Statistical Mechanics

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Contents

1 Thermodynamics (TD)

- TD is motivated by applications: steam engines

- TD deals with macroscopic equilibrium states.

Definition 1.1 (Macroscopic state)**.** A description of a system based macroscopic measurements. Temperature, volume, mass, energy, pressure...

A macroscopic state is not infinitely precise. It doesn't refer to a particle.

Definition 1.2 (Equilibrium state)**.** A macroscopic state that does NOT change in time. No net transfer of energy or particle or of the system.

Definition 1.3 (State function)**.** A function of the small number of quantities that specifies an equilibrium state.

Main Assumption: For every equilibrium state there is a state function called the ENTROPY.

1.1 Postulates of TD

1. **Existence of S**:
$$S \equiv S(U, V, N).$$

The fundamental relation (in the entropy representation)
A macroscopic system has equilibrium states that are characterised uniquely by a small set of extensive variables.

Definition 1.4 (Extensive variables)**.** Provides a measure of the size of a system. Answer "how much" questions. (U: energy, V:Volume, N:Number of particle (mass).)

The fundamental relation gives all TD info about the system. (because you can invert the equation above to get U,V,N)

Figure 1: Box with removable wall.

2. **Maximisation:** The values of the extensive variables of an isolated system in the absence of an internal constraint are those that maximise the entropy over the set of all constrained macroscopic states. We have then:

$$S(U_A, V_A, N_A, U_B, V_B, N_B)$$

$$U = U_A + U_B$$

same for V, N Removing wall, the values of U_A, V_A, N_A will be such that it maximises S.

3. **Additivity**: The entropy of a composite system is additive over its constituent subsystems.

$$S(X_A, X_B) = S(X_A) + S(X_B)$$

This is not true if there exist long range forces but usually well satisfied.
Hold whenever interactions between particles are much shorter than the system size.

4. **Continuity and Differentiability:** The entropy is a continuous and differentiable function of the extensive parameters. (NOT true at phase transitions.)

5. **Extensivity:** The entropy is an extensive function of its extensive variables.

$$S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N) \quad \lambda \in \mathbb{R}$$

(Only holds if surface effects can be neglected.)

6. **Monotonicity:** The entropy is a monotonically increasing function of energy for equilibrium volumes of the energy.

$$\frac{\partial S}{\partial U}|_{V,N} > 0$$

(Something funny happens at negative temperature.)

7. **Nernst postulate:** The entropy of any real physical system is non-negative.(Only applies to QM systems. Doesn't apply to f.eks ideal gas.)

Definition 1.5 (Temperature in TD)**.**

$$\left(\frac{\partial S}{\partial U}\right)|_{N,V} \equiv \frac{1}{T}$$

1.2   TD laws

- If two systems are in equilibrium with a third system, they are also in equilibrium with each other. (Their intensive variables are equal)

- Heat is energy and energy us conserved.

- After the release of a constraint in a closed system, the entropy never decreases.

- The entropy of a quantum mechanical system goes to a constant as $T \to 0$.

0th law: It follows from P.2(maximisation) and P.3(additivity).

$$S = S(U_A, V_A, N_A) + S(U_B, V_B, N_B)$$

$$U_B = U - U_A$$

Caclulations

2 Small Changes: Inexact and exact differentials

Consider a function of 2 variables $F(x, y)$ The differential of this is:

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy \tag{1}$$

This is an exact differential.
Exact differential gives a **unique (does not depend on the integration path)** function (up to a constant) when integrated.

$$\int_{(0,0)}^{(x,y)} df = \int_{(0,0)}^{(,y)} \frac{\partial f}{\partial y} dy + \int_{(0,y)}^{(x,y)} \frac{\partial F}{\partial x} dx$$

Condition for exact differential:
$$\left(\frac{\partial f}{\partial y}\right)_x = \left(\frac{\partial g}{\partial x}\right)_y$$

But not every differential

$$đf = f(x, y)dx + g(x, y)dy$$

is exact For instance:

$$đF = -ydx + xdy$$

is not exact. (The integral is path dependant.)

$$\int_{(0,0)}^{(x,y)} đF = \int_{(0,0)}^{(x,0)} -ydx + \int_{(x,0)}^{(x,y)} xdy = xy,$$

$$\int_{(0,0)}^{(x,y)} đF = \int_{(0,0)}^{(0,y)} x\, dy + ...$$

Not the same.

We can always find an integrating non unique factor (function) so that

$$dG = r(x, y) \; đF$$

For

$$đF = -ydx + xdy$$

want

$$dG = (-r(x, y)y)dx + (r(x, y)x)dy$$

$r = \frac{1}{xy}$

This is the same thing as used when solving first order diff.equation.

Next: work and heat are not exact.

Conservation of energy: $dU = đQ$(Heat added) $+ đW$(work done **on** the system) U is a state function so dU is exact. $đQ$ and $đW$ are inexact as they cannot be derived.

2.0.1 Work

$$đW = \vec{F_{outer}} \cdot d\vec{x} > 0 \tag{2}$$

$$F_{outer} = -F_{inside}$$

$$đW = -F_{inner} \cdot dx$$

$$đW = -pdV$$

$$-\frac{1}{p}đW = dV$$

Here $-1/p$ plays the role of an integrating factor.

$$\int_{(0,0)}^{(p,v)} = \int_{(0,0)}^{p,0} + \int_{(p,0)}^{p,V} -pdV = -pV$$

$$\int_{(0,0)}^{(p,v)} = \int_{(0,0)}^{(0,v)} -pdV = 0$$

Path dependant work can also be magnetic or electric.

2.0.2 Heat

$$dS = S(U + đQ, V, N) - S(U, V, N)$$

$$= \left(\frac{\partial S}{\partial U}\right)_{(v,N)} đQ$$

$$\implies đQ = TdS$$

$$dS = \frac{1}{T}đQ$$

2.0.3 Conservation of energy

$dU = đQ + đW$

$$dU = TdS - pdV$$

(N const)

$$U = U(S, V, N)$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN$$

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T$$

$$\left(\frac{\partial U}{\partial V}\right)_{S,N} = -P$$

$$\left(\frac{\partial V}{\partial N}\right)_{(S,V)} \equiv \mu$$

With N varying:

$$dU = TdS - PdV + \mu dN$$

In entropy representation:

$$S = S(U, V, N)$$

$$dS = \left(\frac{\partial S}{\partial U}\right)_{(V,N)} + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN$$

$$dS = \frac{1}{T}dV + \frac{P}{T}dV - \frac{\mu}{T}dN$$

2.1 TD Processes

For all processes in a closed system,
$$dS \geq 0$$

$dS = 0$ when system is already in equilibrium.
Processes when $dS > 0$ in termed irreversible.

2.1.1 Quasistatic process

Definition 2.1. In the limit of infinitesimal changes at an equilibrium system (very slow ideal process)
$$\Rightarrow dS = 0$$

It's an idealisation, doesn't exist.

2.1.2 Heat Engines

Produce work from heat (steam engine).

