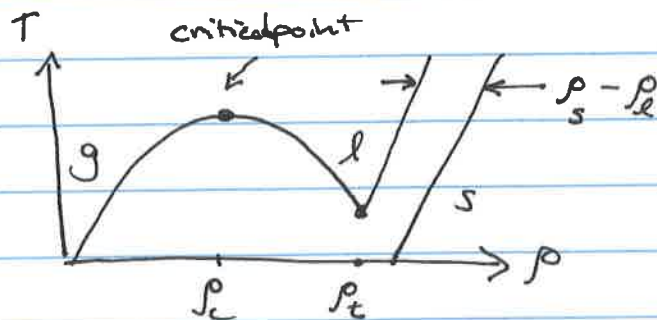
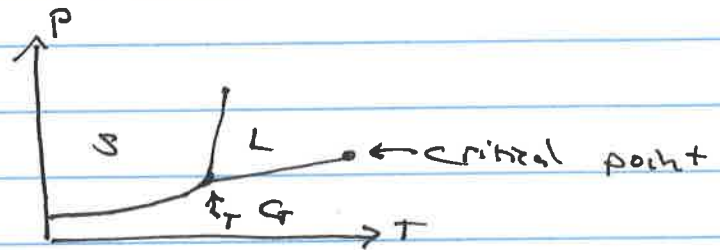


What is a liquid?

①

Dense fluid



$$\rho = \left\langle \frac{N}{V} \right\rangle$$

= bulk particle density

Rough scaling of special points:

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

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

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

A dense fluid is one which has $\rho \geq 2\rho_c$

In this region, the isothermal compressibility

$$\chi = \left(\frac{\partial \rho}{\partial (P\rho)} \right)_T \quad (P = \frac{1}{k_B T})$$

is small $\chi \approx \frac{1}{50}$

Remember:

$$\chi_{\text{ideal gas}} = 1$$

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

Suppose the molecular diameter $\approx \sigma$
 (Roughly speaking σ will be the distance between nearest neighbors in a solid)
 $\rho \sigma^3 \approx 1$ $\leftarrow \sigma^3$ a volume of a molecule in a solid

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

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

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

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

$$= \underbrace{\frac{1}{\chi}}_{\text{unitless}} \underbrace{\left(\frac{k_B T}{\sigma^3} \right)}_{\parallel} \underbrace{\Delta \rho \sigma^3}_{\substack{\text{dimensionless} \\ 1.3 \times 10^2 (T(K)/\sigma^3(\text{\AA}^3)) \text{ atm}}}$$

For Argon, $T \approx 100\text{K}$, $\sigma \approx 3.41 \text{\AA}$

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

So it requires around 1000 atm to produce density changes of $\sim 10\%$ in a liquid!

Another way of looking at this: 1 atm is a very low pressure. Typically $1 \text{ atm} \approx P_{\text{triple}}$ so on earth we are often observing liquids near their triple points!

(3)

Consider the bulk density fluctuations in a liquid:

$$\langle (\delta N)^2 \rangle = \langle (N - \langle N \rangle)^2 \rangle = \left(\frac{\partial \langle N \rangle}{\partial (\beta \mu)} \right)_T$$

μ is the chemical potential.

One of the Maxwell relations in thermodynamics gives us:

$$\left\langle \left(\frac{\partial \rho}{\partial (\beta \mu)} \right)_T \right\rangle = \rho \left(\frac{\partial \rho}{\partial (\beta \mu)} \right)_T$$

$$\begin{aligned} \text{So: } \frac{\langle (\delta \rho)^2 \rangle}{\rho^2} &= \frac{\langle (\rho - \langle \rho \rangle)^2 \rangle}{\langle \rho \rangle^2} \\ &= \frac{\langle \left(\frac{N}{V} - \langle \frac{N}{V} \rangle \right)^2 \rangle}{\left\langle \frac{N}{V} \right\rangle^2} \\ &= \frac{\langle (N - \langle N \rangle)^2 \rangle}{\langle N \rangle^2} \end{aligned}$$

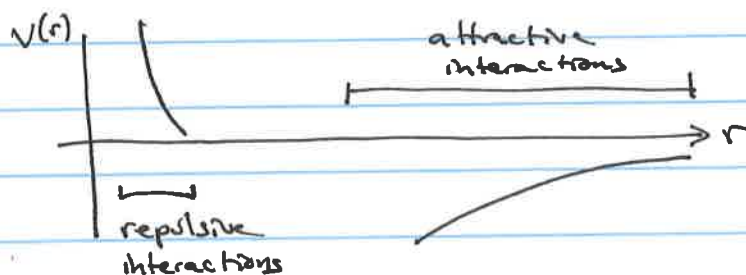
$$\therefore \frac{\langle (\delta \rho)^2 \rangle}{\rho^2} = \frac{1}{\langle N \rangle} \chi$$

So low $\chi \Rightarrow$ small density fluctuations

At a macroscopic level, therefore, liquids aren't very interesting.

