Lecture 2: The classical limit

Recap: Fundamental assumption of statistical mechanics (statistical postulate) ⤳ Ensemble Theory

Construction of probability densities of microscopic states under macroscopic constraints

Central object to compute in equilibrium statistical mechanics

Partition function ⟷ Thermodynamic potential.

For example, canonical partition function (N,V,T) fixed.

$$Z(N,V,T) = \mathrm{Tr}\left[e^{-\beta\hat{H}}\right] = \sum_\nu \langle\nu|e^{-\beta\hat{H}}|\nu\rangle = \sum_\nu e^{-\beta E_\nu} = \sum_n \Omega(E_n)e^{-\beta E_n}$$

Trace over a complete set of states.

n levels

with $\hat{H}|\nu\rangle = E_\nu|\nu\rangle$

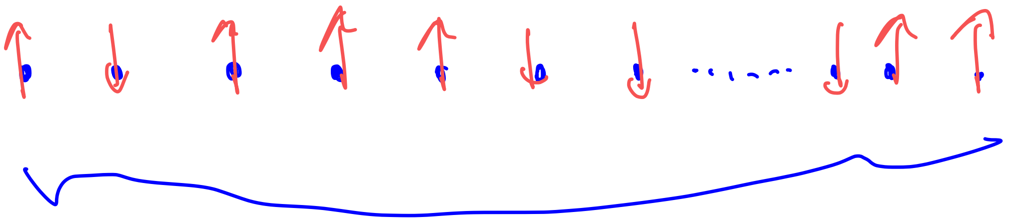
$\{|\nu\rangle\}$ energy eigenstates.

Thermodynamic potential: $\beta F(N,V,T) = -\log Z$.

In some cases $Z(N,V,T)$ can be computed analytically.

For example, 1D Ising model (Wilhelm Lenz, 1920)

Model for (anti) ferromagnet



$s_i = \pm 1$

$J > 0$ (ferromagnet)

Microstate $\{s_i\}$ ⟶ $E_\nu(\{s_i\}) = -J\sum_{\langle i,j\rangle} s_i s_j - \mu H\sum_i s_i$

In 1D exactly solvable (Ising, 1925) ⤳ Transfer matrix method.

2D " " (Onsager, 1944)

Ising model is a lattice model, what about more realistic systems?

$$\hat{H} = \sum_{i=1}^{N} \frac{\hat{p}_i^2}{2m} + \Phi(\hat{\vec r}_1, \dots \hat{\vec r}_N)$$

Quantum systems $\rightsquigarrow$ later

Classical systems (no internal degrees of freedom): degrees of freedom $\{\vec p^N, \vec r^N\}$, so we expect

$$Z(N,V,T) = C \underbrace{\int d\vec p^N \int d\vec r^N}_{(\text{angular momentum})^{3N}} e^{-\beta \underbrace{H(\vec r^N,\vec p^N)}_{\hookrightarrow \text{classical Hamiltonian.}}} \quad (*)$$

$C \rightarrow$ dimensionless (log(...))

Previous courses: $\epsilon_{\vec k} = \frac{\hbar^2 \vec k^2}{2m}$ $\quad \vec k = \left(\frac{2\pi}{L}\right)\vec n$ ← quantum number. $n_i \in \mathbb{Z}$ (periodic boundary conditions)

Compute partition function in two ways: $Z = \mathrm{Tr}\left[e^{-\beta \hat H}\right]$

or with (*) and compare.

But we can give more straightforward method.

For example, classical limit of $\hat H = \underbrace{\frac{\hat{\vec p}^2}{2m}}_{\text{kinetic energy}} + \underbrace{V(\hat{\vec r})}_{\text{external potential}}$ (single particle in an external potential)

$[\hat{\vec r}, \hat{\vec p}] = i\hbar \mathbb{1}$.

Recall completeness relations: $\int d\vec r \, |\vec r\rangle\langle \vec r| = \mathbb{1}$ with $\hat{\vec r}|\vec r\rangle = \vec r|\vec r\rangle$ (‡)

$\int d\vec p \, |\vec p\rangle\langle \vec p| = \mathbb{1}$. with $\hat{\vec p}|\vec p\rangle = \vec p|\vec p\rangle$

Note that this is position and momentum kets are a complete set of states!

