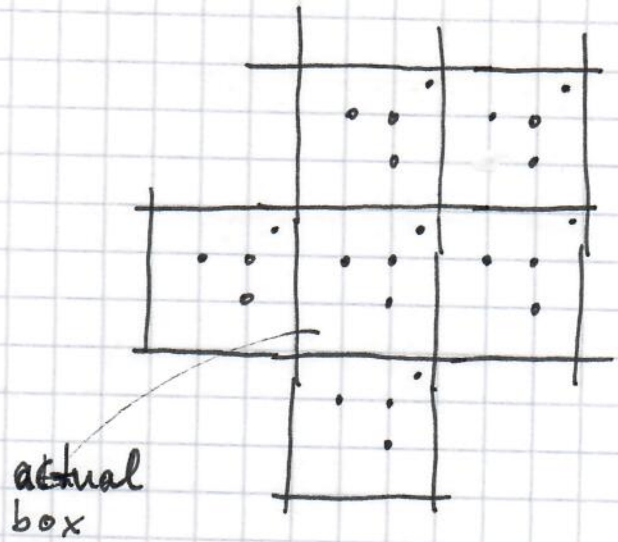
periodic boundary conditions:



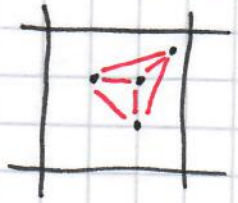
relevant parameter

$$\rho = \frac{N}{V}$$

With periodic boundary conditions, the system has infinite extent → it is infinitely large

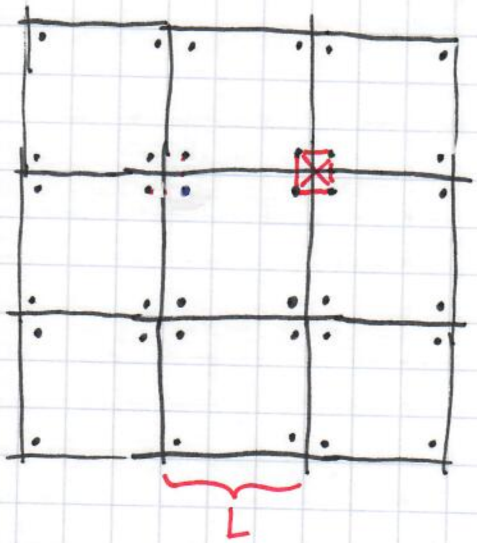
How many two-body interactions do we have in the case shown?

4 particles: $\frac{4 \cdot 3}{2} = 6$ two-body pairs



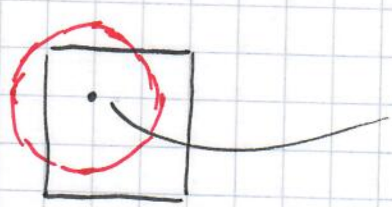
6 two-body pairs

Let's look at a slightly different arrangement



again, 6 two-body pairs

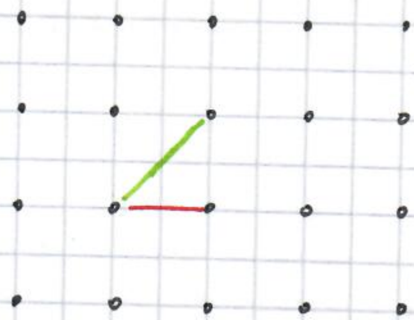
In principle, one would have an infinite number of pairs → in practice (i.e., in computer simulations), one needs to choose a cut-off. Typically, we look for and account for all pairs that have a distance smaller than $\frac{L}{2}$ to all other particles.



this particle interacts w/ all particles located in the circle w/ radius $\frac{L}{2}$

Note: in a lattice, we talk about nearest neighbor and next-to-nearest neighbor interactions

Square lattice:



nearest neighbor interaction

next-to-nearest neighbor interaction

A bit of review from undergrad quantum:

Consider a quantum particle of mass m in a two-dimensional periodic box of area L^2.

note: we are not given the "statistical nature" of the quantum particle, i.e., we don't know whether it's a boson or a fermion.

