Critical Phenomena in Fluids

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Topics

- The needed thermodynamics
- Two-phase coexistence
- Vicinity of the critical point
- Van der Waals Equation
- Spatial Correlations
- Measurement of the critical exponents

The needed Thermodynamics

Potentials and their differential

The inner energy $E(S,V,N)$

$$dE = TdS - pdV + \mu dN$$

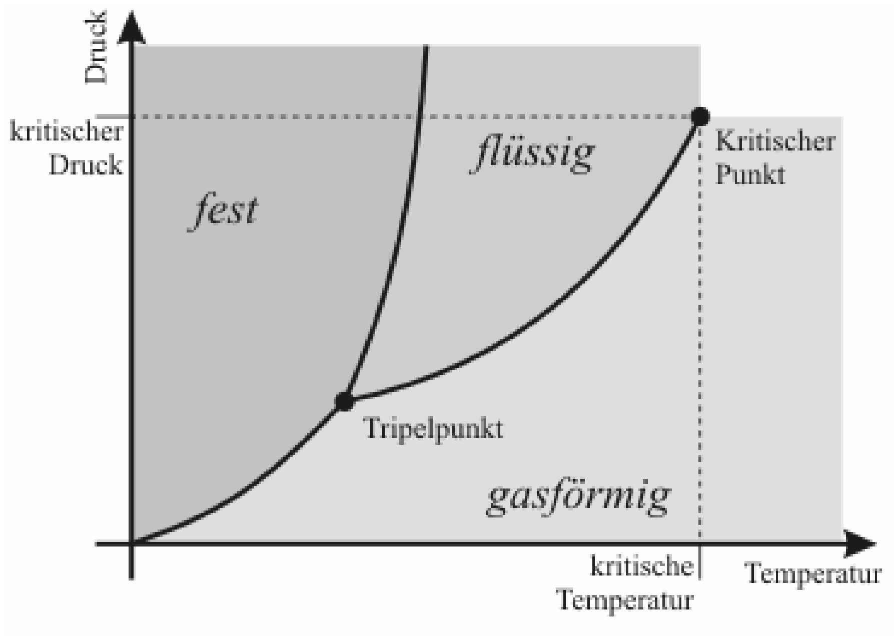
The Helmholtz free energy $F(T,V,N) = E - TS$

$$dF = -SdT - pdV + \mu dN$$

The Gibbs free energy $G(T,p,N) = F + pV = \mu N$

$$dG = -SdT + Vdp + \mu dN$$

Phase diagram

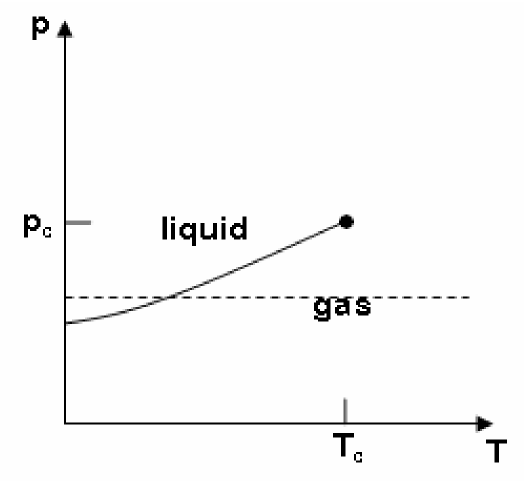


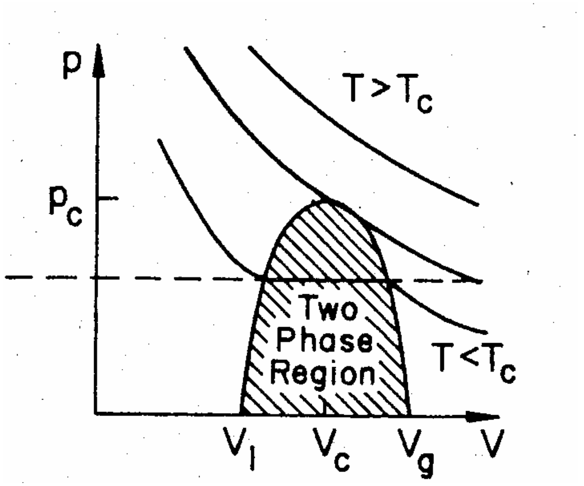
Clausius-Clapeyron relation: $$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta S_m}{\Delta V_m}$$

Landau‘s Symmetry Principle

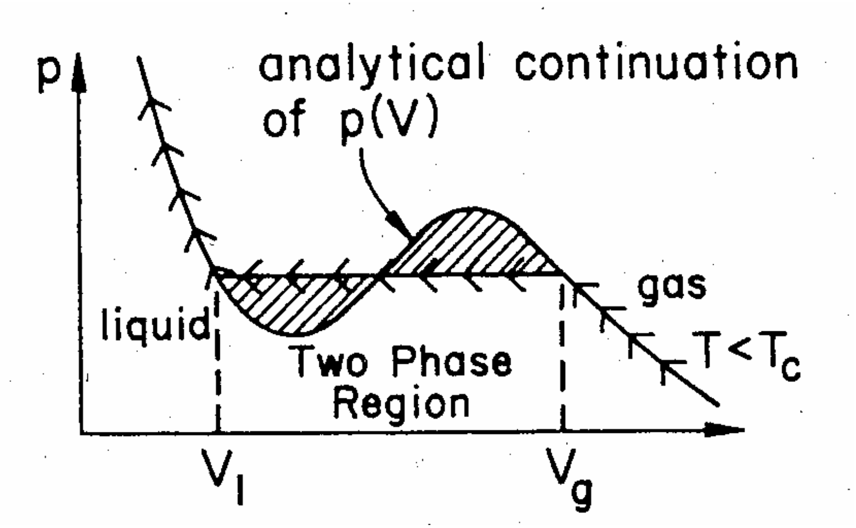
Two-phase coexistence

Fluid at constant pressure / constant Temperature





Maxwell‘s equal area rule:



$$d\mu = -\frac{S}{N}dT + \frac{V}{N}dp$$

$$\mu_l - \mu_g = \int_{gas}^{liq} d\mu = \int_{gas}^{liq} \frac{V}{N}dp = 0$$

Vicinity of the critical point

Compressibility: $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \propto |T - T_c|^{-\gamma}$

