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Surface Thermodynamics
A primer for heat transfer physical scientists

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Partially based on lecture notes by Prof. Gert Ehrlich

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Motivation for understanding thermodynamics of surfaces

- At the nanoscale, atoms and molecules near surfaces and interfaces become a significant fraction of the overall system.
- In this lecture, I will use the term “surface” to describe the transition region between two phases.
- Gibbs (1878) introduced the concept of a “dividing surface” to deal with the thermodynamics of this (often inhomogenous) transition region.
  - See Tolman, J. Chem. Phys. **16**, 758 (1948)

Motivation for understanding thermodynamics of surfaces

- We need thermodynamics to provide insight on
  - Composition and structure of the surface in equilibrium.
  - Driving force for exchange of mass at the surface (evaporation, condensation, adsorption, ripening, coarsening).

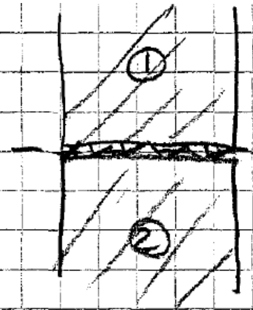
Part I: classical thermodynamics of surfaces

- Surface excess contributions to the extensive variables
  - Gibbs adsorption equation
- Thermodynamic potentials and surface excess free energy
  - Landau thermodynamic potential for multicomponent systems
  - Surface tension, surface energy, surface stress
- Equilibrium shape; Laplace pressure; thermodynamic driving force for coarsening

Part II: statistical mechanics of surfaces

- Landau thermodynamic potential and the grand partition function
  - Equilibrium between 2D and 3D ideal gases
  - Equilibrium between monolayer lattice gas and 3D ideal gas (Langmuir adsorption)
- Comparison to kinetic models for evaporation and condensation
- Connection back to thermodynamics: heat of adsorption

Surface excess of the extensive variables



dividing surface

$$V = V^{(1)} + V^{(2)}$$

volume on side (1) of the dividing surface

$$E = E^{(1)} + E^{(2)} + E^{(s)}$$

internal energy of phase (1) if it was homogeneous all the way to the divid surface

$E^{(s)}$ correction term "surface excess"

similarly the other <u>extensive</u> variables

$$N_i = N_i^{(1)} + N_i^{(2)} + N_i^{(s)} \quad \text{for component } i$$

$$S = S^{(1)} + S^{(2)} + S^{(s)}$$

Surface excess of the extensive variables

Consider a small variation of this system, i.e. infinitesimal process

$$\delta E = T\,\delta S + \sum_i \mu_i\,\delta N_i - P\,\delta V$$

Use the same Gibbs dividing surface idea

$$\delta E = \delta E^{(1)} + \delta E^{(2)} + \delta E^{(s)}$$

$$\delta E^{(s)} = T^{(s)}\,\delta S^{(s)} + \sum_i \mu_i^{(s)} N_i^{(s)} + \gamma\,\delta A$$

let's follow the usual (not great) nomenclature and call this the surface tension

line tension — units of F

surface tension — units of F/m or J/m²

A = area of dividing surface

Surface excess of the extensive variables

Consider a small variation of this system $\Big\}$ i.e. infinitesimal process

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A = area of dividing surface

Relate surface tension to the other intensive variables

energy is extensive

$$\alpha E(S, V, N_i, A) = E(\alpha S, \alpha V, \alpha N_i, \alpha A)$$

$$\alpha = 1+\epsilon \qquad \epsilon << 1$$

$$E = TS - pV + \sum \mu_i N_i + \gamma A$$

now differentiate

$$dE = TdS + SdT + \ldots \gamma dA + A d\gamma$$

and use our earlier result

$$dE = TdS - PdV + \sum \mu_i dN_i + \gamma dA$$

Gibbs Duhem Eq.

$$SdT - VdP + \sum N_i d\mu_i + A d\gamma = 0$$

Gibbs adsorption equation

or if I write just the pieces related to the interface

$$-A\,d\gamma = \sum N_i^{(s)} d\mu_i + S^{(s)} dT$$

Gibbs adsorption equation

For a one component system I can chose $N_i^{(s)} = 0$

then $-A\,d\gamma = S^{(s)} dT$

or if you prefer

$$\frac{S^{(s)}}{A} = -\frac{d\gamma}{dT}$$

Surface excess free energy

and also take a look at the free energy

$$F \equiv E - TS$$

for one component $\quad F = -pV + \mu N + \gamma A$

and $N^{(s)} = 0 \quad F^{(s)} = \gamma A$

so, for a one component system,

$\gamma = \dfrac{F^{(s)}}{A}$ is the surface excess free energy per unit area

more generally, for multicomponent systems we can define a different thermodynamic potential

