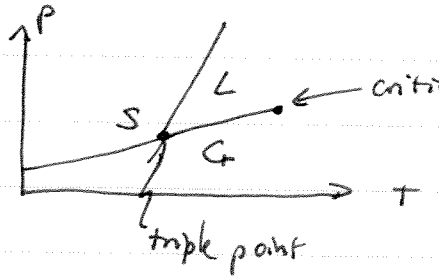
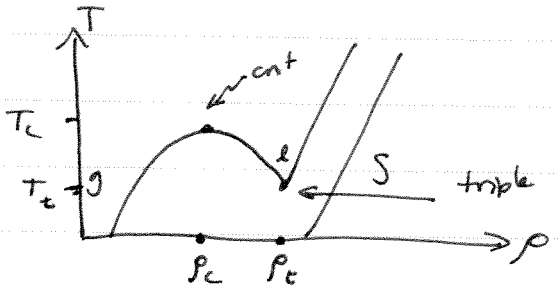
What is a liquid?

Dense Fluid



P = pressure
T = temperature



$\rho = \left\langle \frac{N}{V} \right\rangle$
= bulk density of particles

Rough Scaling of Special points:

$T_t \approx \frac{T_c}{2}$ $\qquad$ $\rho_t \approx 3\rho_c$

Also, change in density upon freezing $\approx 10\%$

$$\frac{\rho_s - \rho_l}{\rho_s} \approx 0.1$$

A <u>Dense</u> fluid is one which has $\rho \geq 2\rho_c$

In this region, the isothermal compressibility:

$$\chi = \left(\frac{\partial \rho}{\partial(\beta p)}\right)_T \qquad \left(\beta = \frac{1}{k_B T}\right)$$

is <u>small</u>:

$$\chi \leq \frac{1}{50}$$

what does a χ of 10^{-2} mean?

$\chi_{ideal\ gas} = 1$

$\chi_{critical\ point} = \infty$

29-2

Suppose the molecular diameter is σ

Roughly speaking, σ will be the distance between Nearest neighbors in a solid: $\rho\sigma^3 = 1$ (σ^3 is the volume of a molecule in the solid)

In a dense fluid $0.6 \leq \rho\sigma^3 \leq 0.9$

Because χ is low, we can estimate how much pressure is required to change ρ by 10%

$$\chi = \left(\frac{\partial \rho}{\partial \beta P}\right) = \frac{\partial \rho}{\partial P}\frac{\partial P}{\partial \beta P} = \frac{\Delta\rho}{\Delta P}\frac{1}{\beta}$$

$$\Delta P\, \beta\chi = \Delta\rho$$

$$\Delta P = \Delta\rho\left(\frac{1}{\beta\chi}\right) = \frac{\Delta\rho\, k_B T}{\chi}$$

$$\Delta P = \chi^{-1}\left(\frac{k_B T}{\sigma^3}\right)\Delta\rho\sigma^3$$

$$\frac{k_B T}{\sigma^3} = 1.3\times10^{2}\left(\frac{T(K)}{\sigma(\text{Å})^3}\right)\ \text{atm}$$

For argon $T \approx 100K$ $\sigma = 3.4$ Å:

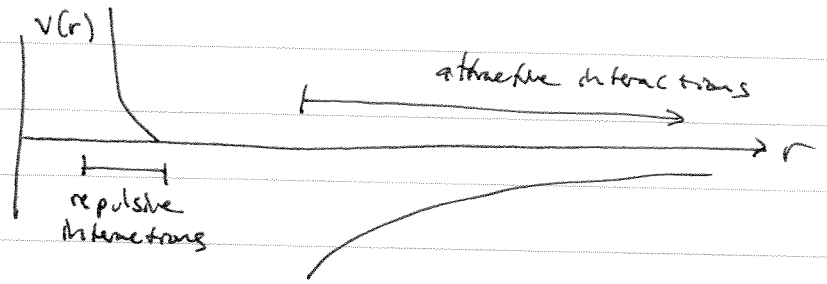
$$\Delta P = 50\left(\frac{100}{40}\right)\cdot 10^2 \times \Delta\rho\sigma^3\ \text{atm}$$

So 10^3 atm are needed to produce density changes of around 10% in a liquid.

1 atm is a very low pressure! And typically 1 atm $\approx P_t$ so we are often viewing liquids near their triple points.

Microscopic models

Since liquids hold themselves together the forces are generally attractive, but since they aren't very compressible, the short range interactions must be repulsive.

