Law of Corresponding States

Rescale the V.d.W equation using P_c, V_c, T_c

$$\tilde{T} = \frac{T}{T_c} \qquad \tilde{V} = \frac{V}{V_c} \quad , \quad \tilde{P} = \frac{P}{P_c}$$

$$\left(\tilde{P}P_c + a\left(\frac{N}{\tilde{V}V_c}\right)^2\right)\left(\tilde{V}V_c - Nb\right) = Nk\tilde{T}T_c$$

and $\boxed{V_c = 3Nb \ , \ kT_c = \frac{8}{27}\frac{a}{b} \ , \ P_c = \frac{1}{27}\frac{a}{b^2}}$

$$\left(\tilde{P} + \frac{1}{\tilde{V}^2}\frac{aN^2}{V_c^2 P_c}\right)\left(\tilde{V} - \frac{1}{3}\right) = \tilde{T}\frac{NkT_c}{P_c V_c}$$

$$\frac{P_c V_c}{kT_c N} = \frac{3}{8} = 0.375$$

He^4: ≈ 0.31
H_2O : 0.23
Ar: 0.292

$$\boxed{\left(\tilde{P} + \frac{3}{\tilde{V}^2}\right)\left(\tilde{V} - \frac{1}{3}\right) = \frac{8}{3}\tilde{T}}$$

law of corresponding states

- when expressed in terms of scaled variables, all fluids should exhibit similar behavior.
- this is true, but they won't be the same as the "V.d.W." gas

⇒ concept of universality is very important
(but not described very well by V.d.W eq.)

Definition of critical exponents

(i)/a $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \sim |T-T_c|^{-\gamma}$ (γ γ' possibly for $T \to T_c \pm 0$)

As we go from the critical point, the coexistence curve has equilibrium volumes $V_e(T) \neq V_g(T)$

(ii)/b $C_{V\,(P)} \sim |T-T_c|^{-\alpha}$ constant V (P) specific heat

(ii) $V_g - V_e \sim \boxed{v_g - v_e \sim |T-T_c|^{\beta}}$ $T<T_c$

specific volume $(v = V/N)$

length of coexistence curve: $\sim$ order parameter

also can be interpreted as the density diff. measured from T_c

$\varphi_g = \frac{V_g - V_c}{V_c}$

$\varphi_e = \frac{V_e - V_c}{V_c}$

$$1/\varphi_e - 1/\varphi_g = \frac{\varphi_g - \varphi_e}{\varphi_g \varphi_e} \simeq \varphi_g - \varphi_e \sim |T-T_c|^{\beta}$$

(iii) <u>on the critical isotherm $T=T_c$</u>

$$|P-P_c| \sim |V-V_c|^{\delta}$$

equivalently:

$$\left|\frac{P-P_c}{P_c}\right| \sim \left|\frac{V-V_c}{V_c}\right|^{\delta}$$

$$|\pi| \sim |\varphi|^{\delta}$$

Critical Behavior of the v.d.W. gas

$$\left(\tilde{P} + \frac{3}{\tilde{V}^2}\right)\left(\tilde{V} - \frac{1}{3}\right) = \frac{8}{3}\tilde{T}$$

critical point $\tilde{P}_c = \tilde{V}_c = \tilde{T}_c = 1$

$\pi \equiv \tilde{P} - 1$, $\varphi = \tilde{V} - 1$, $t = \tilde{T} - 1$

: $\pi = \frac{P - P_c}{P_c} = \tilde{P} - 1$ $\quad \varphi = \frac{V - V_c}{V_c} = \tilde{V} - 1$ $\quad t = \frac{T - T_c}{T_c} = \tilde{T} - 1$

$$\tilde{P} = 8\frac{(1+t)}{2+3\varphi} - \frac{3}{(1+\varphi)^2}$$

assume $t \ll 1$, $\varphi \ll 1$ in the vicinity of the critical point

$\boxed{\text{HW exercise}}$ $\Rightarrow$ $\tilde{P} = 1 + 4t - 6t\varphi - \frac{3}{2}\varphi^3 + o(t\varphi^2, \varphi^4)$

$$\boxed{\pi \simeq 4t - 6t\varphi - \frac{3}{2}\varphi^3}$$

$\boxed{\delta:}$ on the critical isotherm: $(T = T_c)$ $\quad t = 0$

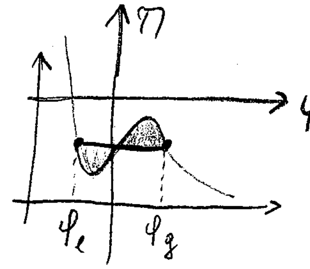
$\pi \simeq -\frac{3}{2}\varphi^3$ $\qquad \left|\frac{P - P_c}{P_c}\right| \sim \left|\frac{V - V_c}{V_c}\right|^\delta$ $\qquad \boxed{\delta = 3}$

