Summary Fys2160

Statistical mechanics

Models

Thermodynamics laws

Thermodynamic processes

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Last days:

- Group sessions: this week and next week
- Problem solving sessions: Tue 12:15-14 this week and next week
- Check that you have 40 points
- Last lecture tomorrow
- Exam: Nov 28, 15:00, 4 hours
  - Approved calculator
  - Rottman: "Matematisk formelsamling"
  - Øgrim and Lian or Angell and Lian: "Fysiske størrelser og enheter"
  - One A4 sheet with notes (2 pages)

2

Statistical mechanics ≈
Thermodynamics of microscopic models

- microstate & macrostate
- fundamental assumption
- NVE
  - multiplicity
  - probability
  - central limit, normal
  - entropy
- NVT
  - Boltzmann factor
  - relative probabilities
  - Partition function, Z
  - Free energy $F = -kT \ln Z$
  - Probability
- μVT
  - Gibbs factor, Gibbs sum Z_G
  - Great potential $\Phi = -kTlnZ_G$
- indistinguishable: $^1/_{N!}$
- equipartition
- Quantum systems
  - Fermi-Dirac
  - Bose-Einstein
  - density of states
  - radiation
- Kinetic theory
  - mean free path
  - mean free time
  - heat capacity
  - thermal conductivity
  - viscosity
  - diffusion coefficient

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Microscopic models

States of microscopic particles, simple enough to calculate multiplicity, partition function or Gibbs sum

- calculate Helmholtz, mean energy, mean particle number,density of states
- find equation of state
- => all can be calculated

- Two state models
  - two-sided box
  - polymer
  - paramagnet
  - random walker
  - hemoglobin
- Einstein crystal
- Ideal gas
- Free electron gas
- Photon gas
- Debye crystal
- Molecular dynamics

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Mentimeter

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exam 2017, problem 2

We will now use a microscopic model of the rubber band made of a polymer. Assume the polymer being stretched consistes of N monomers of length δ The monomers are attached to each other andcan extend either to the right or to the left. That is, each monomer has two possible states

$$s_i = \begin{cases} +1 & \text{høyre} \\ -1 & \text{venstre} \end{cases} \tag{7}$$

that are equally probable. When the rubber band is stretched some of the turns (change of direction between neighbours) are straightened out. The dilatation of the rubber band is then $l = \delta \sum_i s_i$.

(d) If N_h is the number of monomers directed to the right show that the multiplicity of the rubber band is

$$\Omega(N_h, N) = \binom{N}{N_h} \tag{8}$$

and use Stirling's approxmation $\ln(N!) \approx N \ln N - N$ to find the entropy.

(9)

(e) show that the force is given by

$$f = \frac{kT}{2\delta} \ln \frac{N\delta + l}{N\delta - l} \tag{10}$$

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exam 2017, problem 2

The analysis of the rubber band model shows that the force is related to the entropy, that is, how ordered the polymer is. In order to test if the internal energy matters we wil make a model where each monomer has the energy $\delta\epsilon$ independent of s_i. This signifies that the (total internal) energy of the polymer in state i is $\epsilon_i = N\delta\epsilon$. We may now write the partition function as

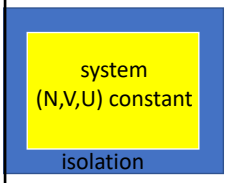
$$Z = \sum_i e^{-\epsilon_i/kT} = \Omega(N_h, N)e^{-N\delta\epsilon/kT}. \quad (12)$$

(k) Use the partition function to find an expression for the force and compare to the expression we found for the microcanonical ensemble. Comment the result.

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Isolated system at equilibrium

microcanonical



Multiplicity of macrostate (N, V, U)

$\Omega(N, V, U)$=number of "equally probable"* accessible microstates
indistinguishable particles: $N!$ permutations do not count =>
$\frac{1}{N!}\Omega'(N, V, U)$

Probability of a microstate s (for a given macrostate (N, V, U)):

$$P(s) = \frac{1}{\Omega(N,V,U)}$$

Boltzmanns entropy:

$$S(N, V, U) = k \ln \Omega(N, V, U)$$
$$= -k \sum_s P(s) \ln P(s)$$

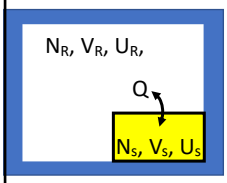
*fundamental assumption of statistical mechanics

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Mentimeter

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System in a thermal bath
canonical (NVT)



Exchanges Q with (NVE) reservoir to keep T constant

probability ratio: $\frac{P(s_1)}{P(s_2)} = \frac{e^{-\beta\varepsilon(s_1)}}{e^{-\beta\varepsilon(s_2)}}$

Boltzmann factor: $e^{-\beta\varepsilon_i}$

Partition function = weighted sum over all microstates: $Z = \sum_i e^{-\beta\varepsilon_i}$

N distinguishable, ident, indep. $Z_N(V,T) = Z_1^N(V,T)$

N indistinguishable, ident, indep. $Z_N(V,T) = \frac{1}{N!} Z_1^N(V,T)$

Boltzmann distribution = Probability of a microstate: $P_i = {e^{-\beta\varepsilon_i}}/{Z}$