Such engines are cyclic,
$$dU = 0, \quad dS = 0, \quad dV = 0, \quad dN = 0$$
in a cycle.
$$dU = 0 \implies đQ + đW = 0$$
$$\implies -đW = đQ$$

$$dS = 0$$
$$TđQ = 0$$

This shit doesn't do any work, new engine: Need a hot and a cold reservoir (to dump heat)

$$\frac{đQ_i}{T_i} - \frac{đQ_o}{T_o} = 0$$

$$\implies đQ_o = \frac{T_i}{T_o}đQ_i$$

$$đQ_i - đQ_0 + đW = 0$$

$$\implies -đW = đQ_i(1 - \frac{T_o}{T_i})$$

Efficiency

$$\eta = \frac{-đW}{đQ_i} = 1 - \frac{T_o}{T_i} = \frac{T_i - T_o}{T_i}$$

2.1.3 Fridge and Air conditioners

Diagram

Fridges are heat engines run in reverse.

$$ \text{d}W + \text{d}Q_I - \text{d}Q_o = 0 \quad (dU = 0) $$

$$ \frac{\text{d}Q_I}{T_I} - \frac{\text{d}Q_o}{T_o} \quad dS = 0 $$

Coefficient of Performance is

$$ COP_{cooling} = \frac{-\text{d}Q_o}{\text{d}W} $$

$$ \implies \text{d}Q_I = T_I \frac{\text{d}Q_o}{T_o} $$

$$ \left(\text{d}W + (\frac{T_I}{T_o} - 1)\text{d}Q_o \right) = 0 $$

Reduce efficiency as $T_o \to 0$.

2.1.4 Heat Pumps

Same as refridgerators, but inside of fridge is outside of the house.

$$ COP_{heating} = \frac{\text{d}Q_I}{\text{d}W} = \frac{1}{1 - \frac{T_o}{T_I}} = \frac{T_I}{T_I - T_O} $$

with

$$ \text{d}Q_O = \frac{T_o}{T_I}\text{d}Q_I $$

$$ \text{d}W + \text{d}Q_I - \frac{T_o}{T_I}\text{d}Q_I = 0 $$

$$ \text{d}W = \text{d}Q_I \left(\frac{T_O}{T_I} - 1 \right) $$

For a non-reversible engine:

$$ dS = \frac{\text{d}Q_I}{T_I} - \frac{\text{d}Q_O}{T_O} + \text{d}A $$

A is the positive entropy generated in a cycle.

3 TD Potentials

Fundamentlal relation:
$$S = S(U, V, N) \text{ or } U = U(S, V, N)$$

from this we can derive all TD.

Example 3.1 (Ideal Gas).
$$S = N k_B \left(\frac{3}{2} ln(\frac{V}{N}) + ln(\frac{V}{N}) + ln X \right)$$

where X is independent of U, V, N

$$\frac{1}{T} = \frac{\partial S}{\partial V}_{V,N} = \frac{3}{2} N k_B \frac{1}{U}$$

$$\implies U = \frac{3}{2} N k_b T$$

$$\frac{P}{T} = \frac{\partial S}{\partial V}_{V,N} = \frac{N k_b}{V}$$

$$\implies PV = N k_B T$$

$$-\frac{\mu}{T} = \frac{\partial S}{\partial N}_{U,V} = \frac{S}{N} - N k_B \frac{5}{2} \frac{1}{N} = \frac{S}{N} - \frac{5}{2} k_B$$

$$\implies S = \frac{5}{2} k_B N - \frac{\mu N}{T}$$

These are all equations of states, not fundamental relations.

How can we extract TD info at constant T, P etc. ?
$$T = \frac{\partial U}{\partial S}_{V,N} - \frac{\partial U}{\partial V}_{S,N}$$

3.1 Legendre Transform

Given $y = y(x)$ let's call $\frac{\partial y}{\partial x} = p$
$$\tilde{y}(p)$$

Try $\tilde{y} = y$ and make a table.
  Useless, no way to know where on the x-axis.

$$\begin{array}{cc} p & y \\ \dots & \dots \end{array}$$

Second try: replace $\tilde{y}$ by the y-intercept of the curved tangent. This works, but requires $\frac{\partial y}{\partial x}$ monotonic (as temperature is).

$$y - \tilde{y} = px$$
$$\tilde{y} = y - px$$

Example 3.2.

$$y = x^2$$

$$p = \frac{\partial y}{\partial x} = 2x \implies x = \frac{p}{2}$$

$$\tilde{y}(p) = y - px = x^2 - px = \frac{p^2}{2} - p\frac{p}{2} = -\frac{p^2}{y}$$

Inverse:

$$y(x) = \tilde{y} + px = -\frac{p^2}{y} + px = \frac{-(2x)^2}{y} + 2x^2 = x^2$$

Differentials:

$$d\tilde{y} = dy - pdx - dpx = -xdp$$

$$dy = d\tilde{y} + xdp + pdx = pdx$$

Switches and negative.

3.2 Helmholtz free energy

$$U = U(S, V, N)$$

want a function of T, V, N that gives all TD info.

$$T = \frac{\partial U}{\partial S}\bigg|_{V,N}$$

$$F = U - TS$$

eliminate U, S in favour of T, V, N

$$= F(T, V, N)$$

(is a fundamental relation.)

$$dF = dU - TdS - sdT$$

recall $dU = TdS - PdV + \mu dN$

$$= -sdT - PdV + \mu dN$$

$$\implies -S = \frac{\partial F}{\partial T}\bigg|_{V,N} \quad -p = \frac{\partial F}{\partial V}\bigg|_{T,N} \quad \mu = \frac{\partial F}{\partial N}\bigg|_{T,V}$$

3.3 Enthalpy

P instead of v.

$$p = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$$

$$H = U + PV$$

want to eliminate V

$$= H(S, P, N)$$

$$dH = TdS + VdP + \mu dN$$

$$T = \frac{\partial H}{\partial S}\bigg|_{P,N} \quad V = \frac{\partial H}{\partial P}\bigg|_{S,N} \quad \mu = \frac{\partial H}{\partial N}\bigg|_{S,P}$$

For experiments at constant P, N Then

$$dH = TdS = đQ$$

or

$$dH = đQ$$

(No integrating factor since it's one dimensional.)

3.4 Gibbs free energy

Double Legendre transform: replace S with T and replace V by P.

$$G = U - TS + PV = G(T, P, N)$$

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

$$-S = \frac{\partial G}{\partial T}\bigg|_{P,N}, \quad V = \frac{\partial G}{\partial P}\bigg|_{T,N} \quad \mu = \frac{\partial G}{\partial N}\bigg|_{P,T}$$

3.5 Summary

- Energy: $U(S, V, N)$

- Helmholtz $F(T, V, N) = U - TS$

- Enthalpy $H(S, P, N) = U + PV$

- Gibbs: $G(T, P, N) = U - TS + PV$

- $f(S, V, \mu) = U - \mu N$

- Grand potential (Landau potential) : $\Omega(T, V, \mu) = U - TS - \mu N$

- $f(S, P, \mu) = U + PV - \mu N$

- $f(T, P, \mu) = U - TS + PV - \mu N$

4 Extensivity

From the postulate,

$$S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N)$$

in systems where surface effect can be neglected.