The "Landau potential" $\quad L \equiv E - TS - \sum_i \mu_i N_i$

$$= -pV + \gamma A$$

therefore $\quad L^{(s)} = \gamma A$

Digression on thermodynamic potentials

closed, isothermal

F Helmholz free energy

$$F \equiv E - TS$$

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

closed, isothermal, constant P

G Gibbs free energy

$$G \equiv E - TS + pV$$

$$G(T, P, N)$$

closed, adiabatic

H enthaply

$$H \equiv E + pV$$

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

open, isothermal

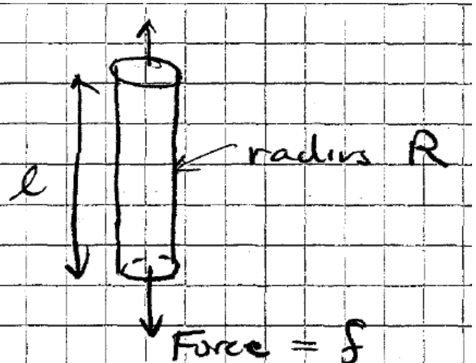
L Landau potential

$$L = E - TS - \sum_i \mu_i N_i$$

$$L(T, V, \mu_i)$$

Difficult to measure the surface tension of a solid

- Need an experiment that can access the reversible mechanical work needed to create new surface
- Zero creep experiment



$$f\,dl = \gamma\, dA$$

$$\gamma = f\,\frac{dl}{dA}$$

for a cylinder at constant volume
important

$$V = \pi R^2 l$$

$$dV = 0 = \pi\, 2R\,dR\, l + \pi R^2 dl$$

$$dR = -\frac{R\,dl}{2l}$$

Use $A = l\, 2\pi R$

$$dA = 2\pi\, dR\, l + 2\pi R\, dl$$

$$dA = \pi R\, dl$$

$$\gamma = \frac{f}{\pi R}$$

Surface tension, surface energy, surface stress

- I usually reserve the term “surface energy” for the surface tension at zero temperature.

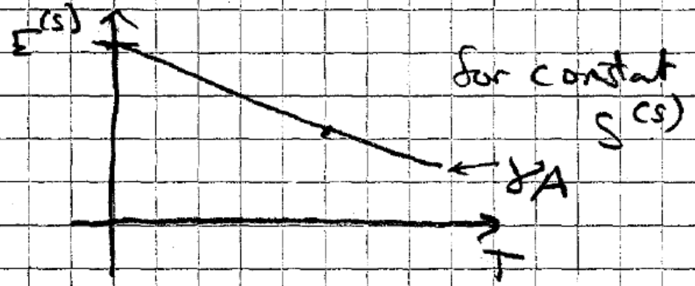
surface energy

$$E^{(s)} = TS^{(s)} + \gamma A$$

$$\left(S^{(s)} = -A \frac{\partial \gamma}{\partial T} \right) \quad = A\left(\gamma - T\frac{\partial \gamma}{\partial T}\right)$$

for dividing surface

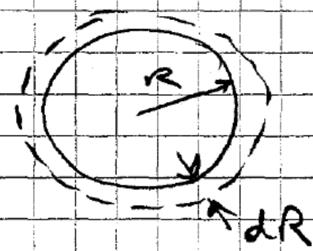
$$\sum \mu_i N_i^{(s)} = 0$$



Surface stress is the work needed to deform a surface

Stretch the area of an isotropic surface

plan view



surface stress

$$dW = \gamma\, 2\pi R\, dR + d\gamma\, \pi R^2$$

$$g\, 2\pi R\, dR =$$

$$g = \gamma + \frac{R}{2}\frac{\partial \gamma}{\partial R}$$

$$g = \gamma + \frac{1}{2}\frac{\partial \gamma}{\partial \epsilon} \qquad d\epsilon = \frac{dR}{R}$$

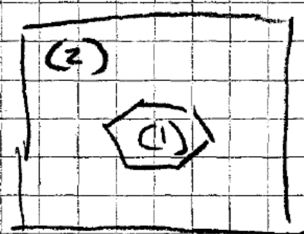
For liquids $\frac{\partial \gamma}{\partial \epsilon}$ is zero because I can't elastically deform a liquid

but for solids $g \neq \gamma$

Equilibrium shape

Fundamental question what is the shape of a crystal in equilibrium?