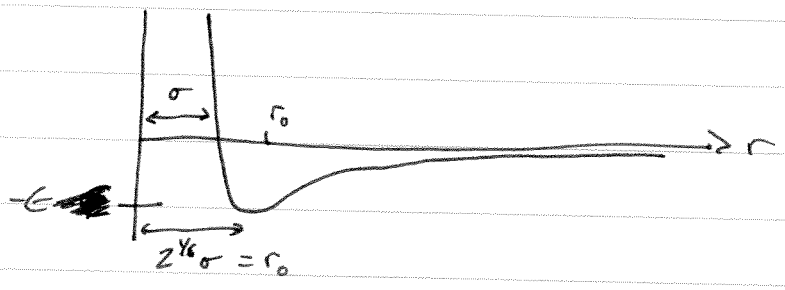


A Lennard-Jones fluid is a classical fluid with

$$U(r^N) = \sum_{i>j=1}^{N} u(r_{ij}) \qquad r_{ij} = |\vec{r}_i - \vec{r}_j|$$

with

$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]$$



This system is characterized by only 3 parameters

ϵ , σ , m

energy length mass of 1 particle

We usually use reduced units to talk about this system

$$T^* = \frac{k_B T}{\epsilon} \qquad \text{and} \qquad \rho^* = \rho \sigma^3$$

The 2 special points have been measured for the LJ system:

$$T_c^* = 1.3 \qquad T_t^* = 0.7$$
$$\rho_c^* = 0.3 \qquad \rho_t^* = 0.9$$

(m plays no role in the phase diagram)

Since the LJ fluid is a classical model, it evolves in time according to Newton's laws: $f = ma$

$$m\ddot{\vec{r}}_i = \vec{F}_i = \text{force acting on particle } i$$

$$= -\frac{\partial}{\partial \vec{r}_i} U(r^N) = -\sum_{j \neq i} \frac{\vec{r}_{ij}}{|r_{ij}|} \frac{\partial u(r_{ij})}{\partial r_{ij}}$$

m governs only the fundamental unit of time:

$$t^* = \left(\frac{\epsilon}{m\sigma^2}\right)^{1/2} t$$

Averages in phase space:

$$(\vec{r}_1, \vec{r}_2 \ldots \vec{r}_N, \vec{p}_1, \vec{p}_2 \cdots \vec{p}_N) = (r^N, p^N)$$

= point in phase space for N-particle system

$$Q = \sum_\nu e^{-\beta E_\nu}$$

$$E_\nu = \mathcal{H}(r^N, p^N) = K(p^N) + U(r^N)$$

$$Q = (\ ) \int dr^N \int dp^N \, e^{-\beta \mathcal{H}(r^N p^N)}$$

$$\sum \int d\vec{r}_1 \int d\vec{r}_2 \cdots \int d\vec{r}_N \int d\vec{p}_1 \int d\vec{p}_2 \cdots \int d\vec{p}_N$$

must make Q dimensionless

$$Q = \frac{1}{N! h^{3N}} \int dr^N \int dp^N \, e^{-\beta K(p^N)} \, e^{-\beta U(r^N)}$$

Read Chapters 7 - 8 in DC's book

Classical Fluids

Averages in Phase Space

$$(\vec{r}_1, \vec{r}_2 \cdots \vec{r}_N ; \vec{p}_1, \vec{p}_2 \cdots \vec{p}_N) = (r^N, p^N)$$

= point in 6N dimensional phase space for an N particle system

$$Q = \sum_{\text{states}} e^{-\beta E_{\text{state}}} \qquad (\beta = \frac{1}{k_B T})$$

$$E_{\text{state}} = \mathcal{H}(r^N, p^N) = K(p^N) + U(r^N)$$

$$Q = (\quad) \underbrace{\int d\vec{r}_1 \int d\vec{r}_2 \cdots \int d\vec{r}_N} \underbrace{\int d\vec{p}_1 \int d\vec{p}_2 \cdots \int d\vec{p}_N} \; e^{-\beta \mathcal{H}(r^N, p^N)}$$

$$\frac{1}{N!\, h^{3N}} \int dr^N \qquad \int dp^N \; e^{-\beta \mathcal{H}(r^N, p^N)}$$

Σ identical indistinguishable particles

to make Q dimensionless

$$Q = \frac{1}{N!\, h^{3N}} \int dr^N \int dp^N \; e^{-\beta \mathcal{H}(r^N, p^N)}$$

30-1.5

Reduced distribution functions

$$P(r^N) = \frac{e^{-\beta U(r^N)}}{\int dr^N e^{-\beta U(r^N)}} = \text{probability of observing system at point } r^N$$

But we often want less detailed information

$$P^{(2/N)}(\vec{r}_1, \vec{r}_2) = \int d\vec{r}_3 \cdots \int d\vec{r}_N \; P(r^N)$$

= joint probability distro for finding particle 1 at $\vec{r}_1$ and particle 2 @ $\vec{r}_2$