Assume that it holds: For energy:

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N)$$

Now vary λ: Differentiate w.r.t λ and let $\lambda = 1$

$$\text{LHS} = \frac{\partial}{\partial \lambda} U(\lambda S, \lambda V, \lambda N) = \frac{\partial}{\partial(\lambda S)} U(\lambda S, \lambda V, \lambda N) \left(\frac{\partial(\lambda S)}{\partial \lambda}\right)_{\lambda=1} + \frac{\partial}{\partial \lambda V} U(\lambda S, \lambda V, \lambda N) \left(\frac{\partial(\lambda V)}{\partial \lambda}\right)_{\lambda=1}$$

$$+ \frac{\partial}{\partial(\lambda N)} U(\lambda S, \lambda V, \lambda N)$$

$$\text{RHS} = U(S, V, N)$$

$$\implies TS - PV + \mu N = U \quad \text{Euler's equation} \tag{3}$$

For the entropy equation:

$$S = \frac{U}{T} + \frac{P}{T} V - \frac{\mu}{T} N.$$

Same stuff.

4.1 Gibbs-Duhem relation

Euler's equation:

$$U = TS - PV + \mu N$$

differentiate:

$$dU = \underbrace{TdS - PdV + \mu dN}_{dU} + SdT - VdP + Nd\mu$$

$$\implies 0 = SdT - VdP + Nd\mu \tag{4}$$

So changes in T, P, N are not independent for an extensive system.

For instance:

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

4.2 TD Potentials and Extensivity

$$\text{Euler's Equation } U = TS - PV + \mu N$$

$$\text{Helmholtz } F = U - TS = -PV + \mu N$$

$$\text{Enthalpy} H = U + PV = TS + \mu N$$

$$\text{Gibbs } G = U - TS + PV = \mu N$$

$$f(T, P, \mu) = U - TS + PV - \mu N = 0 \quad \text{Check on extensivity}$$

5 TD identities

Derivatives: What is held constant matters!
Ideal gas:

$$U = \frac{3}{2}Nk_BT, \quad PV = Nk_BT$$

$$\frac{\partial U}{\partial V}_{T,N} = 0$$

$$\frac{\partial U}{\partial V}_{P,N} = \frac{\partial}{\partial V}(\frac{3}{2}PV)_{P,N} = \frac{3}{2}P$$

$$\frac{\partial U}{\partial V}_{S,N} = -P$$

Other TD potentials

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

See previous section for derivatives. We are often interested in quantities like

$$\frac{\partial V}{\partial P}_{T,N} = \left(\frac{\partial^2 G}{\partial P^2}\right)_{T,N} = -V\kappa_T$$

5.1 Standard Quantities

Coefficient of thermal expansion:

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N} \tag{5}$$

Isothermal compressibility:

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N} \tag{6}$$

The negative sign in front is because most substance shrink when applying pressure.
Specific heat at constant pressure:

$$C_p = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_{P,N} \tag{7}$$

Specific heat at constant volume:

$$C_v = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_{V,N} \tag{8}$$

Heat capacity: = specific heat × N

5.2 Maxwell Relations

For N constant:
$$dU = TdS - PdV$$

because dU is an exact differential (orders of derivative doesn't matter):

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N}$$

From
$$dF = -SdT - PdV + \mu dN$$
$$\frac{\partial S}{\partial V}_{V,N} = \frac{\partial P}{\partial T}_{V,N}$$

and from unnamed potential:
$$\left(\frac{\partial T}{\partial P}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{P,N}$$

6 Manipulating partial derivatives as Jacobians

Jacobian:
$$\frac{\partial(U,V)}{\partial(x,y)} \equiv \begin{bmatrix} \frac{\partial U}{\partial x} & \frac{\partial U}{\partial y} \\ \frac{\partial V}{\partial x} & \frac{\partial V}{\partial y} \end{bmatrix} = \frac{\partial U}{\partial x}\frac{\partial V}{\partial y} - \frac{\partial U}{\partial y}\frac{\partial V}{\partial x} \tag{9}$$

can be extended to any number of variables by adding rows and columns.
Property of Jacobians
$$\frac{\partial(U,V)}{\partial(x,y)} = -\frac{\partial(V,U)}{\partial(x,y)}$$
$$= -\frac{\partial(U,V)}{\partial(y,x)} = \frac{\partial(V,U)}{\partial(y,x)}$$

6.1 Connection to partial derivatives

$$\frac{\partial(U,y)}{\partial(x,y)} = \begin{bmatrix} \frac{\partial U}{\partial x} & \frac{\partial U}{\partial y} \\ \frac{\partial y}{\partial x} & \frac{\partial y}{\partial y} \end{bmatrix} = \left(\frac{\partial U}{\partial x}\right)_y$$

So
$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = \frac{\partial(F,V,N)}{\partial(T,V,N)}$$

Chain rule:
$$\frac{\partial(U,V)}{\partial(x,y)} = \frac{\partial(U,V)}{\partial(r,s)}\frac{\partial(r,s)}{\partial(x,y)}$$

$$= \begin{vmatrix} U_r & U_s \\ V_r & V_s \end{vmatrix} \cdot \begin{vmatrix} r_x & r_y \\ s_x & s_y \end{vmatrix}$$

$$= \begin{vmatrix} U_r r_x + U_s s_x & U_r r_y + U_s s_y \\ v_r r_x + v_s s_x & v_r r_y + v_s s_y \end{vmatrix}$$

Using rule:

$$det(AB) = det(A)det(B)$$

An identity:

$$\frac{\partial(U,V)}{\partial(x,y)} \frac{\partial(a,b)}{\partial(c,d)} = \frac{\partial(u,v)}{\partial(c,d)} \frac{\partial(a,b)}{\partial(x,y)}$$

chain rule gives:

$$\frac{\partial(U,V)}{\partial(x,y)} \frac{\partial(a,b)}{\partial(c,d)} = \frac{\partial(U,V)}{\partial(r,s)} \frac{\partial(r,s)}{\partial(x,y)} \frac{\partial(a,b)}{\partial(r,s)} \frac{\partial(r,s)}{\partial(c,d)}$$

$$= \frac{\partial(U,V)}{\partial(r,s)} \frac{\partial(r,s)}{\partial(c,d)} \frac{\partial(a,b)}{\partial(r,s)} \frac{\partial(r,s)}{\partial(x,y)}$$

$$= \frac{\partial(U,V)}{\partial(c,d)} \frac{\partial(a,b)}{\partial(x,y)}$$

Reciprocals:

$$\frac{\partial(U,V)}{\partial(U,V)} = \begin{vmatrix} \frac{\partial U}{\partial U} & \frac{\partial U}{\partial V} \\ \frac{\partial V}{\partial U} & \frac{\partial V}{\partial V} \end{vmatrix} = \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix}$$

chain rule:

$$1 = \frac{\partial(U,V)}{\partial(U,V)} = \frac{\partial(U,V)}{\partial(x,y)} \frac{\partial(x,y)}{\partial(U,V)}$$

$$\implies \left(\frac{\partial U}{\partial x} \right)_y = \frac{\partial(U,y)}{\partial(x,y)}$$

$$= \left(\frac{\partial(x,y)}{\partial(U,y)} \right)^{-1}$$

Example 6.1.