$$L^{(s)} = \oint \gamma \, dA$$



$V^{(1)}, V^{(2)}$ constant

at equilibrium $L^{(s)}$ is minimized

$$dL^{(s)} = d\left[\oint \gamma \, dA\right] = 0$$

γ = constant is easy

$$d\left[\oint dA\right] = 0$$

$$dA = 0$$

minimum area at constant volume is a sphere

Equilibrium shape: Wulff construction

for crystals γ depends on direction

solving $d\left[\oint \gamma \, dA\right] = 0$

become difficult

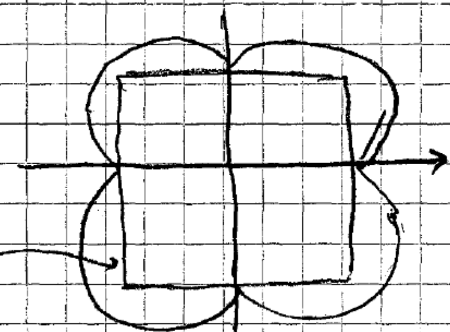
Wulff construction (1901)

for polyhedrons $\dfrac{\gamma_i}{h_i}$ = constant

γ_i = distance from the center to the crystal face

$\gamma \Rightarrow r$

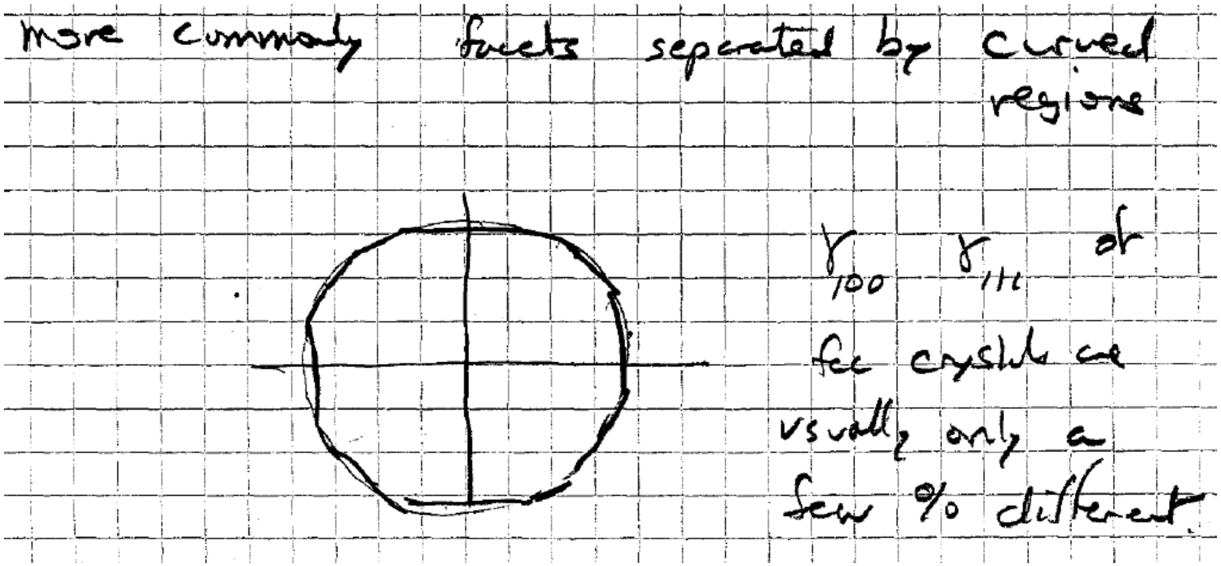
$\theta \to \theta$



Wulff construction

if γ_{100} is much smaller than any other orientation.

Equilibrium shape of most metals is nearly a sphere



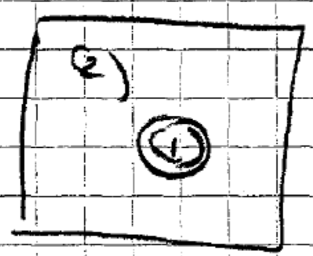
- Need sufficient kinetics (large surface diffusion or fast evaporation/condensation) to observe equilibrium shape

- Most crystal shapes are, in practice, controlled by kinetic limitations (slowest growing facets), not thermodynamics.