30-1.5

Configurational Information

Now, suppose we are interested only in a property of particle coords:

$$\langle A(r^N) \rangle = \frac{\int dr^N \int dp^N \, A(r^N) e^{-\beta \mathcal{H}(r^N, p^N)}}{\int dr^N \int dp^N \, e^{-\beta \mathcal{H}(r^N, p^N)}}$$

Now, since the momentum integrals are identical:

$$= \frac{\int dr^N \, A(r^N) e^{-\beta U(r^N)} \int dp^N e^{-\beta K(p^N)}}{\int dr^N e^{-\beta U(r^N)} \int dp^N e^{-\beta K(p^N)}}$$

we can cancel them:

$$\langle A(r^N) \rangle = \frac{\int dr^N A(r^N) e^{-\beta U(r^N)}}{\int dr^N e^{-\beta U(r^N)}}$$

sometimes called configurational PF

$$=$$

$$Z_N = \int dr^N \, e^{-\beta U(r^N)}$$

$$\langle A(r^N) \rangle = \int dr^N P(r^N) A(r^N)$$

$$P(r^N) = \frac{e^{-\beta U(r^N)}}{\int dr_1^N e^{-\beta U(r^N)}} = \frac{1}{Z_N} e^{-\beta U(r^N)}$$

= probability of observing system at point r_N

$\rho^{(2/N)}$ is a specific reduced dist function (requires specific particles)

$\rho^{(2/N)}(\vec{r}_1, \vec{r}_2)$ = joint distn function for finding a particle at $\vec{r}_1$ and another at $\vec{r}_2$

$$\rho^{(2/N)}(\vec{r}_1, \vec{r}_2) = N(N-1)\, P^{(2/N)}(\vec{r}_1, \vec{r}_2)$$

In general,

$$\rho^{(n/N)}(\vec{r}_1, \vec{r}_2 \cdots \vec{r}_n) = \frac{N!}{(N-n)!} \frac{\int dr^{N-n}\, e^{-\beta U(r^N)}}{\int dr^N\, e^{-\beta U(r^N)}}$$

$$\rho^{(1/N)}(\vec{r}_1) = \frac{N}{V} = \rho = \text{an isotropic fluid}$$

In an ideal gas, particles are uncorrelated, $U = 0$, so

$$\rho^{(2/N)}(\vec{r}_1, \vec{r}_2) = \frac{N(N-1)}{V^2} = \rho^2(1 - N^{-1}) \approx \rho^2 \quad (\text{large } N)$$

In a non-ideal gas, we can define 2 functions that quantify deviation from ideal behavior:

$$g(\vec{r}_1, \vec{r}_2) = \frac{\rho^{(2/N)}(\vec{r}_1, \vec{r}_2)}{\rho^2}$$

$$h(\vec{r}_1, \vec{r}_2) = \left[\rho^{(2/N)}(\vec{r}_1, \vec{r}_2) - \rho^2\right] / \rho^2$$

$$= g(\vec{r}_1, \vec{r}_2) - 1$$

For isotropic fluids, these functions depend only on the difference $r = (\vec{r}_2 - \vec{r}_1)$

that is:

$$g(\vec{r}_1, \vec{r}_2) = g(r)$$
$$h(\vec{r}_1, \vec{r}_2) = h(r) = g(r) - 1$$

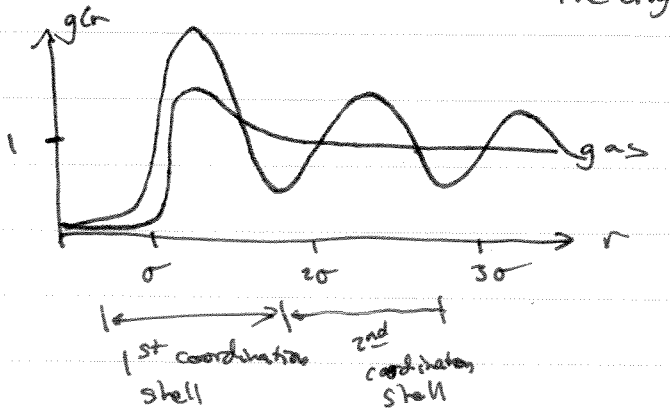
$g(r)$ is called the radial distribution function
or pair correlation function
or pair distribution function

$\rho^{(1/N)}(\vec{r}_1) = \rho$ for a uniform, isotropic system

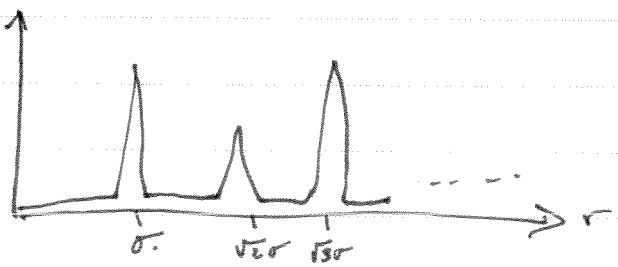
$\rho^{(2/N)}(0, \vec{r}) = \rho\, g(r)$

= conditional probability density that a particle will be found at $\vec{r}$ given that one particle is at the origin.