$|\varphi| \sim |\pi|^{1/3}$

(experiments: $\delta \approx 4-5$)

$\boxed{\beta}$

Coesistense line:
(below T_c)



$\boxed{t<0}$ fixed

$$\int_g^\ell V\,dP = 0 \quad \Rightarrow \quad \int_g^\ell \varphi\, d\Pi = 0 \qquad \text{(Maxwell rule)}$$

$$d\Pi = -6t\,d\varphi - \frac{9}{2}\varphi^2\,d\varphi \qquad t = \text{const}$$

$$\int_{\varphi_g}^{\varphi_\ell} \varphi\left(-6t - \frac{9}{2}\varphi^2\right)d\varphi = 0 \quad \Rightarrow \quad \varphi_\ell = -\varphi_g$$

From the equation of state.

$$\begin{cases} \Pi = 4t - 6t\varphi_g - \frac{3}{2}\varphi_g^3 & (\varphi_g \text{ eqn.}) \\ \Pi = 4t + 6t\varphi_g + \frac{3}{2}\varphi_g^3 & (\varphi_\ell \text{ eqn.}) \end{cases}$$

$$0 = 12t\varphi_g + 3\varphi_g^3$$

$$\varphi_g^2 = -4t \quad \Rightarrow \quad \varphi_g = 2\sqrt{-t} = 2\sqrt{|t|}$$

$v = V/N$ (specific volume: volume per particle)

order param: $\frac{1}{\varphi_\ell} - \frac{1}{\varphi_g} = \frac{\varphi_g - \varphi_\ell}{\varphi_\ell \varphi_g} \sim 2\varphi_g \sim |t|^{1/2}$ $\qquad \boxed{\beta = 1/2}$

↑ densities measured from the critical values

$\boxed{\gamma:}$ isotherm compressibility κ_T:

$$\kappa_T^{-1} = -V\left(\frac{\partial P}{\partial V}\right)_T \sim -\left(\frac{\partial \Pi}{\partial \varphi}\right)_T \simeq -(-6t) \quad \text{at } \varphi = 0$$

$\boxed{\text{for } t>0}$ $\quad \Pi \simeq 4t - 6t\varphi - \frac{3}{2}\varphi^3$

$$\boxed{\kappa_T \sim \frac{1}{6t} \sim \frac{1}{T-T_c}}$$

$\gamma = 1$

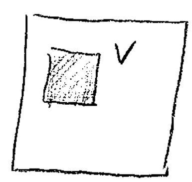
diverges as $T \to T_c^+$

$\boxed{\text{HW exercise:}}$ α (specific heat exponent)

The physical and microscopic interpretation of the divergence in K_T: the behavior of the density-density correlation

Particle number fluctuations and compressibility K_T

$$\boxed{\langle (\Delta N)^2 \rangle = kT\left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{V,T}}$$



$V^{(0)}$

$V << V^{(0)}$

but macroscopic

$N = \langle N \rangle$ for short

from basic thermodynamics: $\boxed{\left(\frac{\partial N}{\partial \mu}\right)_{V,T} = -\frac{N^2}{V^2}\left(\frac{\partial V}{\partial P}\right)_{N,T}}$

$$\Rightarrow \langle (\Delta N)^2 \rangle = kT\frac{N^2}{V^2}\left(-\frac{\partial V}{\partial P}\right)_{N,T} = kT\left(\frac{N}{V}\right)^2 V K_T$$