Equilibrium between a small crystal and its liquid or vapor

$$dL = -P\,dV + \gamma\,dA$$

$$= -p^{(1)}dV^{(1)} - p^{(2)}dV^{(2)} + \gamma\,dA$$



$$dV^{(1)} = -dV^{(2)}$$

$$dL = 0 = p^{(2)} - p^{(1)}dV^{(1)} + \gamma\,dA$$

$$p^{(1)} - p^{(2)} = \gamma\frac{dA}{dV}$$

for a sphere $\quad A = 4\pi R^2$

$$dA = 8\pi R\,dR$$

$$V = \frac{4}{3}\pi R^3$$

$$dV = 4\pi R^2\,dR$$

Equilibrium between a small crystal and its liquid or vapor

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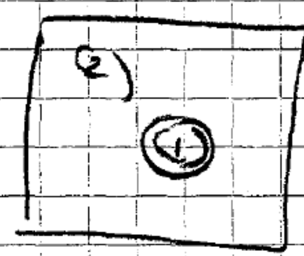

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for a sphere $A = 4\pi R^2$

$$dA = 8\pi R\,dR$$

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$$dV = 4\pi R^2\,dR$$

Equilibrium between a small crystal and its liquid or vapor

$$p^{(1)} - p^{(2)} = \frac{2\gamma}{R}$$

for a faceted crystal this becomes

$$p^{(1)} - p^{(2)} = \frac{2\gamma_i}{h_i}$$

Chemical potential of a small crystal

Gibbs-Duhem constant T, γ

for each phase
$$N^{(1)} d\mu^{(1)} = V^{(1)} dp^{(1)}$$
$$N^{(2)} d\mu^{(2)} = V^{(2)} dp^{(2)}$$

we know from above
$$d\left[p^{(1)} - p^{(2)}\right] = d\left(\frac{2\gamma}{R}\right)$$

$$n^{(2)} = \frac{N^{(2)}}{V^{(2)}} \qquad n^{(1)} = \frac{N^{(1)}}{V^{(1)}}$$

$$n^{(1)} d\mu^{(1)} - n^{(2)} d\mu^{(2)} = d\,\frac{2\gamma}{R}$$

Chemical potential driving force for ripening

if (2) is a gas $n^{(2)} \ll n^{(1)}$

$$n^{(1)} \int_{\mu(R=R_0)}^{\mu(R=\infty)} d\mu^{(1)} = \int_{R=R_0}^{R=\infty} d\,\frac{2\gamma}{R}$$

$$n^{(1)}\left[\mu^{(1)}(R_0) - \mu^{(1)}(\infty)\right] = \frac{2\gamma}{R}$$

$$n^{(1)}\Delta\mu^{(1)} = \frac{2\gamma}{R}$$

for a facetted crystal

$$n^{(1)}\Delta\mu^{(1)} = \frac{2\gamma_i}{h_i}$$

Chemical potential driving force for ripening

Take a look a some numbers

MKS units

$$n = \frac{8}{(5.43 \cdot 10^{-10})^3} \ m^{-3} = 5 \cdot 10^{28}$$

$$\gamma \approx 1 \ J \ m^{-2}$$

$$h_i = 10 \ nm = 10^{-8} \ m$$

$$\Delta\mu = 4 \cdot 10^{-21} J = 0.025 \ eV \approx k_B T \text{ at room } T.$$

Part 2: statistical mechanics to calculate L

$$L = -k_B T \ln \mathcal{Z}$$

grand partition function

$$\mathcal{Z} = \sum_N \exp(N\mu/k_B T)\, Z(N)$$

partition function $\quad Z(N) = \sum_j \exp(-E_j(N,V,T)/k_B T)$

$$F = -k_B T \ln Z(N,V,T)$$

canonical ensemble

$$S = k_B \ln \Omega(N,V,E)$$

micro canonical ensemble

degeneracy

Ideal gas is always the easiest place to start

$$Z(N) = \frac{\zeta^N}{N!}$$ where

$$Z(1) = \zeta(T,V)$$

We'll need to know ζ eventually but let's put that off for a while

$$\mathcal{Z} = \sum_N \frac{\zeta^N}{N!} \exp(N\mu/k_BT)$$

$$= \sum_N \frac{[\zeta \exp(\mu/k_BT)]^N}{N!}$$

call this x

$$\mathcal{Z} = \sum_N \frac{x^N}{N!} = \exp(x)$$

$$\ln \mathcal{Z} = x$$

Need the derivative of L with respect to chemical potential to find N = $N^{(2)}+N^{(s)}$