Microscopic Models

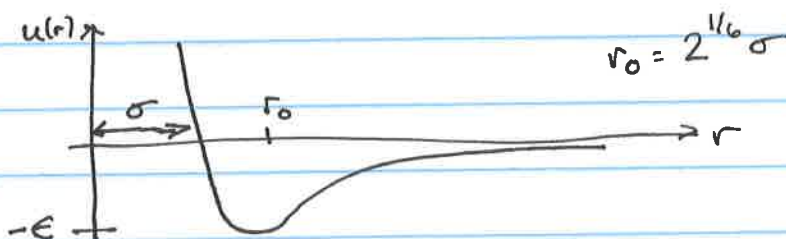
We can reason that since liquids hold themselves together, the forces are attractive, but since they aren't very compressible, the short range interactions must be repulsive:



A Lennard-Jones fluid is a classical fluid with:

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

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



This system is characterized by 3 parameters:

ϵ , σ , m
energy, length, mass of 1 particle

We usually use reduced units to talk about this system

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

(5)

The 2 special points in the phase diagram have been measured for the LJ fluid:

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

(m plays no role in the phase diagram!)

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

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

$$= -\frac{\partial}{\partial \vec{r}_i} U(r^N) = -\sum_{j \neq i} \frac{\vec{r}_{ij}}{|\vec{r}_{ij}|^3} \frac{\partial u(r_{ij})}{\partial r_{ij}}$$

From here on, read Chapters 7 & 8 in Chandlers' book

Classical Fluids

6

Averages in Phase Space

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

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

$$Q = \sum_{\text{states}} e^{-\beta E_{\text{state}}} \quad \text{with } \beta = \frac{1}{k_B T}$$

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

← kinetic ← potential

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

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

identical indistinguishable particles → to make Q dimensionless

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

Configurational information

Suppose we are interested only in a property of particle coordinates:

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

(7)

Now, since the momentum integrals are identical:

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

We can cancel them

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

$$Z_N = \int dr^N e^{-\beta U(r^N)} = \text{sometimes called the configurational partition function}$$

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

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

= probability of observing the system at point r^N

But we often want less detailed information.

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

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

(8)

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

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

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

In general,

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

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

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

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

In a non-ideal gas, we can define 2 functions that measure 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 an isotropic fluid, these 2 functions depend only on the difference

$$r = |\vec{r}_2 - \vec{r}_1|$$

That is,

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

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

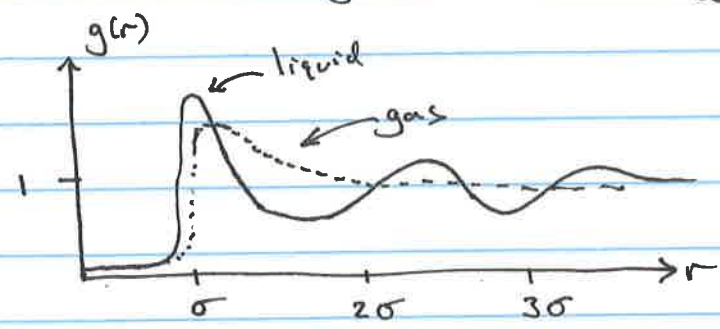
$g(r)$ is called the radial distribution function
or the pair correlation function
or the pair distribution function

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

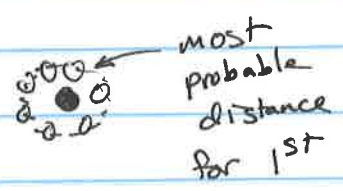
$$\frac{\rho^{(2/N)}(\vec{r}_1, \vec{r}_2)}{\rho} = \rho g(r)$$

= conditional probability density that a particle will be found at \vec{r}_2 given that one particle is at \vec{r}_1

= average density of particles at \vec{r}_2 given that a tagged particle is at \vec{r}_1

