Quiz 5 on Thurs, Apr. 7

Important points from last lecture:

For rotating heteronuclear diatomic molecule AB

$$E_n = n(n+1)\epsilon, \quad d_n = 2n+1, \quad n = 0, 1, 2\cdots$$

$$Z_{rot} = \sum_s e^{-\beta E_s} = \sum_n d_n e^{-\beta E_n} = \sum_n (2n+1) e^{-\beta\epsilon n(n+1)}$$

High-temp behavior $kT \gg \epsilon$

$$Z_{rot} = \sum_n (2n+1) e^{-\beta\epsilon n(n+1)} \simeq \int_0^\infty (2n+1) e^{-\beta\epsilon n(n+1)} dn \simeq \frac{kT}{\epsilon}$$

← approx by integral

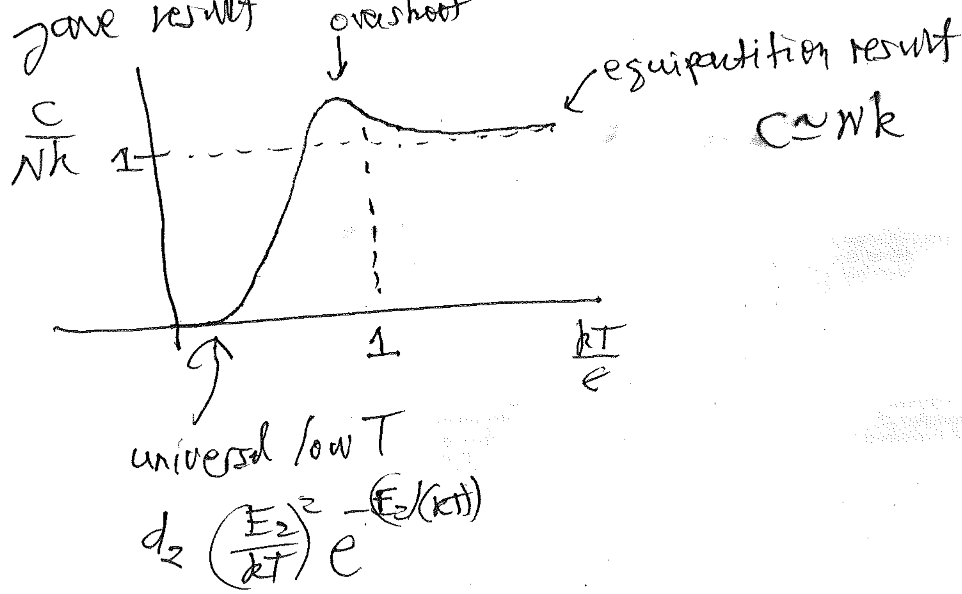
low-temp behavior:

$$Z_{rot} \simeq 1 + e^{-\beta E_2} d_2$$

gives universal low-T form for $\langle \epsilon \rangle = -\frac{\partial \ln Z}{\partial \beta}$, $C = \frac{d}{dT}[N\langle E\rangle]$

numerical calculation of $Z_{rot}$, $\langle E\rangle = -\frac{\partial \ln Z_{rot}}{\partial \beta}$, $C = \frac{d}{dT}[N\langle E\rangle]$

straightforward, gave result



# Boltzmann statistics for classical problems with continuously varying states

So far have considered small quantum systems with <u>discrete</u> energies $E_n$ and corresponding degeneracies $d_n$, e.g. paramagnet, Einstein solid, rotating heteronuclear molecule.

Want to extend discussion to larger classical "small" systems for which classical description is appropriate, using continuous variables like position $\vec{x}$, momentum $\vec{p}$, angle $\theta$, etc.

Ask same question as before: what is probability for small system, in equil. w/ large reservoir with temp $T$, to be in particular state $s$ with energy $E_s$? Assume as before that system and reservoir form <u>closed</u> system so total energy $E_s + E_R = E$ is conserved.

<u>Strictly speaking</u> $P_s = p(x, p, \dots)$ <u>is zero</u> if variables $x, p, \theta, \dots$ are continuous since, in any finite interval, there is $\infty$ of possible values of $x$, $p$, etc. Instead, one has to ask different question, what is probability for system to lie in small intervals

$$[x, x+dx]$$
$$[\theta, \theta+d\theta] \qquad \text{etc}$$
$$[p, p+dp]$$

Let $q$ denote some general continuous coordinate so $E = E(q)$. Then instead of calculating probability $P_q$, we have to work with <u>probability density</u>, also called <u>probability distribution</u>, $\mathcal{D}(q)$, which has physical meaning that $\underline{\mathcal{D}(q)\,dq}$ = prob for $q$ to be in range $q, q+dq$

Densities $\mathcal{D}(q)$ must always appear inside an integral and must always be multiplied by an infinitesimal (sometimes by several infinitesimals) to get a dimensionless probability.