$$dL = -S\,dT - P\,dV + \gamma\,dA - N\,d\mu$$

let's assume the substrate is inert so we will let N μ refer to the adsorbate

$$N = -\frac{\partial L}{\partial \mu} = k_BT \frac{1}{Z}\frac{\partial Z}{\partial \mu}.$$

$$N = k_BT \frac{\partial \alpha}{\partial \mu} = \zeta \exp(\mu/k_BT)$$

or

$$\frac{\mu}{k_BT} = \ln \frac{N}{\zeta}$$

Single particle partition functions

Now we need ζ_{3D} ; ζ_{2D}

normalize each $\Delta x \Delta p_x$ by h

$$\zeta_{3D} = \frac{V}{h^3} \int d^3\vec{p}\, \exp\left(-p^2/2mk_BT\right) \sum_s \exp\left(-\epsilon_s/k_BT\right)$$

integral over continuum of spatial states

integral over continuum of momentum states.

sum over internal states

In general

$$\zeta_{vib} = \sum_v \exp\left(-\epsilon_v/k_BT\right)$$

sum over vibrational states

2D ideal gas in equilibrium with 3D ideal gas

equilibrium $\mu_{3D} = \mu_{2D}$

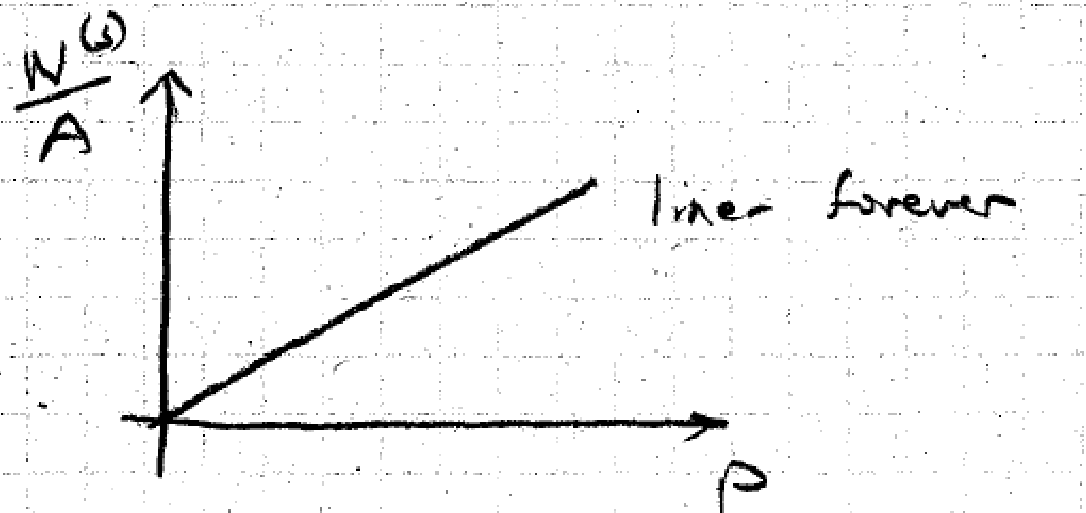
$$\frac{N^{gas}}{\zeta_{3D}} = \frac{N^{(s)}}{\zeta_{2D}}$$

$$PV = N^{gas} k_B T$$

$$\frac{N^{(s)}}{A} = \frac{P\lambda}{k_B T} \exp(\epsilon/k_B T)\, \zeta_{vib}$$

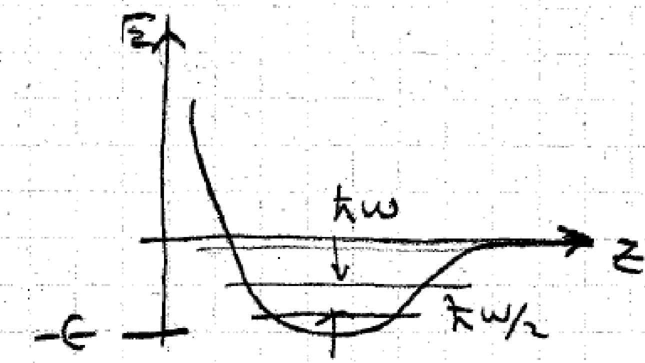
thermal de Broglie wavelength

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$



Perpendicular vibrational partition function

Need to evaluate $\zeta_{vib}\ \exp(\epsilon/k_BT)$



$$\zeta_{vib} = \sum_{v} \exp(\epsilon_v/k_BT)$$

$$= \exp(\hbar\omega/2k_BT)\ \underbrace{\sum_{n=0}^{\infty} \exp(-n\hbar\omega/k_BT)}_{\dfrac{1}{1-\exp(-\hbar\omega/k_BT)}}$$