Equilibrium volumes: $v_g - v_l \propto |T_c - T|^{\beta}$

Specific heat: $C_V \propto |T - T_c|^{-\alpha}$

Shape of the critical isotherm: $|p - p_c| \propto |V - V_c|^{\delta}$

Van der Waals equation

ideal gas equation: $pv = k_b T$

Van der Waals equation: $p = \frac{k_B T}{v-b} - \frac{a}{v^2}$

<u>Determination of the critical point:</u>

- rewrite VdW to cubic-polynomial: $v^3 - \left(b + \frac{k_B T}{p}\right) v^2 \frac{a}{p} v - \frac{ab}{p} = 0$
- the 3 solutions merge at the critical point $(v - v_c)^3 = 0$
- v_c,p_c,T_c are defined through a,b $v_c = 3b; \quad p_c = \frac{a}{27b^2}; \quad k_B T_c = \frac{8a}{27b}$
- universal number: $\frac{p_c v_c}{k_B T_c} = \frac{3}{8}$

Law of corresponding states:

- rescale VdW equation to dimensionless form by rescaling

$$\left(\pi + \frac{3}{\nu^2}\right)(3\nu - 1) = 8\tau$$

- all fluids are predicted to have the same equation of state, with no other parameters involved
- all thermo dynamic properties which follow from this equation are universal
- experimentally, the law of corresponding states is well-satisfied, even by fluids which don‘t obey the VdW equation

Critical Behaviour:

- Now we will calculate the critical exponents of the Van der Waals fluid

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \propto |T - T_c|^{-1}$$

$$v_g - v_l \propto |T_c - T|^{\frac{1}{2}}$$

$$C_V \propto |T - T_c|^0$$

$$|p - p_c| \propto |V - V_c|^3$$

Spatial Correlations

Number fluctuations and compressibility

Grand partition function:

$$e^{-\beta(H-\mu N)}$$

$$\Xi = Tr(e^{-\beta(H-\mu N)})$$

Mean Number of particles in V :

$$\langle N \rangle = k_B T \left(\frac{\partial log \Xi}{\partial \mu} \right)_{T,V}$$

$$\langle N^2 \rangle = \frac{1}{\beta^2} \frac{1}{\Xi} \frac{\partial^2 \Xi}{\partial \mu^2} = \frac{1}{\beta^2} \frac{\partial^2 log \Xi}{\partial \mu^2} + \langle N \rangle^2$$

Fluctuation of particles

$$\Delta N^2 = \frac{k_B T}{\left(\frac{\partial \mu}{\partial N} \right)_{T,V}} = k_B T \rho^2 V \kappa_T$$

$$\left. \frac{\partial \mu}{\partial N} \right|_{V,T} = \frac{\partial(\mu, V)}{\partial(N, V)} = \frac{\partial(\mu, V)}{\partial(N, p)} * \frac{\partial(N, p)}{\partial(N, V)} = \left(\left. \frac{\partial \mu}{\partial N} \right|_{p,T} \left. \frac{\partial V}{\partial p} \right|_{N,T} - \left. \frac{\partial \mu}{\partial p} \right|_{N,T} \left. \frac{\partial V}{\partial N} \right|_{p,T} \right) \left(\left. \frac{\partial V}{\partial p} \right|_{N,T} \right)^{-1}$$

Number Fluctuations and correlations

- Dimensionless two point correlation function:

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

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

- translational invariance implies:

$$\int d^d r d^d r' G(r-r') = V \int d^d r G(r)$$

$$\int d^d r G(r) = k_B T \kappa_T$$

$$G(r) \propto \frac{e^{\frac{|r|}{\xi}}}{|r|^{\frac{(d-1)}{2}} \xi^{\frac{(d-3)}{2}}}$$

Critical Opalescence:

- in a fluid the two-point correlation function also measures the density fluctuations, which are able to scatter light

Structure factor: $$S(k) = \rho \int d^d r e^{-ikr} G(r)$$

$$I \propto S(k) = \frac{k_B T \kappa_T \rho}{1 + k^2 \xi^2(T)}$$

- The divergence of S(k) is observable, because the scattering of light increases dramatically near the critical point.
  This phenomenon is called critical opalescene.

Measurement of critical exponents

- a critical exponent describes only the leading behavior, there are usually corrections to scaling

$$C_V(T) = A\,|t|^{-\alpha}\left(1 + B\,|t|^{\theta} + ...\right)$$

- there are also constants of proportionality like critical amplitudes

Determination of critical exponents

- we need very high resolution thermometry
- the analytic background has to be substracted
- instrumental resolution, impurity effects or the finite size of the system cause rounding of the divergence
- a priori we don`t know T_c
- critical slowing down

$$\tau_0 \propto \xi(T)^z$$