$$\left(\frac{\partial P}{\partial T} \right)_{V,N}$$

in terms standard quantities. Standard quantities:

$$\alpha = \left(\frac{\partial V}{v \partial T} \right)_{P,N}$$

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T,N}$$

$$C_p = \frac{T}{N} \left(\frac{\partial S}{\partial T} \right)_{P,N}$$

$$\left(\frac{\partial P}{\partial T} \right)_{V,N} = \frac{\partial(P,V,N)}{\partial(T,V,N)} = \frac{\partial(P,V,N)}{\partial(P,T,N)} \underbrace{\frac{\partial(P,T,N)}{\partial(T,V,N)}}_{-\partial(V,T,N)} - \left(\frac{\partial V}{\partial T} \right)_{P,N} \left(\frac{\partial P}{\partial V} \right)_{T,N}$$

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$$= \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N} \frac{1}{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N}}$$

$$= \frac{\alpha}{\kappa_T}$$

Example 6.2. $\left(\frac{\partial T}{\partial P}\right)_{H,N}$ in terms of std. quantities.

$$\left(\frac{\partial T}{\partial P}\right)_{H,N} = \frac{\partial(T,H,N)}{\partial(P,H,N)} = \frac{\partial(T,H,N)}{\partial(T,P,N)} \frac{\partial(T,P,N)}{\partial P,H,N} = -\frac{\partial(H,T,N)}{\partial(P,T,N)} \frac{\partial(T,P,N)}{\partial(H,P,N)} = \frac{\left(\frac{\partial H}{\partial P}\right)_{T,N}}{\left(\frac{\partial H}{\partial T}\right)_{P,N}}$$

$$= \frac{V(T\alpha - 1)}{NC_p}$$

$$dH = TdS + VdP + \mu dN$$

$$\left(\frac{\partial H}{\partial P}\right)_{T,N} = T\left(\frac{\partial S}{\partial P}\right)_{T,N} + V = V - T\left(\frac{\partial V}{\partial T}\right)_{P,N}$$

Want $\left(\frac{\partial S}{\partial P}\right)_{T,N}$ Maxwell relation

$$-SdT + VdP + \mu dN = 0$$

$$\implies \left(\frac{\partial S}{\partial P}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{P,N}$$

$$\left(\frac{\partial H}{\partial T}\right)_{P,N} = T\left(\frac{\partial S}{\partial T}\right)_{P,N}$$

$$dH = TdS \implies \Delta H = T\Delta S$$

$$\frac{\Delta H}{\Delta T} = \frac{T\Delta}{\Delta T} = \frac{T(S(T + \Delta T) - S(T))}{\Delta T}$$

$$\frac{\Delta H}{\Delta T} = \frac{T\Delta S}{\Delta T}$$

Which T ? $T, T + \Delta T$ or something else? Check an arbitrary $T + g\Delta T$

$$\frac{\Delta H}{\Delta w T} = \frac{(T + g\Delta T\Delta S)}{\Delta T} = \frac{T\Delta S}{\Delta T} + g\Delta S \to 0 \quad when \Delta \to 0$$

$$\left(\frac{\partial H}{\partial T}\right)_{P,N} = T\left(\frac{\partial S}{\partial T}\right)_{P,N}$$

Example 6.3 (Cp and Cv).

$$C_v = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_{V,N} = \frac{T}{N}\frac{\partial(S,V,N)}{\partial(T,V,N)}$$

$$= \frac{T}{N}\frac{\partial(S,V,N)}{\partial(T,P,N)}\underbrace{\frac{\partial(T,P,N)}{\partial(T,V,N)}}_{\frac{\partial(P,T,N)}{\partial(V,T,N)} = \frac{1}{\left(\frac{\partial V}{\partial P}\right)_{T,N}}}$$

$$= -\frac{T}{NVK_T} \frac{\partial(S,V,N)}{\partial(T,P,N)}$$

$$\frac{\partial(S,V,N)}{\partial(T,P,N)} = \left(\frac{\partial S}{\partial T}\right)_{P,N} \left(\frac{\partial V}{\partial P}\right)_{T,N} - \left(\frac{\partial V}{\partial T}\right)_{P,N} \left(\frac{\partial S}{\partial P}\right)_{T,N}$$

$$= \frac{NVC_P\kappa_T}{T} + (\alpha V)^2$$

$$\implies C_V = \frac{-T}{NVK_T} \left(\frac{-NVK_TC_P}{T} + (\alpha V)^2\right)$$

or

$$C_P = C_V + \frac{T\alpha^2 V}{NK_T}$$

7 Extrema Principles

TD postulate: $S = S(U,V,N,X)$ (N unconstrained extensive variable), is maximized for U, V, N constant as a function of X. X is the position of the wall. In equilibrium:

$$\frac{\partial S}{\partial X}_{U,V,N,X_0} = 0$$

X_0 is the equilibrium value.

$$\frac{\partial^2 S}{\partial x^2}_{U,V,N,X_0} < 0$$

since entropy is max.

Similarly, U = U(S,V,N,X) is minimized for S, V, N constant.

Proof. Near equilibrium at constant V and N

$$dS = \frac{\partial S}{\partial U}_{V,N,X_0,U_0} dU + \frac{\partial S}{\partial X}_{U,V,N,X_0} dX + \frac{1}{2}\left(\frac{\partial^2 S}{\partial X^2}\right)_{U,V,N,X_0} dx^2$$

$$\implies dU = TdS - \frac{T}{2}\left(\frac{\partial^2 S}{\partial X^2}\right)_{U,V,N,Xo} dX^2$$

For S, V, N constant:

$$dU = -\frac{T}{2}\left(\frac{\partial^2 S}{\partial X^2}\right)_{U,V,N,X_0} dX^2 > 0$$

U has a minimum in equilibrium for S, V, N constant. □

Process is where entropy is constant and system minimises energy by doing work on the surroundings.

7.1 Helmholtz Free Energy F

F is minimal in equilibrium for constant T, V, N

A big box with system inside and within the system there's a movable wall with a piston connected to the wall which goes outside of the system and the box. Outside the system inside the box is the reservoir, can exchange heat, but with V, N constant. In equilibrium:

$$\frac{\partial(U + U_R)}{\partial X} = 0 \quad \text{for const. } V + V_R, N + N_R, S + S_R$$

where U is system energy.

$$\frac{\partial^2}{\partial X^2}(U + U_R) > 0$$

Entropy is conserved: $\frac{\partial(S+S_R)}{\partial X} = 0$

$$F = U - TS$$

$$\frac{\partial F}{\partial X} = \frac{\partial U}{\partial X} - \frac{\partial}{\partial X}(T_R S) = \frac{\partial U}{\partial X} - T_R \frac{\partial S}{\partial X}$$

$$= \frac{\partial U}{\partial X} + T_R \frac{\partial S_R}{\partial X}$$

Since reservoir can't do work or anything

$$T dS = dU$$

so

$$= \frac{\partial}{\partial X}(U + U_R) = 0$$

$$\frac{\partial^2 F}{\partial X^2} = \frac{\partial^2 U}{\partial X^2} + \frac{\partial^2 U_R}{\partial X^2} = \frac{\partial^2}{\partial X^2}(U + U_R) > 0$$

The max work that can be extracted:

$$dF = -S dT + đW + \mu dN$$

with $đW = -P dV + đW'$ and $đW'$ is other work For constant T, V, N

$$dF = đW'$$

Free energy Enthalpy and Gibbs free energy are also minimized in equilibrium (see 15.3 and 15.4, Swendsen.)

