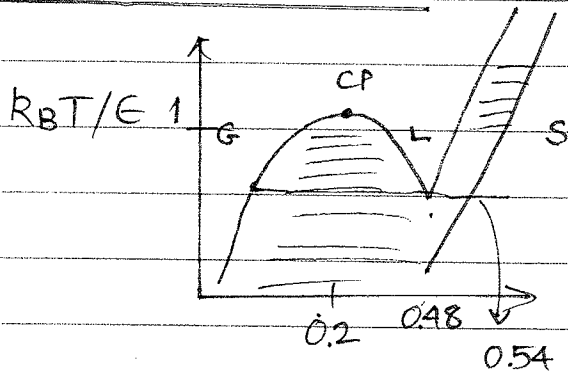


Non-ideal Fluids

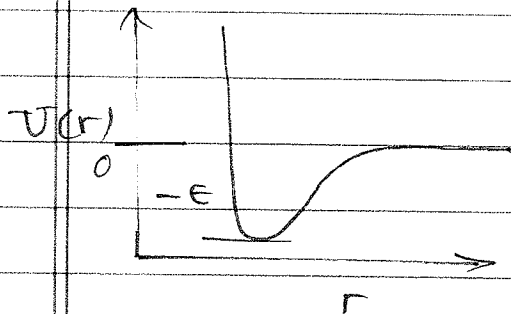


$$\rho^* = \rho \pi \sigma^3 / 6$$

= packing fraction

$$U(r) = LJ$$

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



$$U(\sigma) = 0 \quad \text{so defining } \sigma$$

$$U_{\min} \Rightarrow \left(\frac{dU}{dr} \right)_{r_{\min}} = 0$$

$$U(r_{\min}) = -\epsilon \quad (\text{well depth})$$

LJ is a two parameter pot'l. The computed phase diagram has three phases notable regions:

$$\rho^* \sim 0.10 - 0.20 \quad \text{triple critical point}$$

$$\rho^* = 0.45 (L), 0.54 (S) \quad L \rightleftharpoons S$$

coexistence

$$\rho^* = 0.49 \quad \text{packing of a simple cubic solid}$$

$$\rho^* = 0.74 \quad \text{close packed solid}$$

For $\rho^* > 0.1$, we must include intermolecular potentials into thermo.

Partition functions

So far $Q_N = q^N / N!$ for N -independent
non-interacting
particles.

For dense fluids, this is not valid. Here

$$Q \sim \frac{1}{N!} \int dr_1 \dots dr_N dp_1 \dots dp_N \exp(-\beta H)$$

$$H = \text{Hamiltonian} = \sum_i \frac{p_i^2}{2m} + \sum_{i < j} V(r_{ij})$$

As a tribute to QM, we must include a h
for every $dx dp_x$ volume element, so now

$$Q_N = \frac{1}{N! h^{3N}} \int dr_1 \dots dr_N dp_1 \dots dp_N \exp(-\beta K) \exp(-\beta U)$$

where K is the kinetic energy

$$\text{But } \int dp_{ix} \exp(-p_{ix}^2 / 2m) = \sqrt{2\pi m k_B T}$$

and when we include the h -factors
we have

$$Q_N = \frac{1}{N! \Lambda^{3N}} \underbrace{\int dr_1 \dots dr_N \exp(-\beta U)}_{Z_N}$$

If $\beta U = 0$, then

$$Z_N = V^N \quad \text{and}$$

$$Q_N = \frac{1}{N!} \left(\frac{V}{\Delta^3} \right)^N$$

precisely the
ideal monatomic gas
canonical ensemble
partition function

Focus on Z_N when $\beta U \neq 0$.

$$Z_N = \int dr_1 \dots dr_N \exp(-\beta U)$$

$$\exp(-\beta U) = \prod_{\langle ij \rangle} \exp(-\beta U_{ij})$$

$$\exp(-\beta U_{ij}) \equiv 1 + f_{ij}$$

where f is called
the Mayer f -bond

Now

$$Z_N = \int dr_1 \dots dr_N \prod_{\langle ij \rangle} (1 + f_{ij})$$

$$\prod_{\langle ij \rangle} (1 + f_{ij}) \cong 1 + \frac{N(N-1)}{2} f_{12}$$

(show this
by expanding
the product
for 3 or 4
particles)