→ does not matter for now. Eventually: Degeneracy factor.

(a) What is the number of single-particle quantum states with energy less than E?

(b) What is the density of the single-particle states as a fct. of E?

(a) Since we are considering a quantum particle, we need to solve the 2D Schrödinger equation:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)\psi(x,y) = \varepsilon\,\psi(x,y)$$

We know: $\psi(x,y) = \varphi(x)\,\varphi(y)$

$$\frac{1}{\sqrt{L}}e^{ik_x x} \qquad\qquad \frac{1}{\sqrt{L}}e^{ik_y y}$$

We need to make sure that our eigenstates fulfill the periodic boundary conditions:

$$\varphi(x+L) = \varphi(x)$$

$$\Rightarrow e^{ik_x(x+L)} = e^{ik_x x} \Rightarrow e^{ik_x L} = 1$$

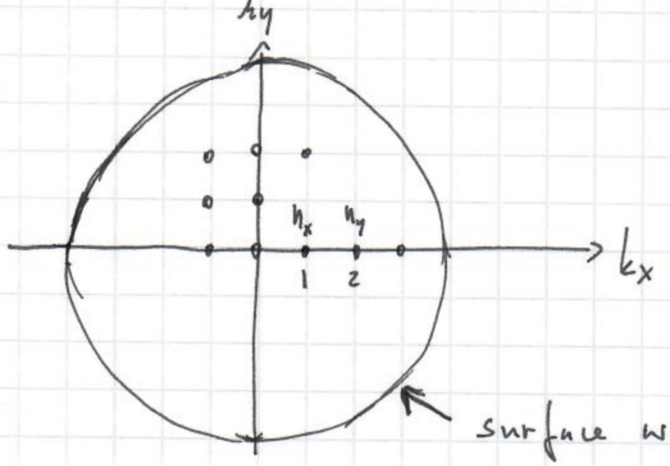
It follows: $k_x = \frac{2\pi}{L} n_x$, where $n_x = 0, \pm 1, \pm 2, \ldots$

Similarly $k_y = \frac{2\pi}{L} n_y$, where $n_y = 0, \pm 1, \pm 2, \ldots$

ε is then given by $\varepsilon = \frac{\hbar^2 k_x^2}{2m} + \frac{\hbar^2 k_y^2}{2m}$

$$= \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2\right) = \frac{(2\pi\hbar)^2}{2mL^2}\left(n_x^2+n_y^2\right)$$

We are looking for the number of states with $\varepsilon \leq E$, where E is fixed.



$$k_x^2 + k_y^2 = k^2$$

$$k = \sqrt{\frac{2mE}{\hbar^2}}$$

surface with $|\vec{k}| = k = \sqrt{\frac{2mE}{\hbar^2}}$

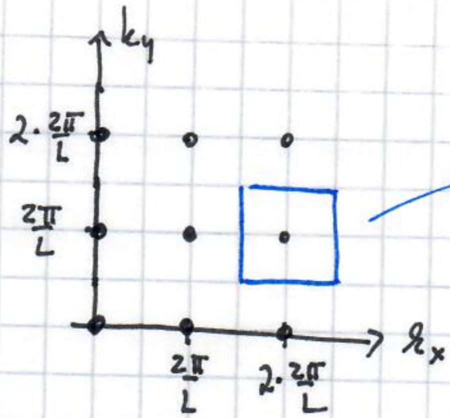
$\Rightarrow$ we need to count all the states that fall inside this circle, which has an area of πk^2.