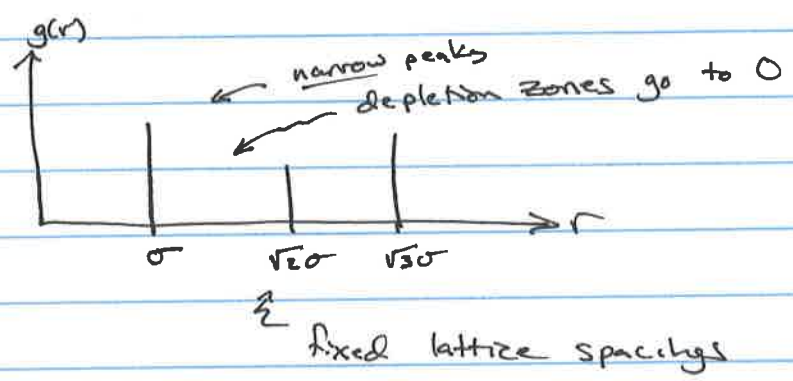


1st coordination shell



most probable distance for 1st coordination shell is 1st peak location

In a crystal:



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

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

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

⚡ These are in 3D. What are equivalent expressions in 2D?

Reversible Work Theorem

①

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

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

where

$$w(r) = \Delta A \leftarrow \begin{array}{l} \text{Helmholtz Free Energy} \\ \text{for this process} \end{array}$$

Proof:

The mean force between particles 1 & 2:

$$-\left\langle \frac{dU(r^{(N)})}{dr_1} \right\rangle_{r_1, r_2} = \frac{-\int \frac{dU(r^{(N)})}{dr_1} e^{-\beta U(r^{(N)})} d\vec{r}_3 \dots d\vec{r}_N}{\int e^{-\beta U(r^{(N)})} d\vec{r}_3 \dots d\vec{r}_N}$$

\uparrow
held fixed
in space

This can also be written:

$$-\left\langle \frac{dU(r^{(N)})}{dr_1} \right\rangle_{r_1, r_2} = \frac{1}{\beta} \frac{d}{dr_1} \ln \int e^{-\beta U(r^{(N)})} d\vec{r}_3 \dots d\vec{r}_N$$

The total number of particles N is a constant as is the total partition function Q with respect to any one coordinate: or Z

$$\frac{d}{dr_1} \ln \frac{N(N-1)}{Z} = 0$$

So this may be added at will!

Therefore:

(2)

$$-\left\langle \frac{d}{d\vec{r}_1} U(r^N) \right\rangle = \frac{1}{\beta} \frac{d}{d\vec{r}_1} \ln \frac{(N-1)N}{z} + \frac{1}{\beta} \frac{d}{d\vec{r}_1} \ln \int e^{-\beta U(r^N)} d\vec{r}_2 \dots d\vec{r}_N$$

$$\therefore -\left\langle \frac{d}{d\vec{r}_1} U(r^N) \right\rangle = k_B T \frac{d}{d\vec{r}_1} \ln \left[N(N-1) \frac{\int d\vec{r}_2 \dots d\vec{r}_N e^{-\beta U(r^N)}}{\int d\vec{r}_1 \dots d\vec{r}_N e^{-\beta U(r^N)}} \right]$$

$$-\left\langle \frac{d}{d\vec{r}_1} U(r^N) \right\rangle_{r_1, r_2} = k_B T \frac{d}{d\vec{r}_1} \ln g(\vec{r}_1, \vec{r}_2)$$

Integrating the average force gives the reversible work

$$w(r_{12}) = \int_{r_{12}}^{\infty} dr_1 \left\langle \frac{dU(r^N)}{dr_1} \right\rangle = k_B T \int_{r_{12}}^{\infty} dr_1 \frac{d}{dr_1} \ln g(r_1)$$

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

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

Also

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

We can also do thermodynamics using $g(r)$

$$U(r^N) = \sum_{i=1}^{N-1} \sum_{j=i+1}^N u(|\vec{r}_j - \vec{r}_i|) = \frac{1}{2} \sum_{ij} u(|\vec{r}_j - \vec{r}_i|)$$

$U(r)$ is a pair potential, which is an approximation for real systems, but we can exploit it:

(3)

