{1}{A} \exp\left(-\frac{mgz}{kT}\right)$$

$n(z) = \rho(z)N$ , where N is total number of particles in the column of atmosphere with base  $dx dy = S$  and infinite height.

$$n(z) = n(0) \exp\left(-\frac{mgz}{kT}\right)$$

$n(0)$  appears in the above equation because it has to give correct concentration at  $z = 0$ .

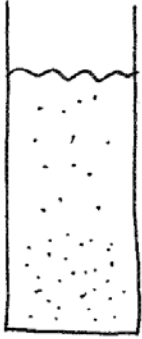
From ideal gas law  $PV = NkT$  we find  $P = kT N/V = kTn$ ,  $n$  – concentration. Because temperature is supposed to be height independent we may write for pressure.

$$P(z) = P(0) \exp\left(-\frac{mgz}{kT}\right) =$$

$$= P(0) \exp\left(-\frac{28 \times 10^{-3} \cdot 9.8z}{6.02 \times 10^{-23} \times 1.38 \times 10^{23} \times 300}\right) \approx P(0) \exp\left(-1.0 \times 10^{-4} \frac{1}{m} z\right)$$

On top of Everest  $h = 8,800$  m pressure is  $P = P(0)0.41$  – incredibly small

### Sedimentation



The distribution of the particles follow the same Boltzman distribution on molecules is in atmosphere. The force instead of  $mg$  is  $(mg - \rho_L v_p g)$   $\rho_L v_p g$  - buoyant force.

Because mass of dust particle is much large than the mass of molecules, concentration of particles decays much faster with height. Say if you have  $100A^0$  particle with  $\rho \approx 4 \text{ g/cm}^2$  in water, than the mass of the particle will be,

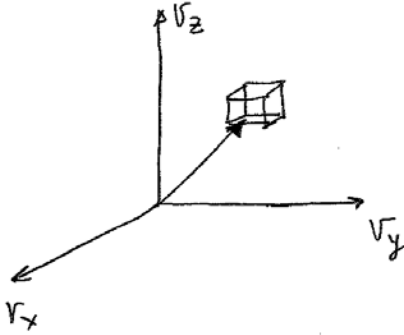
$$4 \frac{\text{g}}{\text{cm}^3} \cdot 10^{-3} \frac{\text{kg}}{\text{g}} \cdot \frac{1}{10^{-6} \text{m}^3 / \text{cm}^3} \cdot (100A^0)^3 \cdot \frac{1}{(10^{10} A^0 / \text{m})^3} = 4 \cdot 10^{-21} \text{g}$$

$$n(z) = n(0) \times \exp\left(-\frac{1}{kT} (mgz - \rho_w v_p gz)\right) =$$

$$= n(0) \exp\left(-\frac{1}{1.38 \times 10^{-23} \times 300} \cdot 3 \cdot 10^{-21} \times 9.8 \times z\right) = n(0) (-7.2z)$$

So the concentration decreases 2.72 (e) times at the height  $h = 1/7.2 \approx 0.14\text{m}$ .

## Maxwell distribution



Let us now consider the experimental arrangement when we do not have any potential field or this field does not change much within the system. We are now interested in the distribution of velocities of molecules in our system. Then the probability to find a molecule with velocity in the range  $(\vec{v}, d\vec{v})$  i.e. within velocity phase volume

$d^3\vec{v} = dv_x dv_y dv_z$  near the velocity  $\vec{v}$  is

$$P_2(\vec{v}) = P_2(v_x, v_y, v_z) = \rho_2(\vec{v}) d^3\vec{v} = A \exp\left[-\beta m \frac{v^2}{2}\right] d^3\vec{v} \int \exp[-bV] d^3\vec{r} = C \exp\left[-\beta m \frac{v^2}{2}\right] d^3\vec{v}$$

The normalization constant C can be found from normalization

$$1 = \int \int \int_{-\infty}^{+\infty} d^3\vec{v} \rho_2(\vec{v}) = \int \int \int_{-\infty}^{+\infty} dv_x dv_y dv_z \rho_2(\vec{v}) = C \int \int \int_{-\infty}^{+\infty} dv_x dv_y dv_z \exp\left[-\beta m \frac{v^2}{2}\right] =$$

$$C \int_{-\infty}^{+\infty} dv_x \exp\left[-\beta m \frac{v_x^2}{2}\right] \times \int_{-\infty}^{+\infty} dv_y \exp\left[-\beta m \frac{v_y^2}{2}\right] \times \int_{-\infty}^{+\infty} dv_z \exp\left[-\beta m \frac{v_z^2}{2}\right]$$