We have exactly one state per $\frac{1}{\left(\frac{2\pi}{L}\right)^2}$

$$\Rightarrow \text{number of states } N(E) = \frac{\pi k^2}{\left(\frac{2\pi}{L}\right)^2} = \frac{L^2 \pi\, 2mE}{(2\pi\hbar)^2}$$

$$\Rightarrow \boxed{N(E) = \frac{mEL^2}{2\pi\hbar^2}}$$

(b) Density of states: $\boxed{\frac{dN(E)}{dE} = \frac{mL^2}{2\pi\hbar^2}}$



one state in each area $\left(\frac{2\pi}{L}\right)^2$

this is an area in k-space and thus has units of length^{-2}

Let's rewrite the density of states expression:

$$\frac{dN(E)}{dE} = \frac{\frac{1}{2\pi}}{\frac{\hbar^2}{mL^2}}$$

this is for a two-dimensional system

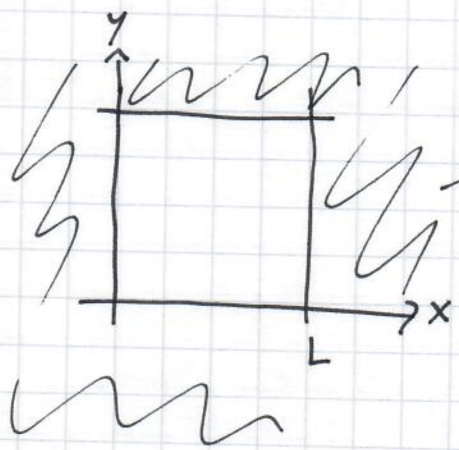
scales as E^0

For a three-dimensional system:

$$\frac{dN(E)}{dE} = \frac{\frac{1}{\sqrt{2}}\,\frac{1}{\pi^2}\left(E \Big/ \frac{\hbar^2}{mL^2}\right)^{1/2}}{\frac{\hbar^2}{mL^2}}$$

this scales as $\sqrt{E}$

Now: Let us consider the 2D system again but let us consider hard wall boundary conditions instead.



infinite potential

$V(x,y) = 0$ for

$0 < x < L$ and $0 < y < L$

Again, we start off by looking at the single-particle SE:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\psi_{\vec{n}}(x,y) = \varepsilon_{\vec{n}}\,\psi_{\vec{n}}(x,y)$$

$$\psi_{\vec{n}}(0,0) = 0 = \psi_{\vec{n}}(L,L) = \psi_{\vec{n}}(x,0) = \psi_{\vec{n}}(0,y) =$$
$$\psi_{\vec{n}}(x,L) = \psi_{\vec{n}}(L,y)$$

$$\psi_{\vec{n}}(x,y) = \frac{2}{L}\sin\left(\frac{n_x \pi x}{L}\right)\sin\left(\frac{n_y \pi y}{L}\right)$$

note: $\underbrace{e^{ikx},\ e^{-ikx}}_{\text{two linearly indep. solutions}} \longrightarrow \underbrace{\sin(kx),\ \cos(kx)}_{\text{two linearly indep. solutions}}$

sin / cos are easier to work with in this case. Since $\cos(0) \neq 0$, the cos solution needs to be discarded.

left with $\sin(k_x x)$ and $\sin(k_y y)$

need $\sin(k_x x) = 0$ for $\underbrace{x = 0}_{\text{naturally fulfilled}}$ and $x = L$

$\Rightarrow \sin(k_x L) = 0$ or $k_x L = n_x \pi$

What values can n_x take?

To start w/ : $n_x = 0, \pm 1, \pm 2, \ldots$

problem: if $n_x = 0$, then

$\sin(k_x x) = 0$

$\Rightarrow$ we don't find the particle anywhere

What about $n_x = \pm 1$?

$n_x = +1$: $\sin\left(\pi \frac{L}{x}\right)$

$n_x = -1$: $\underbrace{\sin\left(-\pi \frac{L}{x}\right) = -\sin\left(\pi \frac{L}{x}\right)}$

the +/- solutions are not linearly independent

$\Rightarrow$ $n_x = -1$ needs to be excluded!

So: $\boxed{\begin{array}{l} n_x = 1, 2, 3, \ldots \\ n_y = 1, 2, 3, \ldots \end{array}}$

$$\underbrace{\varepsilon_{\vec{n}} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} \frac{\pi^2}{L^2} \left(n_x^2 + n_y^2\right)}$$

these differ!

