1/3/06

Liquid-gas phase transition

p: pressure, $\rho = N/V$ = density, T = temperature.

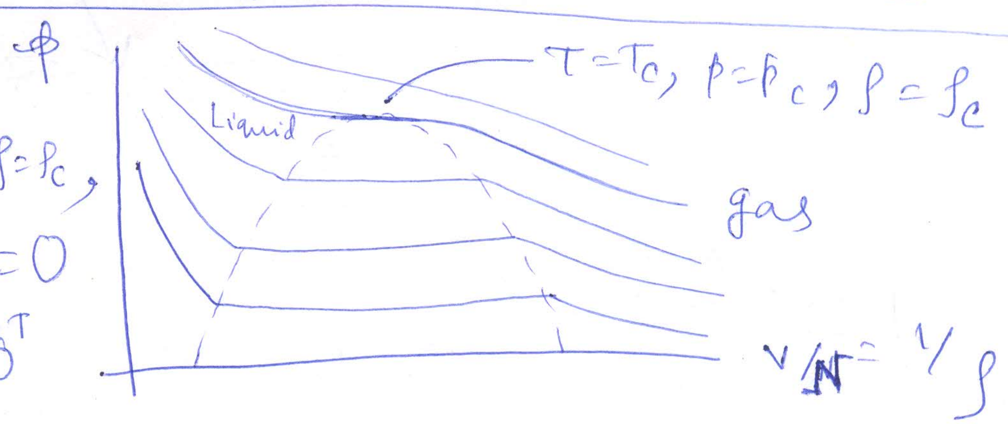
Equation of state:– $p = g(\rho, T)$ → some function

Relation betn. ρ & T

$$p/kT = \frac{\partial}{\partial V} \ln Q = \frac{1}{V} \ln Q$$

Since $\ln Q \propto V f(z, \beta)$

Phase diagram for Liquid-gas system



At $T=T_c$, $p=p_c$, $\rho=\rho_c$,

$$\left(\frac{\partial p}{\partial V}\right)_{N,T} = 0, \left(\frac{\partial^2 p}{\partial V^2}\right)_{N,T} = 0$$

$\Rightarrow \partial p/\partial \rho = 0$, $\frac{\partial^2 p}{\partial \rho^2} = 0$

Q) Can we understand this from Statistical mechanics?

$$p = p_c + a(\rho - \rho_c)^3 \quad \text{at } T = T_c.$$

$$\rho - \rho_c = \left(\frac{p - p_c}{a}\right)^{1/3}$$

$$\partial\rho/\partial p \propto (p - p_c)^{-2/3} \longrightarrow \infty \text{ as } p \to p_c.$$

There is some kind of non analyticity in the fn. det. $\rho - \rho_c$ in terms of $p - p_c$

In order to understand phase transition from statistical mechanics, we need to understand the origin of non-analyticity.

[we haven't gotten this diag. from stat. mech. Till now we have used only thermodyn. relations]

$\Rightarrow$ ρ is discontinuous as a fn. of p.

Model of imperfect gas (classical)

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

$$V = \sum_{i<j} v(\vec{r}_i - \vec{r}_j)$$

Assumptions

1. $v(\vec{r}) = \infty$ for $|\vec{r}| \le a$.
2. $v(\vec{r}) \ge -\epsilon_0$ for $a < |\vec{r}| < r_0$
3. $v(\vec{r}) = 0$ for $r \ge r_0$

known as Hard sphere interaction

Hard core int.

Molecules are rep. for very near approach

It is possible that v never becomes -ve

But it can't be arbitrarily large negative

ϵ_0 can be +ve or -ve

In the realistic case ϵ_0 should be positive bcos there is some attractive component