7.2 Exergy

$$dU = T dS - P dV + đW_X + \mu dN$$

$đW_X$ is work on system by moving internal wall. For constant T, P, N, G is minimized

$$dG = -S dT + V dP + \mu dN + đW_X$$

$$\implies dG = \text{đ}W_X$$

at $P = P_0, T = T_0$ standard $T_0 = $ room temp, $P_0 = 1$atm.

$$Exergy = G(T_0, P_0, X) - G(T_0, P_0, X_0)$$

This is the amount of work that can be extracted at standard pressure and temperature. (Important in engineering for machines in real environment.)
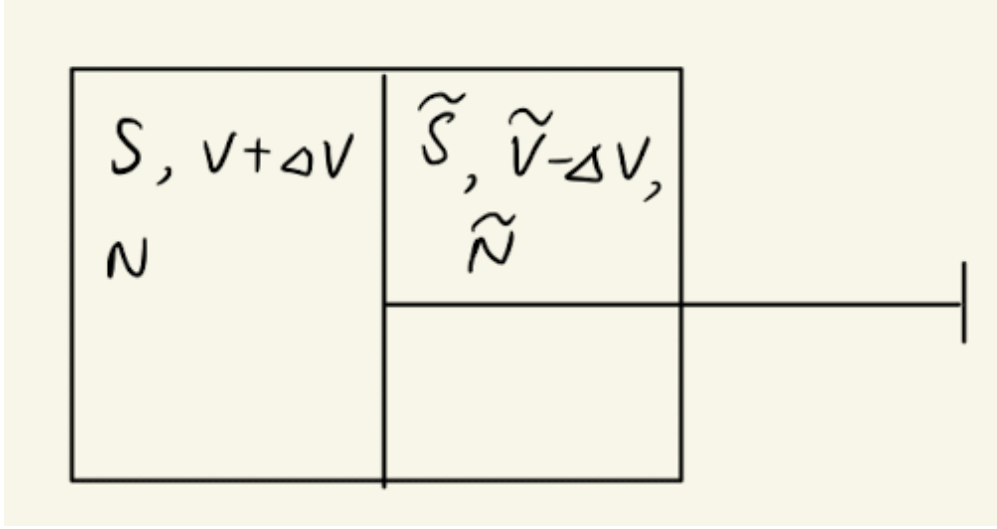
8 Stability Conditions

8.1 Composite system

Figure 2: Composite system

Using the additivity postulate:

$$\Delta U = U(S, V + \Delta V, N) + \tilde{U}(\tilde{S}, \tilde{V} - \Delta, \tilde{N}) - (U(S, V, N) + U(\tilde{S}, \tilde{V}, \tilde{N})) \geq 0 \qquad (10)$$

The second term is the equilibrium energy, and it's minimised.

Specialise to identical systems:

$$\tilde{U} = U$$

Then

$$\Delta U = U(S, V + \Delta V, N)v + U(S, V - \Delta V, N) - 2U(S, V, N) \geq 0$$

For ΔV infinitesimal:

$$\frac{\partial^2 U}{\partial V^2}(\Delta V)^2$$

$$\implies \left(\frac{\partial^2 U}{\partial V^2}\right)_{S,N} \geq 0$$

$$dU = TdS - PdV + \mu dN$$

$$\frac{\partial U}{\partial V}_{S,V} = -P$$

$$\left(\frac{\partial^2 U}{\partial^2}\right)_{S,N} = -\frac{1}{\left(\frac{\partial V}{\partial P}\right)_{S,V}}$$

$$= \frac{1}{VK_s} \geq 0$$

$$K_s > 0 \qquad (11)$$

where K_s is the isentropic compressibility.

8.2 Heat Transfer

$$\Delta U = U(S + \Delta S, V, N)v + U(S - \Delta S, V, N) - 2U(S, V, N) \geq 0$$

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_{V,N} \geq 0$$

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T \implies$$

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_{V,N} = \left(\frac{\partial T}{\partial S}\right)_{V,N} = \left[\left(\frac{\partial S}{\partial T}\right)_{V,N}\right]^{-1}]$$

$$= \left[\frac{N}{T}\frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_{V,N}\right]^{-1} \geq 0$$

8.3 Volume Exchange for Helmholtz Free Energy

$$\Delta F = F(T, V + \Delta V, N) + F(T, V - \Delta V, N) - 2F(T, V, N) \geq 0$$

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

$$\implies \left(\frac{\partial F}{\partial V}\right)_{T,N} = -P$$

$$\left(\frac{\partial^2 F}{\partial V^2}\right)_{T,N} = \left(\frac{\partial P}{\partial V}\right)_{T,N} = \left[v\frac{1}{-v}\left(\frac{\partial V}{\partial P}\right)_{T,N}\right]^{-1}$$

$$\frac{1}{V K_T} \geq 0$$

$$\implies K_T \geq 0$$

8.4 Heat Exchange for Enthalpy

$$H(S + \Delta S, P, N) + H(S - \Delta S, P, N) - 2H(S, P, N) \geq 0$$

$$\implies \left(\frac{\partial^2 H}{\partial S^2}\right)_{P,N} \geq 0$$

$$\left(\frac{\partial H}{\partial S}\right)_{P,N} = T$$

$$\left(\frac{\partial^2 H}{\partial S^2}\right)_{P,N} = \left[\left(\frac{\partial S}{\partial T}\right)_{P,N}\right]^{-1} \geq 0$$

$$\implies C_p \geq 0$$

8.5 What about intensive variables?

We use TD relations.