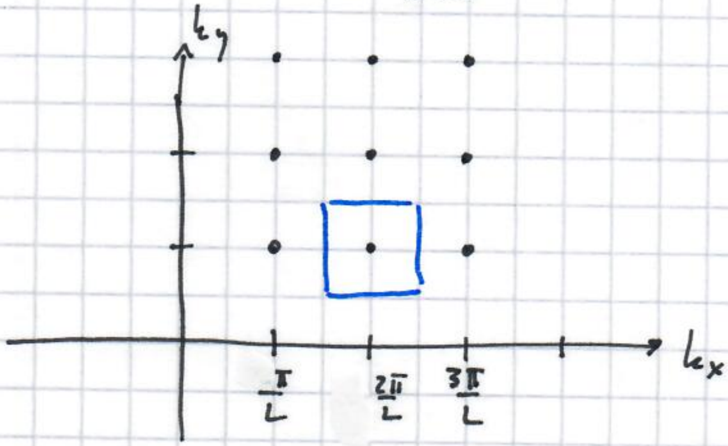
single-particle energy for hard wall boundary conditions

Compare: Periodic BC: $\varepsilon_{\vec{n}} = \frac{\hbar^2}{2m} \frac{\pi^2}{L^2}\, 4 \left(n_x^2 + n_y^2\right)$

$n_x, n_y = 0, \pm 1, \pm 2, \ldots$

How many states do we have w/ energy less than or equal to E?

look at $E = \frac{\hbar^2 k^2}{2m}$ or $k = \sqrt{\frac{2mE}{\hbar^2}}$



these are the allowed states in k-space

→ note: no allowed states at negative k_x or negative k_y

different from periodic BC case → the area in k-space is $\left(\frac{\pi}{L}\right)^2$

If we are looking at states with $\leq E$ or $\leq k$, then we see that area taking up in k-space is $\frac{1}{4}\pi k^2$ (quarter of area of circle)

we are only looking at positive k since this is what is being imposed by the hard wall boundary conditions

$$\Rightarrow N(E) = \frac{\frac{1}{4}\pi k^2}{\left(\frac{\pi}{L}\right)^2}$$

number of states for 2D case - hard wall BCs

$$= \frac{\frac{1}{4}\pi \frac{2m}{\hbar^2} E}{\frac{\pi^2}{L^2}}$$

$$= \frac{\frac{1}{2\pi} E}{\frac{\hbar^2}{mL^2}} = \frac{1}{2\pi} E \frac{1}{\frac{\hbar^2}{mL^2}}$$

same as in case of periodic BCs

Density of states for hard wall case:

$$\frac{dN(E)}{dE} = \frac{1}{2\pi} \frac{1}{\frac{\hbar^2}{mL^2}}$$

same as in case of periodic BCs

8 Quantum Statistical Mechanics

What did we do for the canonical ensemble?

physical situation: energy exchange

Partition function $Q(V,T,N)$: or $Q_N(V,T)$

classical!

$$Q(V,T,N) = \frac{1}{N!\,h^{3N}} \int e^{-\beta \mathcal{H}(\vec{p},\vec{q})}\, d^{3N}\vec{p}\, d^{3N}\vec{q}$$

$$= \mathrm{Tr}\left(\exp(-\beta \mathcal{H}(\vec{p},\vec{q}))\right)$$

view this equation as a definition of the trace (Tr) in classical statistical mechanics when working in the canonical ensemble

trace implies prefactors and that we are integrating over the entire phase space

$$-\beta A = \log\left(Q(V,T,N)\right)$$

We had defined

$$\langle f \rangle = \frac{\int \exp(-\beta \mathcal{H})\, f \; d^{3N}\vec{p}\; d^{3N}\vec{q}}{\int \exp(-\beta \mathcal{H})\; d^{3N}\vec{p}\; d^{3N}\vec{q}}$$

mean value of observable f (or ensemble average)

Let's rewrite this:

$$\langle f \rangle = \frac{\frac{1}{N!\, h^{3N}} \int \exp(-\beta \mathcal{H})\, f \; d^{3N}\vec{p}\; d^{3N}\vec{q}}{Q(V,T,N)}$$

Let's define a density (matrix) $\rho_{can}(\vec{p},\vec{q})$:

$$\rho_{can}(\vec{p},\vec{q}) = \frac{e^{-\beta \mathcal{H}(\vec{p},\vec{q})}}{Q(V,T,N)}$$

$$\Rightarrow \langle f \rangle = \frac{1}{N!\, h^{3N}} \int \rho_{can}(\vec{p},\vec{q})\, f \; d^{3N}\vec{p}\; d^{3N}\vec{q}$$

$$= \mathrm{Tr}\left(\rho_{can}\, f\right)$$

We haven't done anything new!