$$= 1 \qquad kT \ll \hbar\omega$$

$$= \frac{kT}{\hbar\omega} \qquad kT \gg \hbar\omega$$

Compare to a kinetic view of condensation=evaporation

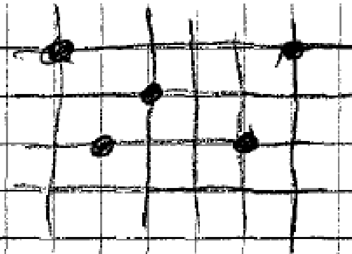
2D ideal gas adsorption $\quad kT \ll \hbar\omega$

$$\frac{P}{\sqrt{2\pi m k T}} = \frac{N^{(s)}}{A}\frac{k_B T}{h}\exp\left(-\epsilon_0/k_B T\right)$$

At room T $\quad \dfrac{k_B T}{h} = 6\times 10^{12}\ \mathrm{s}^{-1}$

This looks like an impingement rate set equal to an evaporation rate but note that we derived the equation without considering kinetics.

Lattice 2D gas (Langmuir adsorption)



Langmuir's model of adsorption

Still no interaction between adsorbates (that's very hard) but now we only allow adsorption on lattice sites of the substrate

before $$Z(N) = \frac{\zeta_{gas}^N}{N!}$$ ideal gas

now $$Z(N) = \frac{\zeta_L^N}{N!} \frac{N_s!}{(N_s - N)!}$$

where N_s = number of surface sites

$$N < N_s$$

Lattice 2D gas (Langmuir adsorption)

put this into the grand partition function

sum over all possible values of N

$$\mathcal{Z} = \sum_{N=0}^{N_s} \exp\left(N\mu/k_BT\right) \frac{N_s!}{N!\,(N_s-N)!}\, \xi^N$$

Same form as the binomial expansion

$$(x+y)^n = \sum_{k=0}^{n} \frac{n!}{k!\,(n-k)!}\, x^{n-k}\, y^k$$

example $n=3$

$$(x+y)^3 = x^3 + 3x^2y + 3xy^2 + y^3$$

$$\frac{3!}{1\cdot 2!}$$

Lattice 2D gas (Langmuir adsorption)

define $x = \zeta \exp\left(\mu / k_B T \right)$

$$Z_1 = (1+x)^{N_s}$$

$$L = -k_B T \ln Z_1$$

$$= -kT N_s \ln(1+x)$$

$$\left(\frac{\partial L}{\partial \mu}\right)_{T, V, A} = -N$$

so $N = \dfrac{kT N_s}{1+x} \dfrac{\partial x}{\partial \mu}$

$$N = N_s \frac{x}{1+x}$$

$$\frac{N}{N_s} = \frac{x}{1+x} \; ; \quad x = \zeta_L \exp\left(\mu_i / k_B T \right)$$

Equlibrium between 2D lattice gas and 3D ideal gas

from before $\mu = kT \ln \frac{N}{\zeta_{3D}}$

so $\exp(\mu/k_B T) = \frac{N}{\zeta_{3D}}$

rearrange the surface expression

define $\Theta = \frac{N}{N_S}$

$\Theta = \frac{x}{1+x}$ or

$x = \frac{\Theta}{1-\Theta} = \zeta_L \frac{N^{(3D)}}{\zeta_{3D}}$

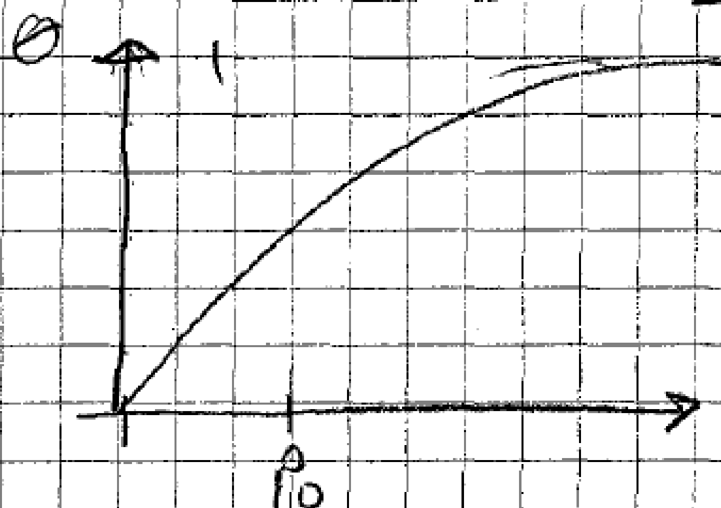
$$\frac{\Theta}{1-\Theta} = \zeta_L \left(\frac{h^2}{2\pi m k T}\right)^{3/2} \frac{p}{kT}$$