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S, \quad \left(\frac{\partial^2 F}{\partial T^2}\right)_{V,N} = -\left(\frac{\partial S}{\partial T}\right) = \frac{-1}{\left(\frac{\partial^2 U}{\partial S^2}\right)_{V,N}} < 0$$

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T, \quad \left(\frac{\partial^2 U}{\partial S^2}\right)_{V,N}$$

so

$$\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,N} < 0 \tag{12}$$

8.6 Van der Waal's gas

Ideal gas:

$$F = -Nk_bT\left[ln(\frac{V}{N}) + \frac{3}{2}ln(k_BT) + X\right]$$

Free, non-interacting particles
Include interactions "treated crudely":

The interaction has two main effects:

1. Energy is lowered by the mean interaction energy $\propto \frac{N}{V}$ per particle.

2. The hard-core potential restricts the volume to $V \to V - Nb$

$$F_{VDW} = -Nk_BT\left[ln(\frac{V - Nb}{N}) + \frac{3}{2}ln(k_BT) + X\right] - a\frac{N^2}{V}$$

where a (measure of attraction) and b (hard-core) are constants. This is an extensive system, meaning we could use the Euler's equation.
Pressure:

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{Nk_BT}{V - Nb} + a\frac{N^2}{V^2}$$

Stability:

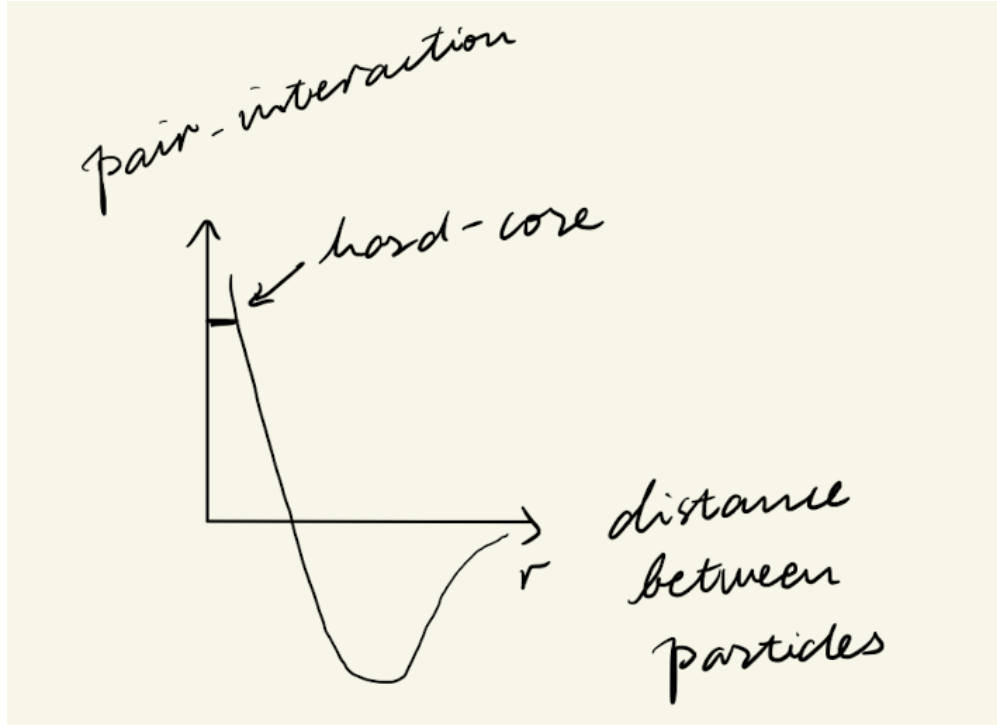$$\left(\frac{\partial^2 F}{\partial V^2}\right)_{T,N} \geq$$

Figure 3: Van der Waal interaction model.

$$\left(\frac{\partial F}{\partial V}\right)_{T,N} = -P$$

$$\left(\frac{\partial^2 F}{\partial V^2}\right)_{T,N} = -\left(\frac{\partial P}{\partial V}\right)_T , N) > 0$$

$$\implies \left(\frac{\partial P}{\partial V}\right)_{T,N} < 0$$

The highlighted part is unstable since $\left(\frac{\partial P}{\partial V}\right)_{T,N} \geq 0$.

Want to calculate the critical temperature T_c:

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

$$\frac{\partial P}{\partial V} = \frac{-Nk_BT}{(V_Nb)^2} + 2a\frac{N^2}{V^3} = 0$$

$$\implies Nk_BTV^3 = 2aN^2(V - Nb)^2$$

$$(\frac{\partial^2 P}{\partial V^2} = \frac{2Nk_BT}{(V - Nb)^3} - 6a\frac{N^2}{V^4} = 0$$
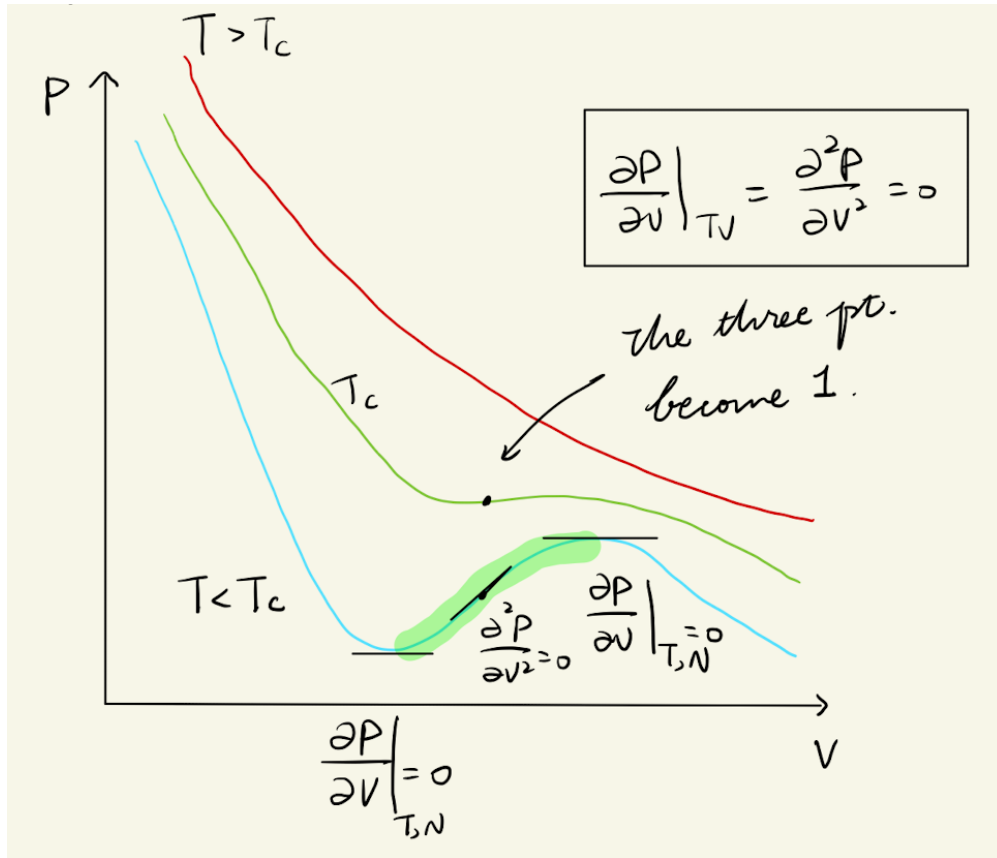
$$\implies 2Nk_BTV^4 = 6aN^2(V - Nb)^3$$

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Figure 4: Pressure vs Volume diagram.