= average density of particles at $\vec{r}$ given that a tagged particle is at the origin.



most probable location for 1st coordination shell



30-4

$$n(r) = 4\pi\rho \int_0^r x^2 g(x)\,dx$$ = # of neighbors within a radius r

$n\left(\frac{3\sigma}{2}\right) \approx 12$ in an atomic liquid

$n(1.3\sigma) = 12$ in an atomic crystalline solid

these are in 3D. what would be the equivalent in 2d?

Reversible Work Theorem

$g(r)$ = radial distribution function, determines reversible work ($w(r)$) associated with moving infinitely separated particles to separation r.

$$g(r) = e^{-\beta w(r)}$$

$w(r) = \Delta A$ ← change in Helmholtz free energy for this process

We also know:

$$g(r) = \frac{\rho^{(2/N)}(r)}{\rho^2} = \frac{N\cdot(N-1)\int d\vec{r}_3 \cdots \int d\vec{r}_N\, e^{-\beta U(r^N)}}{\int d\vec{r}_1 \cdots \int d\vec{r}_2\, e^{-\beta U(r^N)}}$$

$U(r^N)$ = complex function of all atomic positions

Here's a proof: The mean force between particles 1 & 2:

$$-\left\langle \frac{dU(r^N)}{dr_{12}} \right\rangle_{\vec{r}_1,\vec{r}_2} = \frac{-\int \frac{\partial U}{\partial r_{12}} e^{-\beta U(r^N)}\, d\vec{r}_3 \cdots d\vec{r}_N}{\int e^{-\beta U(r^N)}\, d\vec{r}_3 \cdots d\vec{r}_N}$$

averaged over all other particle positions

$\vec{r}_1, \vec{r}_2$ fixed in space

$\vec{r}_1$ & $\vec{r}_2$ are fixed in space

$$-\left\langle \frac{dU(r^N)}{dr_{12}} \right\rangle_{r_1,r_2} = +\frac{1}{\beta}\frac{\frac{\partial}{\partial r_{12}}\int e^{-\beta U(r^N)}\, d\vec{r}_3 \cdots d\vec{r}_N}{\int e^{-\beta U(r^N)}\, d\vec{r}_3 \cdots d\vec{r}_N}$$

Which can be recombined:

$$-\left\langle \frac{dU}{dr_{12}} \right\rangle_{r_1,r_2} = \frac{1}{\beta}\frac{d}{dr_{12}} \ln \int e^{-\beta U(r^N)}\, d\vec{r}_3 \cdots d\vec{r}_N$$

A sneaky trick:

The total # of particles N is a constant, as is the total partition function (Z) with respect to any one coordinate. That is Z is typically reduced to a single number or simple function that does not contain any particle positions

$$\frac{d}{dr_{12}} \ln \frac{N\cdot(N-1)}{Z} = 0$$ ← these are all independent of r_{12}

So we can add this at will to the previous expression

$$\therefore \quad -\left\langle \frac{dU(r^N)}{dr_{12}} \right\rangle_{r_1 r_2} = \frac{1}{\beta}\frac{d}{dr_{12}} \ln \frac{N\cdot(N-1)}{Z} + \frac{1}{\beta}\frac{d}{dr_{12}} \ln \int e^{-\beta U(r^N)} dr_3 \cdots dr_N$$

$$= k_B T \frac{d}{dr_{12}} \ln \frac{N\cdot(N-1)\int e^{-\beta U(r^N)} d\vec{r}_3 \cdots d\vec{r}_N}{\int d\vec{r}_1 \cdots d\vec{r}_N \, e^{-\beta U(r^N)}}$$

$$= k_B T \frac{d}{dr_{12}} \ln g(r_{12})$$

Integrating an average force gives a reversible work or potential of mean force.

$$w(r_{12}) = \int_{r_{12}}^{\infty} dr'_{12} \left\langle -\frac{dU}{dr_{12}} \right\rangle = k_B T \int_{r_{12}}^{\infty} dr'_{12} \frac{d}{dr_{12}} \ln g(r_{12})$$

$$w(r_{12}) = k_B T \ln g(\infty) - k_B T \ln (g(r_{12}))$$

$$w(r_{12}) = -k_B T \ln g(r_{12})$$

Also:

$$w(r) = k_B T \ln \frac{Z(r_{12}=\infty)}{Z(r_{12}=r)} = -\left(A(r_{12}=\infty) - A(r_{12}=r)\right)$$