Equilibrium between 2D lattice gas and 3D ideal gas

define $$p_0 = \frac{kT}{\xi_L}\left(\frac{2\pi m kT}{h^2}\right)^{3/2}$$

$$\frac{\theta}{1-\theta} = \frac{p}{p_0}\ ; \qquad \boxed{\theta = \frac{p}{p+p_0}}$$

Langmuir adsorption isotherm



Single particle partition function for the 2D lattice gas

$$\zeta_L = \exp^{\epsilon/k_BT}\, \zeta_{vib}$$

assume vibrations in the plane are similar frequencies as vibrations perpendicular

$$\zeta_{vib} = \sum \exp(-\epsilon_{vib}/k_BT)$$

Skip a few details

$$= \zeta_\perp^{\,3} \exp\left(-\tfrac{3}{2}\hbar\omega/k_BT\right)$$

so in principle we know everything

$$P_0 = kT\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \frac{\exp(-\epsilon_0/k_BT)}{\zeta_\perp^{\,3}}$$

$$\epsilon_0 = \epsilon - \tfrac{3}{2}\hbar\omega$$

Comparison to a kinetic view of adsorption/desorption

$$\frac{\theta}{1-\theta} = \frac{p}{p_0}$$

assume

$$p(1-\theta) = p_0\theta$$

$$\left[\frac{p}{\sqrt{2\pi m k T}}\right]\underbrace{(1-\theta)}_{\text{free surface sites}} = \left[\frac{kT}{h}\,\frac{2\pi m k T}{h^2}\,\frac{\exp(-\epsilon_0/k_B T)}{\xi_\perp^{\,3}}\right]\theta$$

impingement rate

desorption rate per filled site

filled sites

Compare 2D ideal gas and 2D lattice gas

$$\theta = \frac{P}{P_0} \qquad N^L = N_s \frac{P}{P_0}$$

$$\frac{N^{(2D)}}{A} = \frac{P}{(2\pi m kT)^{1/2}} \frac{h}{kT} \exp \epsilon_0/k_0 T \, \xi_\perp$$

Compare $$\frac{N^{2D}}{N^L} = \frac{A}{N_s} \frac{2\pi m kT}{h^2} \frac{1}{\xi_\perp^2}$$

area per lattice site ($\sim 10^{-15}\,cm^{-2}$)

order unity (usually)

Entropy is (of course) important for determining the equilibrium coverage

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So these are different

even at low θ by a factor

of

$$\frac{2\pi m k T}{h^2} \frac{A}{N_S}$$

$$= \frac{A}{\lambda^2 N_s} \approx 10^5 \text{ for light atoms}$$

thermal de Broglie wavelength

Take a closer look at the entropy of the lattice gas

$$S = S_{conf} + S_{vib}$$

$$S_{conf} = k \ln \Omega_{conf}$$

for Langmuir

# of ways of distributing N identical particles on N_S sites

$$\Omega_{conf} = \frac{N_S!}{N!\,(N_S - N)!}$$

recall $n! = n \ln n - n$ for large n

Take a closer look at the entropy of the lattice gas

$$\frac{S_{conf}}{k_B} = N_S \ln \frac{N_S}{N_S - N} - N \ln \frac{N}{N_S - N}$$

or with $\theta = \frac{N}{N_S}$

per particle

$$\frac{S_{conf}}{N k_B} = \frac{1}{\theta} \ln\left(\frac{1}{1-\theta}\right) - \ln\left(\frac{\theta}{1-\theta}\right)$$

Take a closer look at the entropy of the lattice gas

Θ	$\frac{S_{conf}}{Nk}$
10^{-3}	7.9
10^{-2}	5.6
10^{-1}	3.25
0.5	1.4
0.9	0.36
0.99	0.06

$$\frac{S_{vib}}{Nk_B} = \begin{cases} 0 & \text{if } kT \ll \hbar\omega \\ 3\,\frac{kT}{\hbar\omega} & kT \gg \hbar\omega \end{cases}$$