Let us compute:

$$Z = \mathrm{Tr}\left[e^{-\beta \hat H}\right] = \sum_\nu \langle \nu \underset{(‡)}{|} e^{-\beta \hat H} \underset{(‡)}{|} \nu\rangle$$

$$= \sum_{\nu} \langle \nu | \int d\vec{r}\, |\vec{r}\rangle\langle\vec{r}| e^{-\beta\hat{H}} \int d\vec{r}\,' |\vec{r}\,'\rangle\langle\vec{r}\,'|\nu\rangle$$

$$\sum_{\nu} |\nu\rangle\langle\nu| = \mathbb{1}$$

$$\langle\vec{r}\,'|\vec{r}\rangle = \delta(\vec{r}-\vec{r}\,')$$

$$= \int d\vec{r} \int d\vec{r}\,' \langle\vec{r}| e^{-\beta\hat{H}} |\vec{r}\,'\rangle \sum_{\nu} \langle\vec{r}\,'|\nu\rangle\langle\nu|\vec{r}\rangle$$

$$= \int d\vec{r} \int d\vec{r}\,' \langle\vec{r}| e^{-\beta\hat{H}} |\vec{r}\,'\rangle\, \delta(\vec{r}-\vec{r}\,')$$

$$= \int d\vec{r}\, \langle\vec{r}| e^{-\beta\hat{H}} |\vec{r}\rangle . \quad (**)$$

Recall the operator identity $e^{\hat{A}} e^{\hat{B}} = e^{\hat{A}+\hat{B}+\frac{1}{2}[\hat{A},\hat{B}]+\dots}$

$$\Rightarrow e^{-\beta\hat{H}} = e^{-\beta\hat{\vec{p}}^{\,2}/2m}\, e^{-\beta V(\hat{\vec{r}})} + \mathcal{O}(\hbar)$$

$$(**) = \int d\vec{r}\, \langle\vec{r}| e^{-\beta\hat{\vec{p}}^{\,2}/2m}\, e^{-\beta V(\hat{\vec{r}})} |\vec{r}\rangle$$

$$= \int d\vec{r}\, e^{-\beta V(\vec{r})} \langle\vec{r}| e^{-\beta\hat{\vec{p}}^{\,2}/2m} |\vec{r}\rangle$$

$$\int d\vec{p}\, |\vec{p}\rangle\langle\vec{p}|$$

$$= \int d\vec{r}\, e^{-\beta V(\vec{r})} \int d\vec{p}\, e^{-\beta\vec{p}^{\,2}/2m} \langle\vec{r}|\vec{p}\rangle\langle\vec{p}|\vec{r}\rangle$$

Together with $\langle\vec{r}|\vec{p}\rangle = \frac{1}{(2\pi\hbar)^{3/2}} e^{i\vec{p}\cdot\vec{r}/\hbar}$

$$\langle\vec{p}|\vec{r}\rangle = \langle\vec{r}|\vec{p}\rangle^{*}$$

$\Rightarrow$

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

with $H(\vec{p},\vec{r})$ the classical Hamiltonian.

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

In many-body case, we need to use:

$$|\vec{r}_1, \dots\dots, \vec{r}_N\rangle = \frac{1}{\sqrt{N!}} \sum_{P \in S_N} \xi^{P} |\vec{r}_{P(1)}\rangle \dots |\vec{r}_{P(N)}\rangle$$

where $\xi^{P} = \begin{cases} 1 & \text{bosons} \\ \mathrm{sgn}(P) & \text{fermions.} \end{cases}$

Then same can be repeated (see lecture notes):

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

and therefore,

$$F(N,V,T) = -k_B T \log \Big[\underbrace{\frac{1}{N!\,h^{3N}} \int d\vec{r}^{\,N} \int d\vec{p}^{\,N}\, e^{-\beta H(\vec{r}^{\,N},\vec{p}^{\,N})}}_{\text{to be computed.}} \Big].$$

Note that in equilibrium we can introduce a (continuous) probability density on the classical phase space:

$$f_c(\vec{p}^{\,N},\vec{r}^{\,N}) = \frac{1}{Z} e^{-\beta H} \quad \Big(\text{by definition of } Z: \int d\vec{r}^{\,N} \int d\vec{p}^{\,N} f(\vec{r}^{\,N},\vec{p}^{\,N}) = 1\Big)$$

Suppose we have a function of phase space variables: $A(\vec{r}^{\,N},\vec{p}^{\,N})$

Then

$$\langle A(\vec{r}^{\,N},\vec{p}^{\,N})\rangle = \int d\vec{r}^{\,N} \int d\vec{p}^{\,N} A(\vec{r}^{\,N},\vec{p}^{\,N})\, f_c(\vec{r}^{\,N},\vec{p}^{\,N})$$

$$= \frac{1}{Z} \int d\vec{r}^{\,N} \int d\vec{p}^{\,N} A(\vec{r}^{\,N},\vec{p}^{\,N})\, e^{-\beta H(\vec{r}^{\,N},\vec{p}^{\,N})}$$

Ensemble average.