Free energy: Helmholtz $F = -kT \ln Z$

Internal energy: $U(N,V,T) = -\left(\frac{\partial \ln Z}{\partial \beta}\right)_{V,N}$

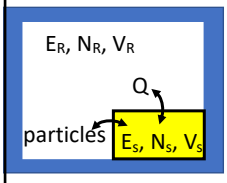
Equation of state: $P(N,V,T) = -\left(\frac{\partial F}{\partial V}\right)_{V,T}$

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Quizz

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System in thermal & particle reservoir
Grand canonical, (μVT)



Exchanges Q & particles with (NVE) reservoir to keep T & μ constant

probability ratio: $\frac{P(s_1)}{P(s_2)} = \frac{e^{-\beta(\varepsilon(s_1)-\mu N(s_1)}}{e^{-\beta(\varepsilon(s_2)-\mu N(s_2)}}$

Gibbs factor: $e^{-\beta(\varepsilon_i-\mu N_i)}$

Gibbs sum: weighted sum over all possible microstates: $Z_G(T,\mu) = \sum_i e^{-\beta(\varepsilon_i-\mu N_i)}$

Probability of a microstate: $P_i = {e^{-\beta(\varepsilon_i-\mu N_i)}}/{Z_G}$

Free energy: Grand potential, $\Phi = -kT \ln Z_G = U - TS - \mu N$

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Thermodynamics

Study of transfers of matter and energy in systems that can be driven (by their surroundings) from one state of equilibrium to another.

Macroscopic, measurable properties, axiomatic (4 «laws»)

Models exchange of energy, work, heat & matter

- from well defined initial equilibrium
- specified thermodynamic operation (change in walls or surroundings)
- => calculate final equilibrium state

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State variables

- A state variable for a system depends only on the equilibrium state of the system and **not the path** to reach that state
- m, V, ρ, N, P, T
- energies: U, H, G, F
- entropy: S
- Example: change of $P(t), V(t)$ with time of ideal gas ($PV = NkT = U$)

$$\Delta U = U(t_1, t_2) = \int_{t_1}^{t_2} P(t)V(t)dt = P(t_2)V(t_2) - P(t_1)V(t_1)$$
$$= \int_{V(t_1)}^{V(t_2)} PdV + \int_{P(t_1)}^{P(t_2)} VdP$$

- Integral depends only on end points.
- State functions have use exact differentials "d" in $dV, dP, dU, \ldots$
- Thermodynamic state variables are only strictly defined in equilibrium

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Path dependent variables

- Heat, Q, and work, W,
  - are not state variables
  - are process quantities / path functions
  - values depend on the path between equilibrium states

$$\Delta W = W(t_1, t_2) = \int_1^2 -PdV \int_{t_1}^{t_2} -P(t)\frac{dV(t)}{dt}dt$$

- $P(t)$ and $V(t)$ must be known along the whole path
- An infinitesimal increment of work $\delta W = -PdV$
- "δ" is an inexact differential, it can only be integrated with full knowledge of path

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First law of thermodynamics

Energy is conserved:

There are two ways of changing the internal energy of a system: heat and work.

$$\Delta U = Q + W$$

Infinitesimal change in U is path dependent:

$$dU = \delta Q + \delta W$$

Schroeder: $dU = Q + W$

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Entropy & second law

For all changes/processes $\Delta S_{tot} \geq 0$

Equilibrium maximizes entropy

N=N_A+N_B, V=V_A+V_B, U=U_A+U_B, all *(N,V,U)* constant, $\alpha \in (N, V, U)$,

$S_{tot} = S_A + S_B$ is maximum in equilibrium $\Longrightarrow \frac{\partial S_B}{\partial \alpha_B} = \frac{\partial S_A}{\partial \alpha_A}$

Thermal equilibrium: $\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}$, $\quad \frac{1}{T} \equiv (\frac{\partial S}{\partial U})_{N,V}$

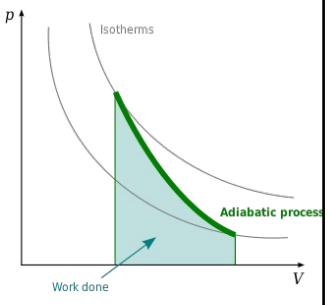
Mechanical equilibrium: $\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B}$, $\quad P \equiv T(\frac{\partial S}{\partial V})_{N,U}$

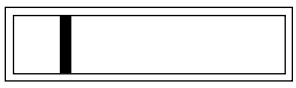
Diffusive equilibrium: $\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B}$, $\quad \mu \equiv -T(\frac{\partial S}{\partial N})_{U,V}$

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Reversible & irreversible processes

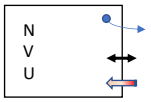
- All processes where $\Delta S_{tot} > 0$ are irreversible
- All real processes are irreversible
- A reversible process, $\Delta S_{tot} = 0$, is
  - quasistatic
  - incremental, infinitesimal changes
  - an idealized, mathematical limit
- Example: Quasistatic volume change:
  - $W = P\Delta V$
  - when $Q = 0$
  - If return along same path
    - $W = 0$
    - $\Delta S = 0$