Compare to entropy of the ideal gas

entropy of the ideal gas

$$\frac{S_{gas}}{Nk} = \ln \frac{kT}{p\lambda^3} + 5/2$$

Ar at atmospheric pressure $\quad \dfrac{S_{gas}}{Nk_B} \approx 15$

Heat of adsorption

Use Gibbs free energy instead of Landau because we want P to be one of the dependent variables (and N but not μ)

before

$$L = -kT \ln \mathcal{Z}$$

$$\mathcal{Z}(\mu, V, T) = \sum_N Z(N, V, T) \exp\left(N\mu / k_B T \right)$$

$$Z(N, V, T) = \sum_j \exp\left(-\epsilon_j / k_B T \right)$$

now

$$\mathcal{Z}'(N, P, T) = \sum_V Z(N, V, T) \exp\left(-PV / kT \right)$$

Heat of adsorption

$$dG = -S\,dT + V\,dP + \gamma\,dA + \sum \mu_i\,dN_i$$

as usual pick $N^{(s)}_{substrate} = 0$

one adsorbate $N^{(s)} = N^{(s)}_{adsorbate}$

$$dG^{(s)} = -S^{(s)}\,dT + \gamma\,dA + \mu\,dN^{(s)}$$

$$\mu_s(T, A, N^{(s)}) = \left(\frac{\partial G^{(s)}}{\partial N^{(s)}}\right)_{T,A}$$

Heat of adsorption

Expand this in terms of the dependent variables

$$d\mu_s = \left(\frac{\partial \mu_s}{\partial T}\right)_{N^{(s)},A} dT + \left(\frac{\partial \mu_s}{\partial A}\right)_{T,N^{(s)}} dA$$

$$+ \left(\frac{\partial \mu_s}{N^{(s)}}\right)_{T,A} dN^{(s)}$$

Next step is to get all the derivatives in the same form $\left(\frac{\partial}{\partial N^{(s)}}\right)_{T,A}$

to do this we need "Maxwell relations"

Heat of adsorption

This leads to for constant $N^{(s)}$, A process

$$d\mu_s = -\left(\frac{\partial S^{(s)}}{\partial N^{(s)}}\right)_{T,A} dT$$

and for the gas phase in equilibrium with the surface

$$d\mu_s = d\mu_{gas} = -\left(\frac{\partial S^{(gas)}}{\partial N^{(gas)}}\right)_{T,P} dT + \left(\frac{\partial V^{gas}}{\partial N^{gas}}\right)_{T,P} dP$$

Heat of adsorption

combine these

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

how does the equilibrium pressure change with T at fixed coverage $N^{(s)}$

simplify for ideal gas

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

Heat of adsorption

and we usually put this in terms of enthalpy

$$H = E + PV \qquad H(S, P, N)$$

or

$$H = G + TS \qquad G(T, P, N)$$

since

$$\left(\frac{\partial G^{(s)}}{\partial N^{(s)}}\right)_{T,A} = \left(\frac{\partial G^{gas}}{\partial N^{gas}}\right)_{T,P}$$

in equilibrium

Heat of adsorption

We can write

$$\frac{T}{P}\left(\frac{\partial P}{\partial T}\right)_{A,N^{(s)}} = \frac{\left(\frac{\partial H^{gas}}{\partial N^{gas}}\right)_{T,P} - \left(\frac{\partial H^{(s)}}{\partial N^{(s)}}\right)_{T,A}}{kT}$$

usually referred to as the isosteric heat of adsorption

q_{iso}

☆ if you know $\left(\frac{\partial P}{\partial T}\right)_{A,N^{(s)}}$ then you know q_{iso}

Heat of adsorption of the 2D ideal gas

our statistical mechanics result for
2D ideal gas (freely mobile adsorbate)
was

$$p = \frac{N^{(s)}}{A\lambda} kT \frac{1}{\xi_+} \exp(-\epsilon_0/k_BT)$$

$$\frac{1}{p}\frac{\partial p}{\partial T} = \frac{\partial \ln p}{\partial T} \qquad \text{let } \xi_+ = 1$$

$$\ln P = \text{constants} + \ln T^{3/2} - \epsilon_0/k_BT$$

$$\frac{\partial \ln P}{\partial T} = 0 + \frac{3}{2}\frac{1}{T} + \epsilon_0/k_BT^2$$

$$q_{iso} = kT^2\left(\frac{\partial \ln P}{\partial T}\right)$$

$$q_{iso} = \epsilon_0 + \frac{3}{2}kT$$