Combine:

$$2V = 3(V - Nb)$$

$$\implies V_c = 3Nb$$

and

$$k_B T_c = \frac{2aN^2(3Nb - Nb)^2}{N(3Nb)^3} = \frac{8}{27}\frac{a}{b}$$

$$P_c = \frac{N_k BT}{V_c - Nb} - a\frac{N^2}{V_c^2} = \frac{1}{27}\frac{a}{b^2}$$

$$\frac{P_c V_c}{N k_B T_c} = \frac{3}{8}$$

Ideal gas: 1

insert Fig.4 Both unphysical, unstable.

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$$

$$\left(\frac{\partial P}{\partial V}\right)_{T,N} = -\left(\frac{\partial^2 F}{\partial V^2}\right)_{T,N} < 0$$

For stability.

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,N}$$

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

second derivative of intensive variabel less than 0 for stability.

insert Fig.5 Cap:Van der Waal's gas at $T < T_C$ Stability

$$\left(\frac{\partial^2 F}{\partial V^2}\right)_{T,N} > 0 \Rightarrow \left(\frac{\partial P}{\partial V}\right)_{T,N} < 0$$

This is violated on D-F. Assumption of homogeneity breaks down. The homogeneous solution is unstable (unphysical. NOT realised) on D-F.

insert Fig.6 Maxwell construct: Choose a line which crosses the graph 3 times which also divides the area into 2 equal parts. In the region B-H there are 3 possible values for V given a P (one is unphysical (DF), but there are still two to choose from.) TD stable state at const. P, T, N minimises **Gibbs free energy**. Calculate G ! Van der Waal's gas is extensive:

$$U = TS - PV + \mu N$$

$$G = U - TS + PV = \mu N$$

Recall Gibbs-Duhem relation:

$$d\mu = -\left(\frac{S}{N}\right)dT + \left(\frac{V}{N}\right)dP = \frac{V}{N}dP$$

$$\Longrightarrow G = \int dG = \int d\mu N = \int dPV$$

Area under the curve.

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,N}$$

At C, G there are two phases that coexists: V_C and V_G Since V_C is bigger than V_G, so V_C describes a gas phase and V_C describes a liquid phase.

insert Fig.8 and 9

$$\rho_C = \frac{N}{V_C}, \quad \rho_G = \frac{N}{V_G}$$

8.7 Phases

C-phase: V_C volume fraction $\frac{V_C}{V} = X_C$ G-phase: V_G volume fraction $\frac{V_G}{V} = X_G$

$$\implies V_C + V_G = V \implies X_C + X_G = 1$$

Total number of particles:

$$N = V_C \rho_C^* + V_G \rho_G^*$$

$$\frac{N}{V} = X_C \rho_C^* + X_G \rho_G^*$$

Set $X_G = 1 - X_C$, $\frac{N}{V}$

$$\rho = X_C \rho_C^* + (1 - X_C)\rho_G^*$$

$$X_C = \frac{\rho - \rho_G^*}{\rho_C^* - \rho_G^*}, \quad X_G = 1 - X_C$$

insert Fig.10 From Helmholtz Free energy, $T < T_C$

insert Fig.11

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$$

insert Fig.12

8.8 Clausius-Clapeyron

Assume extensivity $\implies$ Gibbs-Duhem relation

$$d\mu = -\frac{S}{N}dT + \frac{V}{N}dP = -sdT + \frac{1}{n}dP$$

where $s \equiv \frac{S}{N}, \quad n \equiv \frac{N}{V}$

Liquid

$$\mu_2^l - \mu_1^l = -s(T_2^l - T_1^l) + \frac{1}{n^l}(P_2^l - P_1^l)$$

Gas

$$\mu_2^l - \mu_1^l = -s(T_2^l - T_1^l) + \frac{1}{n^l}(P_2^l - P_1^l)$$

l stands for liquid On the ceexistence line in equilibrium:

$$\mu_1^l = \mu_1^g$$

same with all other variables. Subtract the eqs:

$$0 = (s^g - s^l)(T_2 - T_1) + \left(\frac{1}{n^l} - \frac{1}{n^g}\right)(P_2 - P_1)$$

$$\implies \frac{P_2 - P_1}{T_2 - T_1} = \frac{s^g - s^l}{T_2 - T_1} = \frac{s^g - s^l}{\frac{1}{n^g} - \frac{1}{n^l}}$$

$$\implies \left(\frac{\partial P}{\partial T}\right)_{\text{alone coexistence}} = \frac{(s^g - s^l)}{\frac{1}{n^g} - \frac{1}{n^l}}$$

9 More particle types: Gibbs Phase Rule

$$dU = TdS - PdV + \sum_{i=1}^{K} \mu_i dN_i$$

There are $2 + K$ independent variable. Extensive:

$$U = TS - PV + \sum_{i=1}^{k} \mu_i N_i$$

Gibbs-Duhem:

$$d\mu = -\frac{S}{N}dT + \frac{V}{N}dP + \sum_{i=1}^{k} N_i d\mu_i$$

If we have ϕ phases, then there is a Gibbs-Duhem rel. for each phase.

$$0 = S^1 dT^1 - V^1 dP^1 + \sum_{i=1}^{k} N_i^1 d\mu_i^1$$

phase 1

$$\vdots$$

$$0 = S^\phi dT^\phi - V\phi dP^\phi + \sum_{i=\phi}^{k} N_i^\phi d\mu_i^\phi$$

phase ϕ

At coexistence:

$$T_1 = T_2 = ... = T_\phi \quad P_1 = P_2 = ... = P_\phi \quad \forall i \mu_i^1 = \mu_i^2 = ... = \mu_i^\phi$$

(Can omit superscript from T,P, and μ_i)

$$0 = S^1 dT - V^1 dP + \sum_{i=1}^{k} N_i^1 d\mu_i$$

and for all ϕ equations. There are $2 + k$ variables (T, P, μ_i) and ϕ equations. The number of **free variables** at coexistence determines the dimension of the coexistence manifold (multidimensional object).

$$F = 2 + K - \phi$$

Example 9.1 (K=1).

$$F = 3 - \phi$$

$\phi = 2$ (Two phases coexist) $\implies F = 1$ (line) $\phi = 3$ (Three phases coexist) $\implies F = 0$ (point) $\phi = 4$ cannot coexist.

Example 9.2 (Binary Alloy (Two types of atoms)).

$$K = 2$$

$$F = 4 - \phi$$

Here 4 phases can coexist at a point, 3 along a line and 2 on a surface.

10   3. Law of TD

"The entropy of a (real QM) TD system goes to a constant as $T \to 0$."
Violated for the ideal gas:

$$S = k_B N(\frac{3}{2} ln \left(\frac{U}{N}\right) + ln \left(\frac{V}{N}\right)) + X$$

$$= k_B N \left(\frac{3}{2} ln \left(\frac{3}{2} \frac{N k_B T}{N}\right) + ln \left(\frac{V}{N}\right) + X\right)$$

when $T \to 0$, $S \to -\infty$

Planck said it's 0, but it's **NOT**!