The three integrals have the same value

$$\int_{-\infty}^{+\infty} \exp(-\alpha x^2) dx = \sqrt{\frac{\pi}{2\alpha}} \quad \int_{-\infty}^{+\infty} \exp\left(-\beta \frac{mv_x^2}{2}\right) dv_x = \sqrt{\frac{2\pi}{\beta m}}$$

$$C = \left(\frac{\beta m}{2\pi}\right)^{\frac{3}{2}} = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}$$

As a result we have **the Maxwell velocity distribution**.

$$P_2(v_x, v_y, v_z) = \rho_2(\vec{v}) d^3\vec{v} = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \exp\left[-\beta m \frac{v^2}{2}\right] d^3\vec{v}$$

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The following integrals are useful in computation of different average values:

$$I(n) = \int_0^{\infty} x^n \exp(-ax^2) dx$$

$$I(0) = \frac{1}{2} \sqrt{\frac{\pi}{a}}, \quad I(1) = \frac{1}{2} a^{-1}, \quad I(2) = \frac{1}{4} \sqrt{\pi} a^{-3/2}, \quad I(3) = \frac{1}{2} a^{-2}, \quad I(4) = \frac{3}{8} \sqrt{\pi} a^{-5/2}, \quad I(5) = a^{-3}$$

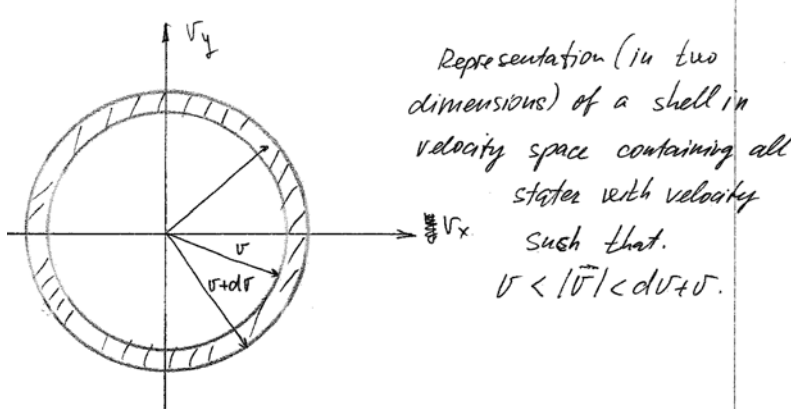
**To compute an average value**  $\langle Q \rangle$  of some quantity  $Q(v_x, v_y, v_z)$  which is a function of the velocity, we use general rule

$$\langle Q \rangle = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} Q(v_x, v_y, v_z) \rho_2(\vec{v}) dv_x dv_y dv_z$$

$$\langle v_x^2 \rangle = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} v_x^2 \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} \exp\left( -\frac{mv^2}{2kT} \right) dv_x dv_y dv_z =$$

$$\left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} \times \int_{-\infty}^{+\infty} v_x^2 \exp\left( -\frac{mv_x^2}{2kT} \right) dv_x \times \int_{-\infty}^{+\infty} \exp\left( -\frac{mv_y^2}{2kT} \right) dv_y \times \int_{-\infty}^{+\infty} \exp\left( -\frac{mv_z^2}{2kT} \right) dv_z = \frac{kT}{m}$$

**Let us introduce probability of certain speed (magnitude of velocity)**



$\rho_3(v)dv$  - is the probability for the molecule to be in **any** position within volume  $V$ , move in **any** direction and have the speed between  $v$  and  $v+dv$ .

To compute  $\rho_3(v)dv$  we have to integrate  $\rho_2(\vec{v})d^3\vec{v}$  over all possible direction. We first convert element volume in velocity space from Cartesian to spherical coordinates  $dv_x dv_y dv_z = \sin\theta d\theta d\phi v^2 dv$ . After this we have

$\rho_2(v, \theta, \phi) \sin\theta d\theta d\phi v^2 dv$  is the probability to find a molecule in **any** position within the volume  $V$  and to have the speed between  $v+dv$ , azimuthal angle between  $\phi+d\phi$  and polar angle between  $\theta$  and  $\theta+d\theta$ . After integration over all angles (which is the same as integration over all possible directions of the speed we have

$$\rho_3(v)dv = \int_0^{2\pi} d\phi \int_0^\pi \rho_2(v, \theta, \phi) \sin\theta d\theta d\phi v^2 dv =$$

$$\int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta v^2 \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} \exp\left( -\frac{mv^2}{2kT} \right) dv = 4\pi v^2 \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} \exp\left( -\frac{mv^2}{2kT} \right) dv$$

The average speed is computed by general method using integral I(3)



$$\langle v \rangle = \int_0^{+\infty} v 4\pi v^2 \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} \exp\left( -\frac{mv^2}{2kT} \right) dv = \sqrt{\frac{8}{\pi}} \sqrt{\frac{kT}{m}}$$