Suppose $(\vec{r}^{\,N}(t),\vec{p}^{\,N}(t))$ is a solution from Hamilton's equations:

$$\overline{A(\vec{r}^{\,N}(t),\vec{p}^{\,N}(t))} = \lim_{\tau\to\infty} \int_0^{\tau} dt\, A(\vec{p}^{\,N}(t),\vec{r}^{\,N}(t)) \quad \text{Time average.}$$

(e.g. obtained from molecular dynamics).

System is ergodic $\Leftrightarrow$ $\langle A(\vec{r}^{\,N},\vec{p}^{\,N})\rangle = \overline{A(\vec{r}^{\,N}(t),\vec{p}^{\,N}(t))}$.

Non-ergodic: glasses, ...

It is straightforward to write probability densities for other ensembles in classical limit.

For example, grand canonical ensemble:

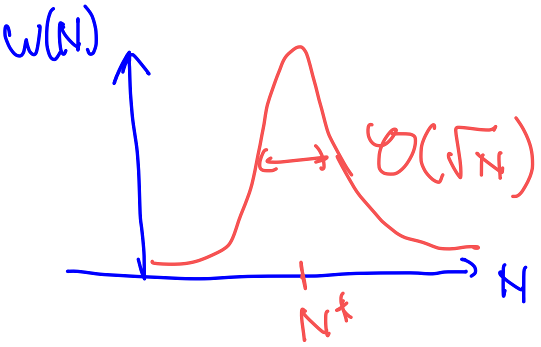
$$\Xi(\mu,V,T) = \sum_{N=0}^{\infty} e^{\beta\mu N} Z(N,V,T)$$ (grand-canonical partition function)

$$\Omega(\mu,V,T) = -k_B T \log \Xi$$ (grand potential)

Note that $\sum_{N=0}^{\infty} \int d\vec{r}^N \int d\vec{p}^N f_g(\vec{r}^N,\vec{p}^N;N) = 1$

Marginal probability density: $W(N) = \int d\vec{r}^N \int d\vec{p}^N f_g(\vec{r}^N,\vec{p}^N;N)$

$$= \frac{e^{\beta\mu N}}{Z(N,V,T)}.$$



General classical Hamiltonians for particles without internal degrees of freedom

$$H(\vec{r}^N,\vec{p}^N) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + \Phi(\vec{r}^N).$$

N-body interaction potential

$$\vec{F}_i = -\frac{\partial \Phi}{\partial \vec{r}_i}.$$

Simplest case: $\Phi = 0$ (ideal gas).

In this case: $$Z(N,V,T) = \frac{1}{N!\,h^{3N}} \underbrace{\prod_{i=1}^{N} \int d\vec{p}_i\, e^{-\beta \vec{p}_i^{\,2}/2m}}_{\text{Gaussian integral}} \cdot \int d\vec{r}^N$$

$$= \frac{V^N}{N!\,\Lambda^{3N}}$$

Here, $\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$ Thermal de Broglie wavelength.

From partition function thermodynamic properties can be inferred:

$$\beta f_{id}(\rho,T) := \frac{\beta F_{id}(N,V,T)}{V} = \rho\left[\log(\rho\Lambda^3)-1\right]$$

where $\rho = \frac{N}{V}$ = constant.

From standard thermodynamic relations, we find: (Check!)

$$\beta E = 3/2 \; ; \; \beta p = \rho \; ; \; \beta\mu = \log(\rho\Lambda^3)$$

$$S/k_B = \frac{5}{2}N - N\ln\rho\Lambda^3$$ (Sackur-Tetrode equation)

Note that above expressions are valid for $\rho\Lambda^3 \ll 1$.

Namely, for $\rho\Lambda^3 > \exp(5/2)$ $S<0$

$\Rightarrow$ Quantum mechanical effects become important!