10.1   Consequences

$$dS = \frac{đQ}{T} \quad đQ = cdT$$

$$dS = c\frac{dT}{T}, S(T) - S(0) = \int_0^T dS = \int_0^T \frac{dT}{T} C$$

Taking $T \to 0$ will give 0 if integral is not diverging. For integral not to diverge $C(T \to 0) = 0$

Also the thermal expansion coefficient:

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_{P,N} = -\frac{1}{V} \left(\frac{\partial S}{\partial P}\right)_{T,N}$$

$$-SdT + VdP.$$

If S goes to a pressure independent const. at $T \to 0$. Then $\alpha = 0$.

11 Statistical Mechanics

11.1 Binomial Distribution

Probability distribution for flipping coins: 1 coin:

$$1:1$$

2 coins:

$$1:2:1$$

3 coins:

$$1:3:3:1$$

Mean value, increases width increases, maximum (probability) decreases.

$$P(N_\uparrow) = \frac{1^\uparrow}{2}\frac{1^\downarrow}{2} = \frac{N!}{N^\uparrow!(N-N^\uparrow)!}\frac{1}{2}^N$$

What is the characteristic of this distribution when N is large. We need $N!$ for N large

$$N! = \int_0^\infty dx\, x^N e^{-x} = \left(-x^N e^{-x}\big|_0^\infty + N\int_0^\infty dx x^{N-1} e^{-x} \quad \text{and so on}\right)$$

Factorial Expansion

$$N! = \int_0^\infty dx e^{-x+Nln(X)} \tag{13}$$

Use Laplace's method. For N large Approximate the integrand by its value close to the maximum of the exponent. Set

$$g(x) = Nln(x) - x$$

$$\left(\frac{\partial g}{\partial x}\right) = \frac{N}{x} - 1 = 0 \implies X_0 = N$$

$$2\left(\frac{\partial g}{\partial x}\right) = -\frac{N}{x^2}\big|_{x=x_0} = -\frac{1}{N} < 0 \implies x_0 \text{is a max.}$$

$$g(x) \approx g(x_0) + \left(\frac{\partial g}{\partial x}\right)_{x_0}(x-x_0) + \frac{1}{2}2\left(\frac{\partial g}{\partial x}\right)_{x=x_0}(x-x_0)^2$$

$$\implies N! = \int_0^\infty dx e^{Nln(N)-N-\frac{1}{2N}(x-N)^2}$$

$$= e^{Nln(N)-N}\int_0^\infty e^{-\frac{1}{2N}(x-N)^2}$$

For $N >> \sqrt{(N)}$width of the Gaussian we can extend the lower limit to $-\infty$ since it's so small.

$$\implies e^{Nln(N)-N}\int_{-\infty}^\infty dx e^{-\frac{1}{2N}x^2}$$

$$= e^{Nln(N)-N}\sqrt{2\pi N}$$

$$ln(P(N_\uparrow)) = ln(N_\downarrow) - ln(N_\uparrow) - ln\left((N - N_\uparrow)!\right) + N_\uparrow ln(P) + (N - N_\uparrow)ln(1 - p)$$

$$= Nln(N) - N - (N_\uparrow ln(N_\uparrow) - N_\uparrow) - ((N - N_\uparrow)ln(N - N_\uparrow) - (N - N_\uparrow)) + N_\uparrow ln(P) + (N - N_\uparrow)ln(1 - P)$$

$$= Nln(N) - N_\uparrow ln(N_\uparrow) - (N - N_\uparrow)ln(N - N_\uparrow) + N_\uparrow ln(\frac{P}{1-p}) + Nln(1 - P)$$

Maximum:

$$\left(\frac{\partial}{\partial N_\uparrow}\right)ln[P(N_\uparrow)] \implies -ln(N_\uparrow) - \frac{N_\uparrow}{N_\uparrow} + ln(N - N_\uparrow) + 1 + ln(\frac{p}{1-p}) = 0$$

$$\implies ln(\frac{p}{1-p}) = ln(\frac{N_\uparrow}{N - N_\uparrow}) = ln\left(\frac{N_\uparrow/N}{1 - N_\uparrow/N}\right)$$

$$\implies P = \frac{N_\uparrow}{N}$$

$$\implies N_\uparrow^{max} = NP$$

Location of the max P is NP. Second derivative:

$$\left(\frac{\partial^2 ln(P)}{\partial N_\uparrow^2}\right) = -\frac{1}{N_\uparrow} - \frac{1}{N - N_\uparrow}$$

$$= -\frac{1}{N}(\frac{1}{N_\uparrow/N} + \frac{1}{1 - N_\uparrow/N}) = -\frac{1}{N}\left(\frac{1}{(N_\uparrow/N)(1 - N_\uparrow/N)}\right)$$

$$\overset{at\,max\,\frac{N_\uparrow}{N}=P}{=} -\frac{1}{N}\frac{1}{p(1-p)}$$

$$ln(P_N)|_{\text{at max}} = NlnN - Np(lnN + lnP) - N(1-p)(ln(N) + ln(1-P)) + NPln(1-p) + Nln(1-p) = 0$$

$$ln[P(N_\uparrow)] = 0 + \underbrace{0}_{\text{first der.}} - \frac{1}{2(Np(1-P))}(N_\uparrow - NP)^2$$

$$P(N_\uparrow) \approx Ae^{-\frac{1}{2N(1-p)}(N_\uparrow - NP)^2}$$

where A is the missing normalisation constant.
Gaussian around $NP \propto N$ and standard derivative $\sqrt{NP(1-P)} \propto \sqrt{N}$

The height is $\frac{1}{\sqrt{N}}$.
If we focus on the fraction of coins being head,

$$\left\langle \frac{N_\uparrow}{N} \right\rangle = p$$

$$\left\langle \left(\frac{N_\uparrow}{N}^2 \right) \right\rangle - \left\langle \frac{N_\uparrow}{N} \right\rangle^2 = \frac{1}{N^2} NP(1 - P) \propto \frac{1}{N}$$

the mean value becomes a precise statment as $N \to \infty$

11.2   Random Independent Variables

We define a random variable F that takes 2 values
1 with Probability p 0 with probability $1 - p$ Then take N such random variables $F_i \quad i = 1 \cdots N$
then

$$N_\uparrow = \sum_{i=1}^{N} F_i$$

The average value of F_i is

$$\langle F_i \rangle\rangle = 1p + 0(1 - p) = p$$

$$\langle N_\uparrow \rangle = \left\langle \sum_{i=1}^{N} F_i \right\rangle = \sum_{i=1}^{N} \langle F_i \rangle = NP$$

Deviation from the average:

$$\left\langle (N_\uparrow - NP)^2 \right\rangle = \left\langle N_\uparrow^2 \right\rangle - 2NP \langle N_\uparrow \rangle + (NP)^2$$

$$\langle N_\uparrow^2 \rangle = \left\langle \left(\sum_{i=1}^{N} F_i \right)^2 \right\rangle = \left\langle \sum_{i=1}^{N} F_i \sum_{j=1}^{N} F_j \right\rangle = \left\langle \sum_{n=0}^{N} F_i^2 + \sum_{i,j} F_i F_j \right\rangle$$

$$= \sum_{i=1}^{N} \langle F_i^2 \rangle + \sum_{i \neq j} \langle F_i F_j \rangle$$