(1) $\quad \boxed{\langle (\Delta N)^2 \rangle = kT\rho^2 V K_T}$

dimensionless two-point correlation function:

$$\boxed{\rho = \frac{N}{V} = \langle \rho(\bar{x}) \rangle} \quad G(\bar{x}-\bar{x}') = \frac{1}{\rho^2}\left[\langle \rho(\bar{x}) \rho(\bar{x}') \rangle - \rho^2 \right]$$

essential $(\bar{x}-\bar{x}')$ dependence in hom. syst

$$|\bar{x}-\bar{x}'| \to \infty \qquad \langle \rho(\bar{x}) \rho(\bar{x}') \rangle \to \langle \rho(\bar{x}) \rangle \langle \rho(\bar{x}') \rangle = \rho^2$$

and

$$\lim_{|\bar{x}-\bar{x}'| \to \infty} G(\bar{x}-\bar{x}') = 0$$

Also note, that

$$\langle (\rho(\bar{x}) - \rho)(\rho(\bar{x}') - \rho) \rangle = \langle \rho(\bar{x}) \rho(\bar{x}') \rangle - \rho^2$$

$$N = \int d^3x \, \rho(\bar{x}) \quad \Rightarrow \quad \langle N \rangle = \int d^3x \langle \rho(\bar{x}) \rangle = \int d^3x \, \rho$$

$$\int d^3x \int d^3x' \, G(\bar{x}-\bar{x}') = \frac{1}{\rho^2}\left[\left\langle \int d^3x \, \rho(\bar{x}) \int d^3x' \, \rho(\bar{x}') \right\rangle - \langle N \rangle^2 \right]$$

$$= \frac{1}{\rho^2}\left[\langle N^2 \rangle - \langle N \rangle^2 \right] = \frac{1}{\rho^2} \langle (\Delta N)^2 \rangle \qquad (2)$$

from the translational invariance of $G(\bar{x},\bar{x}') = G(\bar{x}-\bar{x}')$

$$\int d^3x \int d^3x' \, G(\bar{x}-\bar{x}') = V \int d^3r \, G(\bar{r}) \qquad (3)$$

Combining (1), (2), and (3):

$$\boxed{\int d^3r \, G(\bar{r}) = k_B T \, K_T}$$

$$G(\bar{r}) \propto \frac{e^{-r/\xi(T)}}{r} \qquad d=3$$

<u>away from T_c</u>

$$\xi(T) \xrightarrow[T \to T_c]{} \infty$$

Structure Factor and Critical Opalescence

$$S(\bar{k}) = \rho \int d^3r \, e^{-i\bar{k}\bar{r}} \, G(\bar{r})$$ structure factor

$$\boxed{\lim_{k \to 0} S(\bar{k}) = \rho \int d^3r \, G(\bar{r}) = \rho k_B T K_T}$$

$k \neq 0$ $$\boxed{S(\bar{k}) = \frac{\text{const}}{k^2 + \xi^{-2}(T)}} \xrightarrow{\bar{k} \to 0} \text{const} \cdot \xi^2(T) = \rho k_B T K_T$$

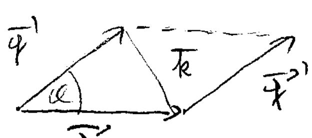
(*) experimental finding

$\xi(T)$ is finite away from T_c,

$$\boxed{S(\bar{k}) = \frac{\rho k_B T K_T}{1 + k^2 \xi^2(T)}}$$

$T \to T_c$ $$S(\bar{k}) \propto \frac{1}{k^{2-\eta}} \xrightarrow[k \to 0]{} \infty$$ and $K_T \to \infty$

Scattering Experiment: elastic scattering of neutron or light



$|\bar{q}'| = |\bar{q}| = \text{const.}$

$$\boxed{|\bar{k}| = 2|\bar{q}| \sin\frac{\vartheta}{2}} = \frac{4\pi}{\lambda} \sin\left(\frac{\vartheta}{2}\right)$$

(*) intensity of scattered radiation:

$$I(\vartheta) \propto S(\bar{k})$$

Two-point function:

$$G(\bar{x},\bar{x}') = \frac{1}{\rho^2}\left[\langle \rho(\bar{x})\rho(\bar{x}')\rangle - \rho^2\right]$$

$\rho = \langle \rho(\bar{x})\rangle$
homogeneous system

$$G(\bar{x},\bar{x}') = \frac{1}{\rho^2}\left[\langle (\rho(\bar{x})-\rho)(\rho(\bar{x}')-\rho)\rangle\right]$$

Thus, $G(\bar{x},\bar{x}') = G(\bar{x},\bar{x}')$ is the measure of the density fluctuations in the system

$$\lim_{|\bar{x}-\bar{x}'|\to\infty} G(|\bar{x}-\bar{x}'|) \to 0 \qquad \text{since} \qquad \lim_{|\bar{x}-\bar{x}'|\to\infty} \langle \rho(\bar{x})\rho(\bar{x}')\rangle \longrightarrow \langle \rho(\bar{x})\rangle\langle \rho(\bar{x}')\rangle = \rho^2$$