Because $\mathcal{D}(q)dq$ has meaning of prob, sum of all possible probabilities must be one (i.e., a physical system must always be observed to have some value). So

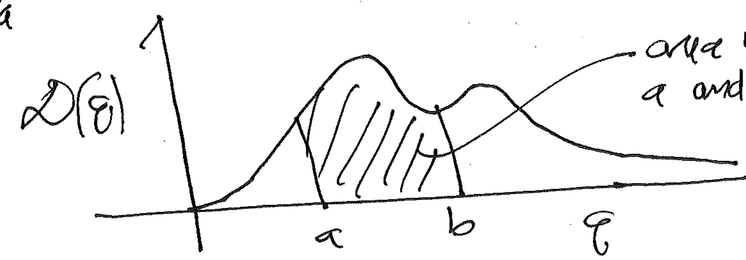
$$\int_{-\infty}^{\infty} \mathcal{D}(q)\,dq = 1$$

Further

$$\int_a^b \mathcal{D}(q)\,dq = \text{prob of observing system to have value } q \text{ in range } a \le q \le b$$

Note if we let $b = a + da$,

$$\int_a^{a+da} \mathcal{D}(q)\,dq \simeq \mathcal{D}(a)\int_a^{a+da} dq = \mathcal{D}(a)\,da$$




area under $\mathcal{D}(q)$ between a and b is probability to be between a and b

In many cases, a physical ~~so~~ system is described by several continuous variables and so the probability density $\mathcal{D}_{12}(q_1, q_2)$ will be a multivariate function. The meaning is

$$\mathcal{D}_{12}(q_1, q_2)\, dq_1\, dq_2 =$$ probability to observe system to have variable $q_1$ in range $q_1, q_1+dq_1$, $q_2$ in range $q_2, q_2+dq_2$

To be a probability density, all probabilities must add up to 1

$$\int_{-\infty}^{\infty} dq_1 \int_{-\infty}^{\infty} dq_2\, \mathcal{D}_{12}(q_1, q_2) = 1$$

From a multivariate probability density, one can obtain several new probability densities that depend on fewer variables. For example

$$\mathcal{D}_1(q_1) = \int_{-\infty}^{\infty} \mathcal{D}_{12}(q_1, q_2)\, dq_2 =$$ probability density to observe variable $q_1$ in range $q_1, q_1+dq_1$ independently of the value of $q_2$

$$\mathcal{D}_2(q_2) = \int_{-\infty}^{\infty} \mathcal{D}_{12}(q_1, q_2)\, dq_1 =$$ prob density for $q_2, q_2+dq_2$ independently of the value of $q_1$

You can easily verify that these new probability densities that depend on fewer variables are indeed probability densities whose "areas" add to 1, e.g.

$$\int_{-\infty}^{\infty} \mathcal{D}_1(q_1)\,dq_1 = \int_{-\infty}^{\infty}\left[\int_{-\infty}^{\infty} \mathcal{D}_{12}(q_1,q_2)\,dq_2\right]dq_1 = \int_{-\infty}^{\infty} dq_1 \int_{-\infty}^{\infty} dq_2\, \mathcal{D}_{12}(q_1,q_2)$$

$$= 1$$

and similarly for $\mathcal{D}_2(q_2)$.

Another way to get new probability densities from a given probability density is to change variables. For example, if we are given a prob. density $\mathcal{D}(q)$ such that

$$\int_{-\infty}^{\infty} \mathcal{D}(q)\,dq = 1 \qquad \text{normalization condition}$$

we can change variables $q = q(p)$ to a new variable $p$. Then $dq = \frac{dq}{dp}dp$ and the normalization condition can be written

$$1 = \int_{-\infty}^{\infty} \mathcal{D}(q)\,dq = \int_{-\infty}^{\infty}\left[\mathcal{D}(q(p)) \cdot \frac{dq}{dp}\right] \cdot dp.$$

This last equation says that the quantity

$$\mathcal{D}\left[q(p)\right]\frac{dq}{dp}$$

is a probability density for the new variable $p$.