The average energy:

$$\langle E \rangle = \langle K(p^N) \rangle + \langle U(r^N) \rangle$$

$$= N \left\langle \frac{p^2}{2m} \right\rangle + \left\langle \sum_{i>j=1}^N u(r_i - r_j) \right\rangle$$

equipartition

of pairs

average pair potential

$$= \frac{3}{2} N k_B T + \frac{N(N-1)}{2} \langle u(r_{12}) \rangle$$

$$\frac{N(N-1)}{2} \langle u(r_{12}) \rangle = \frac{N(N-1)}{2} \frac{\int dr^N u(r_{12}) e^{-\beta U(r^N)}}{\int dr^N e^{-\beta U(r^N)}}$$

$$= \frac{N(N-1)}{2} \frac{\int d\vec{r}_1 \int d\vec{r}_2 u(r_{12}) \int d\vec{r}_3 \dots d\vec{r}_N e^{-\beta U(r^N)}}{\int dr^N e^{-\beta U(r^N)}}$$

$$= \frac{1}{2} \int d\vec{r}_1 d\vec{r}_2 \rho^{(2/N)}(\vec{r}_1, \vec{r}_2) u(r_{12})$$

For a uniform, isotropic system,

$$\rho^{(2/N)}(\vec{r}_1, \vec{r}_2) = \rho^2 g(r_{12})$$

$$\vec{r}_{12} = \vec{r}_2 - \vec{r}_1, \quad \text{so} \quad \vec{r}_1 = -\vec{r}_{12} + \vec{r}_2 = \vec{r}_2 - \vec{r}_{12}$$

For fixed \vec{r}_2 , $d\vec{r}_1 = -d\vec{r}_{12}$

$$\therefore \frac{N(N-1)}{2} \langle u(r_{12}) \rangle = \frac{1}{2} \int d\vec{r}_2 \int d\vec{r}_{12} \rho^2 g(r_{12}) u(r_{12})$$

$$\begin{aligned} \therefore \frac{N(N-1)}{2} \langle u(r_{12}) \rangle &= \frac{V\rho^2}{2} \int d\vec{r} g(r) u(r) \\ &= \frac{N}{2} \int d\vec{r} \rho g(r) u(r) \end{aligned}$$

Putting this all together:

$$\langle E \rangle = \frac{3}{2} N k_B T + \frac{N}{2} \rho \int d\vec{r} g(r) u(r)$$

$$\frac{\langle E \rangle}{N} = \frac{3}{2} k_B T + \frac{\rho}{2} \int d\vec{r} g(r) u(r)$$

↑
thermodynamic
property

↑ ↑
structural
property microscopic
energy function

Back to reversible work:

$$w(r) = u(r) + \Delta w(r)$$

↑ potential of mean force ↑ pair potential ↙ contribution due to surrounding particles in the liquid

That is $\Delta w(r)$ is the change in the Helmholtz free energy of the solvent due to moving particles 1 & 2 from $|\vec{r}_2 - \vec{r}_1| = \infty$ to $|\vec{r}_2 - \vec{r}_1| = r$

$$\lim_{\rho \rightarrow 0} \Delta w(r) = 0$$

$$\therefore g(r) = e^{-\beta u(r)} [1 + O(\rho)]$$

(5)

That is, at low densities
 $g(r) \approx e^{-\beta u(r)}$

We can put this in to the thermodynamic expression...

$$\frac{\Delta E}{N} = \frac{\rho}{2} \int d\vec{r} g(r) u(r) \approx \frac{\rho}{2} \int d\vec{r} e^{-\beta u(r)} u(r) [1 + O(\rho)]$$

We also have a connection between Helmholtz F.E. and ΔE :

$$\frac{\Delta E}{N} = \frac{\partial(\frac{\beta \Delta A}{N})}{\partial \beta}$$

ΔA is the excess Helmholtz free energy

$$\text{Also: } -\beta \Delta A = \ln \left(\frac{Q}{Q_{\text{ideal}}} \right)$$

$$\therefore -\frac{\beta \Delta A}{N} = \frac{\rho}{2} \int d\vec{r} f(r) + O(\rho^2)$$

$$\text{where } f(r) = e^{-\beta u(r)} - 1$$

$$\text{So: } \rho^2 \frac{\partial(\frac{\beta \Delta A}{N})}{\partial \beta \rho} = \beta P - \rho$$

$$\beta P = \rho + \rho^2 B_2(T) + O(\rho^3)$$

$$B_2(T) = -\frac{1}{2} \int d\vec{r} f(r) \quad \text{which is the second virial coefficient}$$