$\boxed{\text{HW:}}$ working in the canonical ensemble and writing $\boxed{\rho(\bar{x}) = \sum_{i=1}^{N} \delta(\bar{x}-\bar{x}_i)}$ show that

(i) $\langle \rho(\bar{x})\rangle = \frac{N}{V}$ constant

(ii) $\langle \rho(\bar{x})\rho(\bar{x}')\rangle$ = function of $(\bar{x}-\bar{x}')$

assuming that the interaction part of the Hamiltonian is homogeneous, i.e., $U(\bar{x}_1,\bar{x}_2,\dots,\bar{x}_N) = \sum_{i<j} U(\bar{x}_i-\bar{x}_j)$

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extending the definition of $G(\bar{x},\bar{x}')$ to the G.C. ensemble to allow number of particle fluctuations, we found

$$\boxed{\int d^d r\, G(\bar{r}) = k_B T\, \kappa_T}$$

d dimension

using $\frac{N}{V}$ and $\frac{\langle N\rangle}{V}$ interchangeably

$$\boxed{\lim_{\bar{k}\to 0} S(\bar{k}) = \rho\, k_B T\, \kappa_T}$$

Structure Factor

$$\rho = \frac{N}{V}$$

$$S(\bar{k}) = \rho \int d^d r \, e^{-i\bar{k}\bar{r}} G(\bar{r}) =$$ (Fourier tr. of two-point density correlations)

$$= \frac{1}{\rho} \int \Big[\underbrace{\langle \rho(\bar{x}) \rho(\bar{x}') \rangle}_{\text{func. of } (\bar{x}-\bar{x}')} - \rho^2 \Big] e^{-i\bar{k}\bar{r}} d^d r$$

$$= \frac{1}{\rho}\frac{1}{V} \int \Big[\sum_{ij} \langle \delta(\bar{x}-\bar{x}_i)\, \delta(\bar{x}'-\bar{x}_j) \rangle \, e^{-i\bar{k}(\bar{x}-\bar{x}')} d^d x \, d^d x' - \rho \, \delta_{\bar{k},0} V$$

$$\boxed{= \frac{1}{N} \sum_{ij} \left\langle e^{-i\bar{k}(\bar{x}_i - \bar{x}_j)} \right\rangle - N \delta_{\bar{k},0}}$$

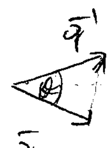
$$\left(\delta_{\bar{k},0} V = (2\pi)^d \delta(\bar{k}) \right)$$

<u>elastic scattering application:</u> (plane wave scattering approx.)

incoming beam: $\psi_{\bar{q}}(\bar{x}) = \frac{1}{\sqrt{V}} e^{+i\bar{q}\bar{x}} = |\bar{q}\rangle$

outgoing (scattered) beam: $\psi_{\bar{q}'}(\bar{x}) = \frac{1}{\sqrt{V}} e^{+i\bar{q}'\bar{x}} = |\bar{q}'\rangle$

$|\bar{q}'| = |\bar{q}|$



$\Delta\bar{q} = \bar{k}$

$$|\bar{k}| = 2 \sin\frac{\theta}{2} \, |\bar{q}| = \frac{4\pi}{\lambda_{\text{light}}} \sin\left(\frac{\theta}{2}\right)$$

model interaction between the system of N particles and the probe (light or neutrons): $\sum_{i=1}^{N} u(\bar{x}-\bar{x}_i)$

$$W_{\bar{q}\to\bar{q}'} = \frac{2\pi}{\hbar} \left| \langle \bar{q}+\bar{k} | \sum_{i=1}^{N} u(\bar{x}-\bar{x}_i) | \bar{q} \rangle \right|^2 \delta(\varepsilon_{\bar{q}'} - \varepsilon_{\bar{q}})$$

QM average.