As an illustration of these ideas, consider a probability density

$$\boxed{\mathcal{D}_{xyz}(x,y,z) = \left(\frac{c}{\pi}\right)^{3/2} e^{-c(x^2+y^2+z^2)}}$$

where $c$ is some positive constant. You should verify that

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \left[\left(\frac{c}{\pi}\right)^{3/2} e^{-c(x^2+y^2+z^2)}\right] = 1$$

so this is indeed a prob. density. If we are just interested in the probability of finding the system in a narrow range $x, x+dx$ no matter what are the values of the coordinates $y$ and $z$, we simply add up all the probabilities corresponding to all possible values of $y$ and $z$

$$\mathcal{D}_x(x) = \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \left[\left(\frac{c}{\pi}\right)^{3/2} e^{-c(x^2+y^2+z^2)}\right] = \sqrt{\frac{c}{\pi}}\, e^{-cx^2}$$

and you can easily verify that

$$\int_{-\infty}^{\infty} \mathcal{D}_x(x)\,dx = \int_{-\infty}^{\infty} \sqrt{\frac{c}{\pi}}\, e^{-cx^2}\,dx = 1$$

Similarly, we can obtain 2-dim prob density for finding system with variables in range

$$y, y+dy, \quad z, z+dz$$

independent of x by integrating over the x variable

$$\mathcal{D}_{yz}(y,z) = \int_{-\infty}^{\infty} dx \cdot \mathcal{D}_{xyz}(x,y,z) = \frac{c}{\pi} e^{-c(y^2+z^2)}$$

Finally, we can switch from Cartesian to spherical coordinates

$$(x,y,z) \rightarrow (r,\theta,\varphi)$$

to discover the probability density $\mathcal{D}_{r,\theta,\varphi}(r,\theta,\varphi)$ for finding the system to have variables in the range

$$r, r+dr \quad \theta, \theta+d\theta \quad \varphi, \varphi+d\varphi$$

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz\; \mathcal{D}_{xyz}(x,y,z) = \int_0^{\infty} dr \int_0^{\pi} d\theta \int_0^{2\pi} d\varphi \Big[ \mathcal{D}_{xyz}(r,\theta,\varphi) \cdot r^2 \sin\theta\, dr\, d\theta\, d\varphi \Big]$$

where $\mathcal{D}_{xyz}(r,\theta,\varphi) = \mathcal{D}_{xyz}(r\sin\theta\cos\varphi,\ r\sin\theta\sin\varphi,\ r\sin\theta)$

For our simple prob density

$$\mathcal{D}_{xyz}(r,\theta,\varphi) = \left(\frac{c}{\pi}\right)^{3/2} e^{-cr^2} \quad \text{since } x^2+y^2+z^2=r^2$$

So the prob density in spherical coordinates, w.r.t variables $r,\theta,\varphi$, is given by

$$\boxed{\mathcal{D}_{r\theta\varphi}(r,\theta,\varphi) = \left(\frac{c}{\pi}\right)^{3/2} e^{-cr^2} r^2 \sin\theta \cancel{dr\,d\theta\,d\varphi}}$$

In turn, we can find further prob densities that depend ~~too~~ two or one spherical coordinate. For example

$$\mathcal{D}(r) = \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta\, \mathcal{D}_{r\theta\varphi}(r,\theta,\varphi) = \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \left[\left(\frac{c}{\pi}\right)^{3/2} e^{-cr^2} r^2 \sin\theta\right]$$

$$= 4\pi r^2 \left(\frac{c}{\pi}\right)^{3/2} e^{-cr^2}$$

is the prob. density to observe the system to have a radial coordinate in the range $r, r+dr$ ind. of value of $\theta, \varphi$

$$\mathcal{D}(\theta) = \int_0^{\infty} dr \int_0^{2\pi} d\varphi \left[\left(\frac{c}{\pi}\right)^{3/2} e^{-cr^2} r^2 \sin\theta\right]$$

$$= \frac{1}{2}\sin\theta$$

is the probability density for $\theta, \theta+d\theta$ independent of $r, \varphi$ values

you can verify $\mathcal{D}(\varphi) = \frac{1}{2\pi}$ since original density $\mathcal{D}(x,y,z) = e^{-cr^2}$ symmetric, independent of $\varphi$.