All we did on pages 153/154 is to rewrite the known classical statistical mechanics expressions for the canonical ensemble in a "fancy" compact notation: Tr

ρ_{can}

Why? "Trace" and "density matrix" are concepts well established in quantum mechanics.

Idea: Use quantum mechanical density matrix $\hat{\rho}_{can}$ and quantum mechanical "Tr operation" and adopt all formalism / equations from classical statistical mechanics.

Let's try to make this more explicit.

What does $Q_N(V,T) = \mathrm{Tr}\left(e^{-\beta \mathcal{H}}\right)$ mean in quantum statistical mechanics?

$\mathcal{H} \longrightarrow \hat{\mathcal{H}}$

this becomes an operator

classically,
$\mathcal{H} = \mathcal{H}(\bar{p}, \bar{q})$

$\Rightarrow \mathrm{Tr}\left(e^{-\beta \hat{\mathcal{H}}}\right) = \ldots ?$

if we have an operator, then we need to act on "s.th."...

Moreover, if we have an operator in the exponent, then we need to do a Taylor expansion of the exponential, then act with each term in the infinite sum onto "s.th.", then hopefully collect or resum infinite set of terms to get compact expression.

Let's do it: $e^{-x} = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} x^n$

$$\Rightarrow e^{-\beta \hat{\mathcal{H}}} = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \underbrace{(\beta \hat{\mathcal{H}})^n}_{\beta^n \underbrace{\hat{\mathcal{H}}^n}_{\underbrace{\hat{\mathcal{H}} \cdot \hat{\mathcal{H}} \cdot \ldots \cdot \hat{\mathcal{H}}}_{n \text{ factors}}}}$$

What next? Let $\{\psi_n\}$ be a <u>complete</u> set of eigenstates of $\hat{\mathcal{H}}$.

Note: In general, we don't know the ψ_n, especially not if we are dealing with an interacting N-particle system!

$$\hat{\mathcal{H}} |\psi_n\rangle = E_n |\psi_n\rangle$$

eigenstate

eigenenergy

Closure relation: $\boxed{\sum_n |\psi_n\rangle\langle\psi_n| = 1}$ the sum goes over a complete set of states!

Importantly: the sum extends over all eigenstates of the complete set!

if we have sc. states, the sum turns into integral

So: $$\exp(-\beta\hat{\mathcal{H}}) = \exp(-\beta\hat{\mathcal{H}}) \underbrace{\sum_m |\psi_m\rangle\langle\psi_m|}_{=\hat{I}}$$

$$= \sum_n \frac{(-1)^n}{n!}\beta^n\hat{\mathcal{H}}^n \sum_m |\psi_m\rangle\langle\psi_m|$$

$$= \sum_m \sum_n \frac{(-1)^n}{n!}\beta^n \underbrace{\hat{\mathcal{H}}^n |\psi_m\rangle}_{\hat{\mathcal{H}}\hat{\mathcal{H}}\cdots\hat{\mathcal{H}}|\psi_m\rangle \to E_m|\psi_m\rangle \;\Rightarrow\; (E_m)^n|\psi_m\rangle}\langle\psi_m|$$

$$= \underbrace{\sum_m \sum_n \frac{(-1)^n}{n!}\beta^n (E_m)^n}_{\exp(-\beta E_m)} |\psi_m\rangle\langle\psi_m|$$

$$= \sum_m \exp(-\beta E_m)|\psi_m\rangle\langle\psi_m|$$

So: $$e^{-\beta\hat{\mathcal{H}}} = \sum_m \exp(-\beta E_m)|\psi_m\rangle\langle\psi_m|$$