So a rough measure when quantum effects become important

$\rho\Lambda^3 \approx 1$

Then $\Lambda \sim \frac{h}{\sqrt{\langle\vec{p}^{\,2}\rangle}}$

Note that classical effects dominate when $m\uparrow$ $T\uparrow$ $\rho^{-1/3}\uparrow$

What systems behave classically?

microscopic ¦ mesoscopic ¦ macroscopic.

$\mathcal{O}(1\,\text{nm})$ $\mathcal{O}(10\,\text{nm})$

- Macroscopic objects
- Simple fluids (one-component, atomic, molecular, ...)
- Complex liquids (milk, blood, polymer melt, liquid crystals, proteins ....)

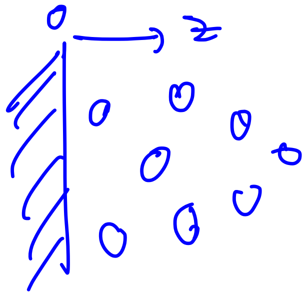
Interacting classical fluids. ($\Phi \neq 0$)

Generally, we can write.

$$\Phi(\vec{r}^N) = \underbrace{\sum_{i=1}^{N} V_{ext}(\vec{r}_i)}_{\substack{\text{one-body} \\ \text{(external potential)}}} + \underbrace{\sum_{i=1}^{N} \sum_{j>i} v(|\vec{r}_i - \vec{r}_j|)}_{\substack{\text{two-body interactions} \\ \text{(isotropic, translational invariance)}}} + \ldots\ldots$$

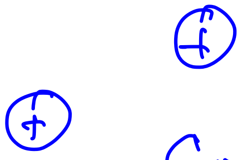
three-body
four-body etc.

Examples



hard wall.

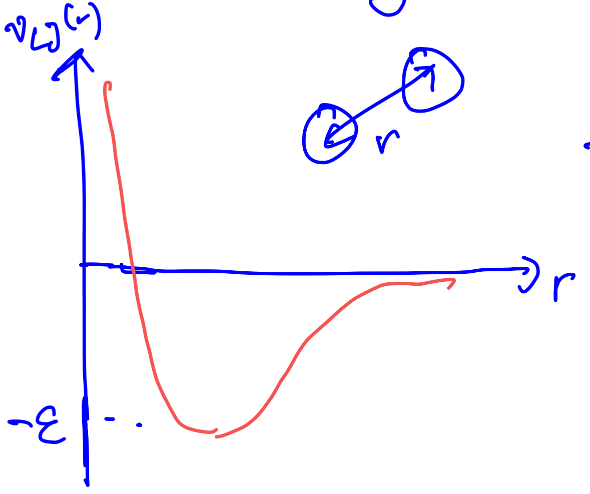
$$V_{ext}(z) = \begin{cases} \infty & z<0 \\ 0 & z>0 \end{cases}$$



Coulomb

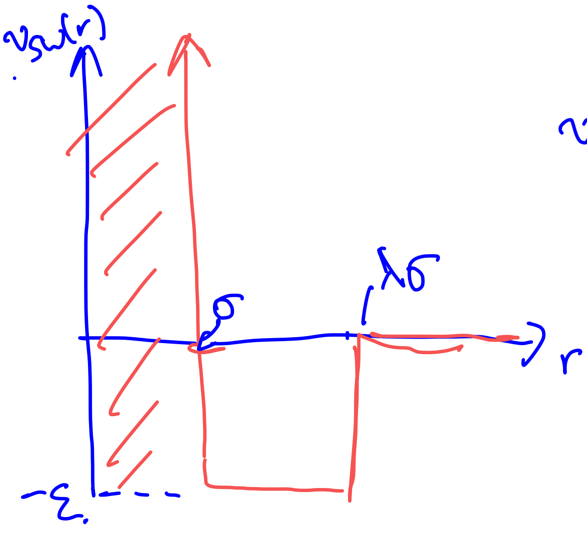
$$v(r) = \frac{e^2}{4\pi\epsilon_0 r}$$

For classical systems, we often use various model potentials:



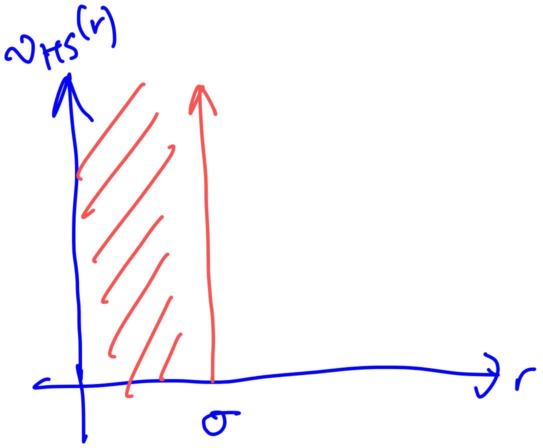
Lennard-Jones potential (empirical)

$$v_{LJ}(r) = 4\epsilon\left[\underbrace{\left(\frac{\sigma}{r}\right)^{12}}_{\substack{\text{Pauli exclusion} \\ \text{+ Born repulsion.}}} - \underbrace{\left(\frac{\sigma}{r}\right)^{6}}_{\substack{\text{Van der Waals} \\ \text{interaction.}}}\right]$$



$$v_{SW}(r) = \begin{cases} \infty & r<\sigma \\ -\varepsilon & \sigma<r<\lambda\sigma \quad (\lambda>1) \\ 0 & r>\lambda\sigma. \end{cases}$$

Square-well potential. When $\varepsilon>0$ also called sticky hard spheres.



$$v_{HS}(r) = \begin{cases} \infty & r<\sigma \\ 0 & r>\sigma. \end{cases}$$

Hard-sphere potential.

Non-isotropic potentials:

$$v_{GB}(\vec r, \vec u_1, \vec u_2) = \epsilon(\hat u_1,\hat u_2,\hat r)\left[\left(\frac{\sigma_0}{r-\sigma(\hat u_1,\hat u_2,\hat r)+\sigma_0}\right)^{12} - \left(\frac{\sigma_0}{r-\sigma(\hat u_1,\hat u_2,\hat r)+\sigma_0}\right)^{6}\right].$$

Gay-berne potential.

Dipole-dipole interaction:

$$v(r,\vec\mu_1,\vec\mu_2) = \underbrace{\frac{1}{4\pi\epsilon_0 r^3}}_{\text{distance}} \underbrace{\left[\vec\mu_1\cdot\vec\mu_2 - 3(\vec\mu_1\cdot\hat r)(\vec\mu_2\cdot\hat r)\right]}_{\text{orientiational part.}}$$

In general, all these model potential are so-called effective interaction potentials! (Integrated out degrees of freedom).

Note that for $H(\vec r^N, \vec p^N) = \sum_{i=1}^{N} \frac{\vec p_i^{\,2}}{2m} + \Phi(\vec r^N)$

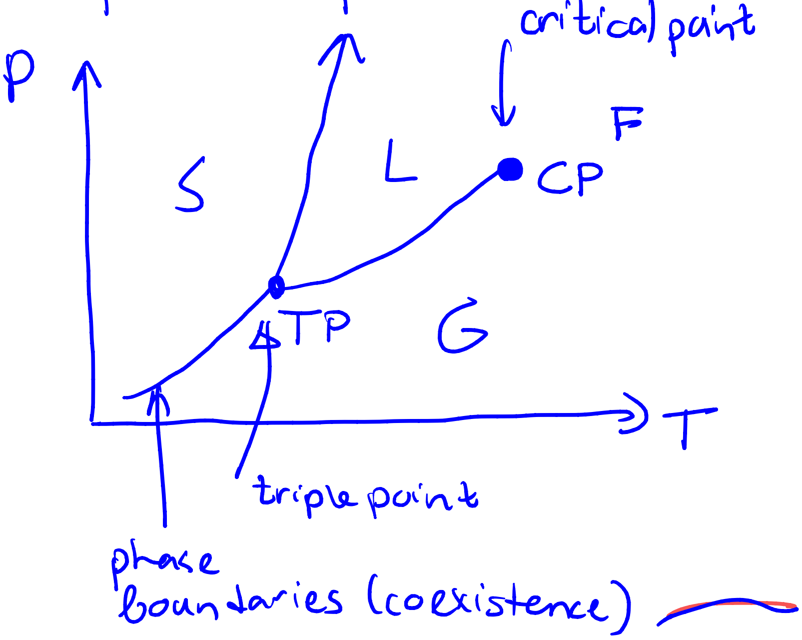
that $Z(N,V,T) = \dfrac{Q(N,V,T)}{\Lambda^{3N} N!}$ where $\underbrace{Q(N,V,T) = \int d\vec r^N e^{-\beta\Phi(\vec r^N)}}_{\text{configurational integral.}}$