One more observation before giving several examples to illustrate the ideas! for system with continuous label $q$, the expression

$$\mathcal{P}(q) = \frac{e^{-\beta E(q)}}{Z} \qquad Z = \int_{-\infty}^{\infty} e^{-\beta E(q)}\, dq$$

now has physical dimension

now has meaning of probability density rather than probability

Thus average of some quantity $X(q)$ that varies with $q$ now given by

$$\langle X \rangle = \int_{-\infty}^{\infty} X(q) \cdot \underbrace{\mathcal{P}(q)\, dq}_{} \equiv \sum_s X_s \cdot P_s$$

dimensionless since $\frac{1}{Z}$ has dimensions of $\frac{1}{q}$

$$= \int_{-\infty}^{\infty} X(q) \left( \frac{e^{-\beta E(q)}}{Z} \right) dq$$

$$= \frac{1}{Z} \int_{-\infty}^{\infty} X(q)\, e^{-\beta E(q)}\, dq$$

$$\boxed{\langle X \rangle = \frac{\int_{-\infty}^{\infty} X(q)\, e^{-\beta E(q)}\, dq}{\int_{-\infty}^{\infty} e^{-\beta E(q)}\, dq}} \equiv \frac{1}{Z} \sum_s e^{-\beta E_s} X_s$$

note how this has physical dimension of $X$ since dimensions of $q$ cancel out between numerator and denominator

For $X(q) = E(q)$ equal to the energy of the system, the same formula holds as before:

$$\langle E \rangle = \frac{\int_{-\infty}^{\infty} E(q)\, e^{-\beta E(q)}\, dq}{\int_{-\infty}^{\infty} e^{-\beta E(q)}\, dq} = -\frac{\partial \ln Z}{\partial \beta}$$

Application 1: Equipartition theorem    Section 6.3, pages 238-240 of Schroeder

Assume $E(q) = cq^2$ varies quadratically with some parameter $q$.

Then:

$$Z = \int_{-\infty}^{\infty} e^{-\beta E(q)}\, dq = \int_{-\infty}^{\infty} e^{-\beta c q^2}\, dq = \frac{1}{\sqrt{\beta c}} \int_{-\infty}^{\infty} e^{-x^2}\, dx = \sqrt{\frac{\pi}{\beta c}}$$

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = -\frac{1}{Z} \cdot \frac{\partial Z}{\partial \beta} = \frac{kT}{2}$$

each quadratic term contributes $\frac{kT}{2}$

General case: $E = \sum_{i=1}^{f} c_i q_i^2$    $q_1, q_2, \ldots, q_f$ separate degrees of freedom

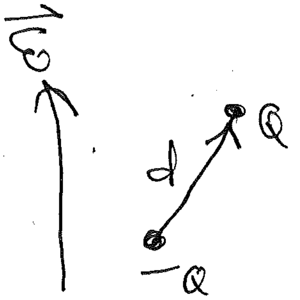
$$Z = \int_{-\infty}^{\infty} dq_1 \cdots \int_{-\infty}^{\infty} dq_f \cdot e^{-\beta(c_1 q_1^2 + \cdots + c_f q_f^2)}$$

$$= \prod_{i=1}^{f} \left( \int_{-\infty}^{\infty} dq_i\, e^{-\beta c_i q_i^2} \right) = \sqrt{\frac{\pi}{\beta c_1}} \cdot \sqrt{\frac{\pi}{\beta c_2}} \cdots \sqrt{\frac{\pi}{\beta c_f}}$$

$$Z = C \cdot \beta^{-f/2}$$

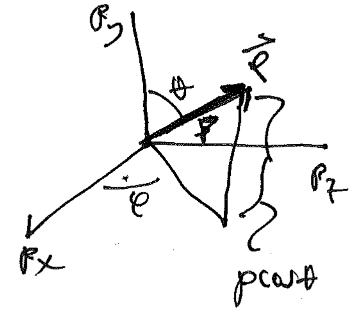
you can finish proof

Application 2: electric dipole in external uniform electric field $\vec{\mathcal{E}}$




Consider 3d electric dipole $\vec{p} = (p_x, p_y, p_z)$
$= Q d \hat{n}$

corresponding to two opposite equal charges $Q, -Q$ separated by distance $d$. Many molecular dipoles, e.g. in dielectric of a capacitor, are big enough to treat classically and so continuously. Orientation of dipole w.r.t. external field $\vec{\mathcal{E}} = \mathcal{E}\hat{z}$ given by angle $(\theta, \varphi)$ of spherical coordinate system.




