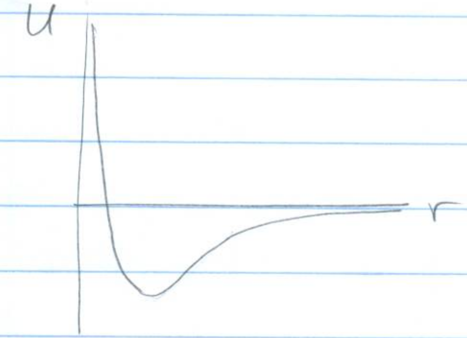
Goldenfeld, Chapter 4

Exercise 4-1

(a) A typical form for the pair potential $U(r)$ is



The partition function for the gas in the canonical ensemble is

$$Z_N = \frac{1}{N!} \frac{(2\pi m kT)^{3N/2}}{h^{3N}} \int d^3r_1 \cdots \int d^3r_N \exp\left\{-\beta \sum_{i<j=2}^{N} U(r_{ij})\right\}$$

Suppose the pair potential has the form $U(r) = \epsilon u(r/\sigma)$. Then the integral over the positions reduces by dimensional analysis to V^N multiplied by a function of N and two dimensionless intensive variables: $v^* = V/N\sigma^3$ and $T^* = kT/\epsilon$. The integral can be expressed in the form

$$\int d^3r_1 \cdots \int d^3r_N \exp\left(-\beta\epsilon \sum_{i<j=2}^{N} u(r_{ij}/\sigma)\right)$$

$$= V^N \exp\left(N C(v^*, T^*, N)\right)$$

The partition function is

$$Z_N = \frac{1}{N!}\left(\frac{(2\pi mkT)^{3/2}V}{h^3}\right)^N \exp\left(N\,C(v^*,T^*,N)\right)$$

The free energy is

$$F_N = -kT \log Z_N$$

$$= -kT\left[N\log\frac{(2\pi mkT)^{3/2}V}{h^3} + N\,C(v^*,T^*,N) - \log N!\right]$$

In the thermodynamic limit, the free energy reduces to

$$F = -NkT\left[\log\frac{(2\pi mkT)^{3/2}V}{h^3} + C(v^*,T^*,\infty) - \log N + 1\right]$$

$$= -NkT\left[\log\frac{(2\pi mkT)^{3/2}V}{h^3N} + C(v^*,T^*,\infty) + 1\right]$$

The pressure is

$$P = -\frac{\partial F}{\partial V}$$

$$= NkT\left[\frac{1}{V} + \frac{\partial C}{\partial v}(v^*,T^*,\infty)\frac{1}{N\sigma^3}\right]$$

We can define the scaled pressure by

$$p^* = \frac{P\sigma^3}{\epsilon}$$

The equation of state then reduces to

$$p^* = T^* \left[\frac{1}{v^*} + \frac{\partial c}{\partial v^*}(v^*, T^*, \infty) \right]$$

The right side is a function of v^* and T^* only:

$$p^* = \pi(v^*, T^*)$$

(b) At the critical point, the 1st and second derivative of the pressure with respect to the volume at fixed temperature must vanish. Therefore the critical variables satisfy

$$\frac{\partial \pi}{\partial v^*}(v^*, T^*) = 0$$

$$\frac{\partial^2 \pi}{\partial v^{*2}}(v^*, T^*) = 0$$

We denote the simultaneous solution of these two equations by v_c^* and T_c^*. The critical value of the scaled pressure is therefore

$$p_c^* = \pi(v_c^*, T_c^*)$$

The critical values of the pressure, temperature and volume per particle are

$$P_c = p_c^* \frac{\epsilon}{\sigma^3}$$

$$kT_c = T^* \epsilon$$

$$v_c = v_c^* \sigma^3$$

They satisfy

$$\frac{P_c v_c}{kT_c} = \frac{p_c^* v_c^*}{T_c^*}$$

This combination is independent of the energy scale ϵ and length scale σ that characterize the fluid.