$$\langle \bar{q}+\bar{k} | \sum_{i=1}^{N} u(\bar{x}-\bar{x}_i) | \bar{q} \rangle = \frac{1}{V}\int d^3x \, e^{-i(\bar{q}+\bar{k})\bar{x}} \sum_{i=1}^{N} u(\bar{x}-\bar{x}_i) \, e^{+i\bar{q}\bar{x}}$$

$$= \frac{1}{V}\sum_{i=1}^{N} \int d^3x \, e^{-i\bar{k}\bar{x}} u(\bar{x}-\bar{x}_i) = \frac{1}{V}\sum_{i=1}^{N} \underbrace{\int d^3x \, e^{-i\bar{k}(\bar{x}-\bar{x}_i)} u(\bar{x}-\bar{x}_i)}_{u(\bar{k})} e^{-i\bar{k}\bar{x}_i}$$

$$= \frac{1}{V}\sum_i e^{-i\bar{k}\bar{x}_i} u(\bar{k}) = \frac{1}{V} u(\bar{k}) \sum_{i=1}^{N} e^{-i\bar{k}\bar{x}_i}$$

$\bar{k} = \bar{q}' - \bar{q}$

scattered intensity:

$$I(\bar{k}) \propto \left\langle \frac{1}{V^2}|u(\bar{k})|^2 \left| \sum_{i=1}^{N} e^{-i\bar{k}\bar{x}_i} \right|^2 \right\rangle$$

thermal average

$$= \frac{1}{V^2}|u(\bar{k})|^2 \left\langle \sum_{i,j} e^{-i\bar{k}(\bar{x}_i-\bar{x}_j)} \right\rangle = \frac{N}{V^2}|u(\bar{k})|^2 S(\bar{k})$$

form factor

for $\bar{k} \neq 0$

e.g. for neutron scattering: $u(\bar{x}-\bar{x}_i) \propto \delta(\bar{x}-\bar{x}_i)$

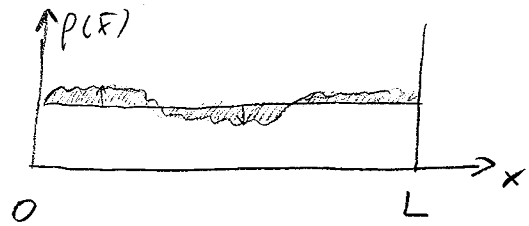
$|u(\bar{k})| \propto$ const. (slowly varying func)

$$\boxed{I(\bar{k}) \propto S(\bar{k})}$$

i.e., the structure factor of the material/system will be proportional to the scattered beam

$\hat{\rho}(\bar{x}) = \rho(\bar{x}) - \rho$ density fluctuations about the average

$\hat{\rho}_{\bar{k}} = \int \hat{\rho}(\bar{x})\, e^{-i\bar{k}\bar{x}}\, d^3x$



$\boxed{\text{HW:}}$ (show that)

Kronecker delta

$$\langle \hat{\rho}_{\bar{k}}\, \hat{\rho}_{\bar{k}'} \rangle = \delta_{\bar{k},-\bar{k}'}\, N S(\bar{k})$$

i.e., $\langle \hat{\rho}_{\bar{k}}\, \hat{\rho}_{-\bar{k}} \rangle = N\, S(\bar{k})$ or $\boxed{S(\bar{k}) = \frac{1}{N} \langle \hat{\rho}_{\bar{k}}\, \hat{\rho}_{-\bar{k}} \rangle}$

Experimental evidence

$T \gtrless T_c$ $\quad S(\bar{k}) \propto \dfrac{1}{k^2 + \xi^{-2}}$ $\qquad G(\bar{r}) = \dfrac{1}{\rho} \displaystyle\int \frac{d^dk}{(2\pi)^d}\, e^{i\bar{k}\bar{r}}\, S(\bar{k})$

$\xi(T)$ can be measured

$$= \frac{1}{(2\pi)^{d/2}} \frac{1}{(r\xi)^{\frac{d-2}{2}}} K_{\frac{d-2}{2}}(r/\xi)$$

$$\overset{r/\xi \to \infty}{\simeq} \frac{1}{r^{\frac{d-2}{2}}} \cdot \frac{1}{r^{1/2}}\, e^{-r/\xi}$$

$$= \frac{1}{r^{\frac{d-1}{2}}}\, e^{-r/\xi}$$

$d = 3$ $\quad G(r) \propto \dfrac{e^{-r/\xi}}{r}$

$T \to T_c:$ $\quad S(\bar{k}) \propto \dfrac{1}{k^{2-\eta}}$ $\qquad G(r) \propto r^{2-d-\eta} = \dfrac{1}{r^{d-2+\eta}}$

$\Downarrow$

diverging $\int G(r)\, d^dr$