Freshman physics tells us that

$$E = -\vec{p}\cdot\vec{\mathcal{E}} = -p\,\mathcal{E}\cos\theta$$

Then:

$$Z = \sum_n d_n e^{-\beta E_n} \longrightarrow \underbrace{\int_0^{2\pi}}_{\varphi} \underbrace{\int_0^{\pi}}_{\theta} \cdot\, e^{-\beta\left[-p\mathcal{E}\cos\theta\right]} \underbrace{\sin\theta\, d\theta\, d\varphi}_{\text{degeneracy}}$$

where $\sin\theta\, d\theta\, d\varphi = d\Omega$ can be thought of as degeneracy of vectors $\vec{p}$ lying in direction $\theta, \varphi$ with range $\theta, \theta + d\theta$ $\quad \varphi, \varphi + d\varphi$

$$Z = \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta\, e^{\beta p \mathcal{E}\cos\theta} \sin\theta = 4\pi\, \frac{\sin\left[\beta p \mathcal{E}\right]}{\beta p \mathcal{E}}$$

3/29

Average dipole moment $\langle p_z \rangle = \langle p\cos\theta \rangle$ when dipole is in equilibrium with reservoir of temperature T given by:

$$\langle p_z \rangle = \langle p\cos\theta \rangle = \int p\cos\theta \cdot \frac{e^{+\beta p \mathcal{E}\cos\theta}}{Z} \cdot d\Omega$$

$$= \frac{1}{Z}\int p\cos\theta \cdot e^{+\beta p \mathcal{E}\cos\theta}\, d\Omega$$

$$= \frac{kT}{Z}\frac{\partial Z}{\partial \mathcal{E}}$$ ← notice common trick of differentiating w.r.t. parameter to bring down quantity of interest

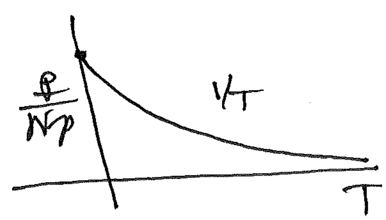
$$\langle p_z \rangle = p\left[\coth(\beta p \mathcal{E}) - \frac{1}{\beta p \mathcal{E}}\right]$$ ← please do the algebra and verify this result

Macroscopic dipole moment for N ~~do~~ identical non-interacting dipoles

$$P = \langle P_z \rangle = N\langle p_z \rangle = Np\left[\coth(\beta p \mathcal{E}) - \frac{1}{\beta p \mathcal{E}}\right]$$ = polarization

Predicts Curie-like law: for large T, small $\beta$

$$P = \text{polarization} \propto \frac{\mathcal{E}}{T}$$




at high temperature, orientations randomize, no net polarization

## Application 3: The Maxwell speed distribution

Gas of molecules in equilibrium at temperature T can be thought of as single system consisting of single molecule in equilibrium with remaining molecules that make up the large reservoir.

If gas is ideal and particles are non-interacting, energy of system is

$$E(\vec{v}) = \frac{1}{2}mv^2$$

and distribution function to observe molecule with velocity $\vec{v}$ with components in range

$$v_x, v_x+dv_x \quad v_y, v_y+dv_y \quad v_z, v_z+dv_z$$

given by

$$\mathcal{D}(v_x,v_y,v_z) = \frac{e^{-\beta\cdot\frac{1}{2}mv^2}}{\int dv_x\int dv_y dv_z\, e^{-\beta m v^2/2}} = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\beta m v^2/2}$$

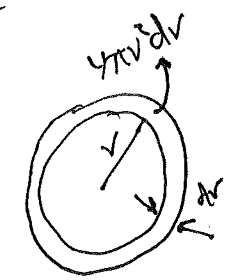
If we are not interested in orientation of velocities but just their magnitude, we can switch to spherical coordinates in velocity space like this

$$\mathcal{D}(v_x,v_y,v_z)dv_x dv_y dv_z = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\beta m v^2/2} \cdot v^2 \sin\theta\, dv\, d\theta\, d\varphi$$

and we can then integrate over $0\le\varphi\le 2\pi$, $0<\theta<\frac{\pi}{2}$, to get prob of $v, v+dv$ independent of angle. This gives prob to observe molecule to have speed $v, v+dv$ ind. of orientation $= \boxed{\left(\frac{m}{2\pi kT}\right)^{3/2} \cdot 4\pi v^2 \cdot e^{-\beta m v^2/2}\, dv}$

$= \mathcal{D}_m(v)\,dv$

The expression $\mathcal{D}_m(v)$ is called the <u>Maxwell-Boltzmann speed distribution</u> of an equilibrium ideal gas of identical molecules of mass $m$. Has intuitive interpretation:




$$\mathcal{D}(v) \propto \underbrace{4\pi v^2 dv}_{\text{degeneracy of } \vec{v}} \times \underbrace{e^{-\beta m v^2/2}}_{\text{probability of molecule having velocity } \vec{v}}$$

You can verify that, as is the case for any prob density,

$$\int_0^\infty \mathcal{D}(v)\,dv = 1$$

Also $\int_{v_1}^{v_2} \mathcal{D}(v)\,dv =$ prob for speed to lie in range $v_1 \le v \le v_2$