To lowest order,

$$Z_N = \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \left[1 + \frac{N(N-1)}{2} f_{12} + \dots \right]$$

$$= V^N + V^{N-2} \frac{N(N-1)}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 f_{12}$$

$$= V^N \left[1 + \frac{N^2}{2V^2} \underbrace{\int d\mathbf{r}_1 d\mathbf{r}_2 f_{12}}_V \right]$$

$$\ln Z_N = \ln V^N + \ln \left(1 + \frac{N^2}{2V} \int d\mathbf{r}_{12} f_{12} \right)$$

Define $B_2 = -\frac{1}{2} \int d\mathbf{r}_{12} f_{12} = \text{second virial coef}$

$$\ln Z_N = \ln V^N + \frac{N^2}{2V} \int d\mathbf{r}_{12} f_{12}$$

$$= \ln V^N - \frac{N^2}{V} B_2(T)$$

Now assemble $A = -k_B T \ln Q_N$

$$\ln Q_N = \ln \left(\frac{1}{N!} \Delta^{3N} \right) + \ln V^N - \frac{N^2}{V} B_2(T)$$

$$= \ln \left(\frac{V^N}{N! \Delta^{3N}} \right) - \frac{N^2}{V} B_2(T)$$

and $A = -k_B T \ln Q^{\text{ideal}} + \frac{k_B T N^2 B_2(T)}{V}$

$$P = - \left(\frac{\partial A}{\partial V} \right)_T = \rho k_B T + k_B T \frac{N^2}{V^2} B_2(T)$$

$$= \rho k_B T \left[1 + B_2(T) \rho \right]$$

first term of the virial expansion.

$$\langle E \rangle = \frac{3}{2} N k_B T + \frac{N(N-1)}{2} \frac{\int dr_1 \dots dr_N e^{-\beta U} U(r_{ij})}{\int dr_1 \dots dr_N e^{-\beta U}}$$

Define

$$g(r_{12}) = \frac{V^2}{Z_N} \int dr_3 \dots dr_N \exp(-\beta U)$$

and

$$\langle E \rangle = \frac{3}{2} N k_B T + \frac{N^2}{2V} \int dr_{12} U(r_{12}) g(r_{12})$$

$$= N \left\{ \frac{3}{2} k_B T + \frac{1}{2} \rho \int dr_{12} U(r_{12}) g(r_{12}) \right\}$$

average intermolecular potential energy.

Can also write

$$\beta P = \rho - \left(\frac{\rho^2}{6 k_B T} \right) \int dr \left(r \frac{\partial U}{\partial r} \right) g(r)$$

Many ideas here:

$$1) \beta P = \rho [1 + B_2(T) \rho + B_3 \rho^2 + \dots]$$

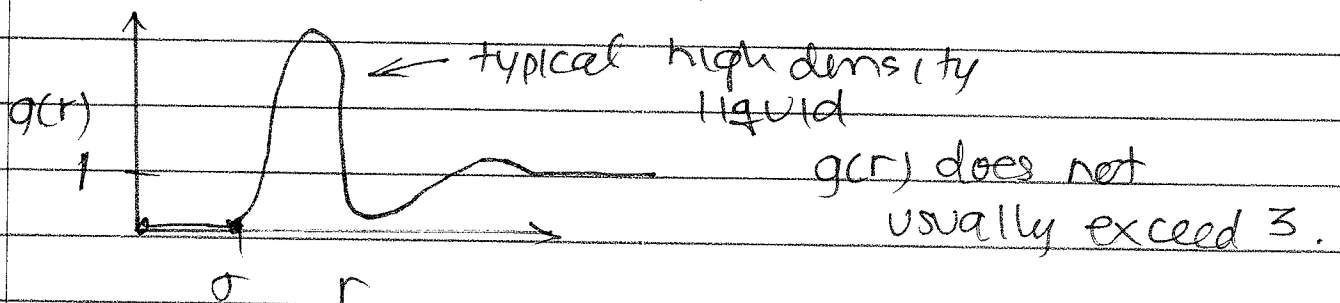
$$VB_2 = \text{---} \int dr_1 dr_2 f_{12}$$

$$VB_3 = \text{---} \int dr_1 dr_2 dr_3 f_{12} f_{23} f_{31}$$

$$VB_4 = \text{---} + \text{---} + \text{---} \int dr_1 dr_2 dr_3 dr_4 f_{12} f_{23} f_{34} f_{41} f_{24}$$

Each virial coef can be described by a set of ^{all} connected diagrams where the vertices are connected by f-bonds.

$g(r)$: With this function, we can calculate "all" thermo functions, $\langle E \rangle$, P , C_V , $\dots kT \dots$



$$\int_0^R \rho dr g(r) = \# \text{ of neighbors around a specific particle at the coordinate system origin.}$$