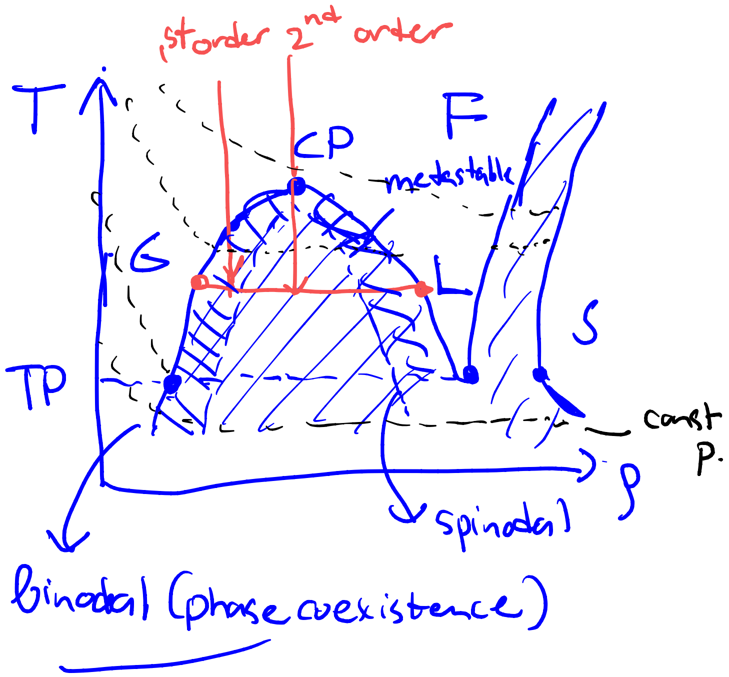
Note that for ideal gas $Q(N,V,T) = V^N$.

Interactions can lead to non-trivial phase behaviour

* Phase diagrams: Conditions under which phases coexist.

Simplest example:

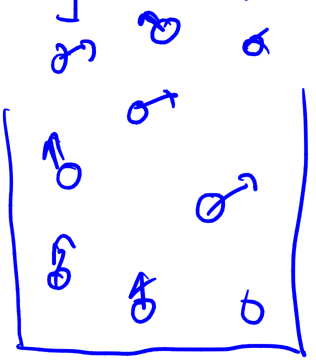




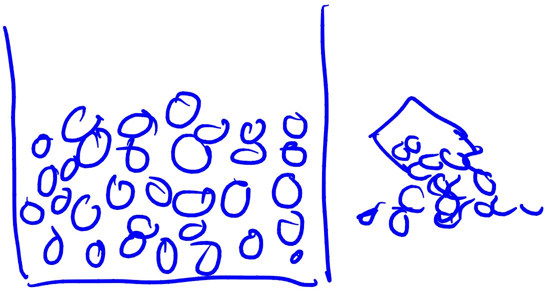
in coexisting phases, all intensive thermodynamic variables are constant!

S: solid G: gas

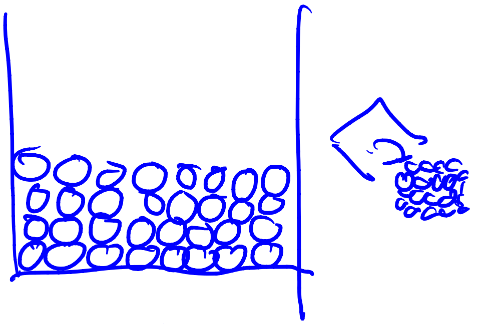
L: liquid F: fluid.



gas



liquid



solid.

- ☐ volume not fixed
- ☐ low density
- ☐ non-fixed shape
- ☐ high compressibility
- ☐ translational inv.
- ☐ potential energy

$$\langle K \rangle > \langle \Phi \rangle$$

kinetic energy

- ☐ fixed volume
- ☐ high density
- ☐ non-fixed shape
- ☐ low compressibility
- ☐ translational inv.
- ☐ $\langle K \rangle \sim \langle \Phi \rangle$

- ☐ fixed volume
- ☐ high density
- ☐ fixed shape
- ☐ low compressibility
- ☐ Translational symmetry broken (crystal) or invariant (amorphous)

$$\langle \Phi \rangle > \langle K \rangle$$

Phase diagrams can be very complicated (e.g. water ...)