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Thermodynamic identity



- Change in entropy due to *energy, volume, particle number* has a total differential:

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

- Use definitions: $\frac{1}{T} \equiv (\frac{\partial S}{\partial U})_{N,V}$, $P \equiv T(\frac{\partial S}{\partial V})_{N,U}$, $\mu \equiv -T(\frac{\partial S}{\partial N})_{U,V}$

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

- => Thermodynamic identity for $U(S,V,N)$

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

- The *thermodynamic identity* holds *true* for any infinitesimal change in a system

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exam 2017, problem 2

A rubber band of length $L(T) = l_0(T) + l(T)$ is stretched with a force f at each end. When $f = 0$ the length is $L = l_0$ and when $f > 0$ the dilatation is $l > 0$.

(a) Write an expression for the thermodynamic identity of the rubber band.

(b) Show that the thermodynamic identity for the Helmholtz free energy, F, can be written

$$dF = fdl - SdT \tag{4}$$

(c) Show that the force f for a given dilatation l can be written as a derivative of Helmholtz free energy:

$$f = \left(\frac{\partial F}{\partial l}\right)_T \tag{5}$$

and by the entropy:

$$f = -T\left(\frac{\partial S}{\partial l}\right)_E. \tag{6}$$

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Quizz

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Quasistatic processes

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

True for
- quasistatic,
- infinitesimal changes

TDI, N=const $dU = TdS - PdV$

1st law: $dU = \delta Q + \delta W$ $(dU = Q + W)$

=> $\delta Q = TdS, \quad \delta W = -PdV$ $(Q = TdS, \quad W = -PdV)$
- still path dependent!
- heat always produces entropy!

Some (rare) processes are not
- quasistatic,
- infinitesimal changes

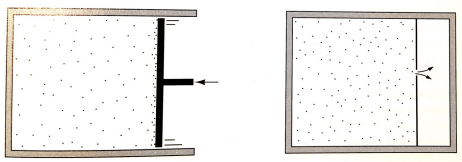


Figure 3.16. Two types of non-quasistatic volume changes: very fast compression that creates internal disequilibrium, and free expansion into a vacuum.

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exam 2017, problem 2

(i) When the rubber band is stretched slowly, will there be heat flowing into the band, out of the band or will there be no heat flow? Justify your answer.

(j) Draw a cyclic process in a $f - L$-diagram where the force $f = 0$ in state 1) and 3) and $f > 0$ in state 2). Along the path 1)→2) the rubber band is stretched slowly. Along the path 2)→3) the force is quickly reduced. Along the path 3)→1) the force on the rubber band is not changed. Indicate the heat flow, the type of process of each path and justify the shape of the path (straight, curved...)

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Engines & refrigerators

- efficiency e=W/Q
- COP=Q/W
- Rubber band exam could be continued with efficiency of a rubber engine.
- Quizz:

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Mentimeter

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Exam 2017, Problem 1

a) The Gibbs free energy of two phases *A* and *B* of a pure substance are equal at the coexistence line in a phase diagram: $G_A=G_B$. Explain why the coexistence line is inclined.

b) For ``ordinary substances" there are coexistence lines between gas-liquid, gas-solid, liquid-gas and between different crystalline solid phases. Why does only the coexistence line between gas and liquid end in a critical point? (All the other coexistence lines end in another coexistence line or in (*TPV*) equals zero or infinity:)

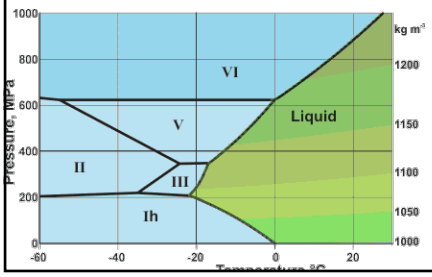
c) Explain the principle of corresponding states

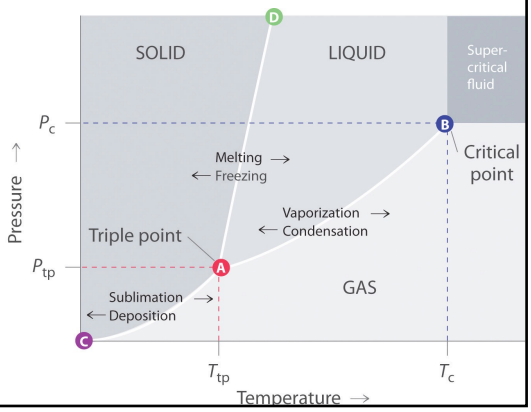
d) Do systems obeying the 1) ideal gas 2) van der Waals equation of state have a critical point?

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Phase equilibria

- Phases = states of matter
- In all state space (P,T,V...) at least one phase exists
- Boundaries = phase coexistence line = equilibrium
  - $G_A = G_B$ at the coexistence line
  - $dG_A = dG_B$ to stay on the line, $dG = VdP - SdT$
  - $dP/dT = \Delta S/\Delta V = \Delta H/(T\,\Delta V)$
  - Clausius-Clapeyron





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Quizz

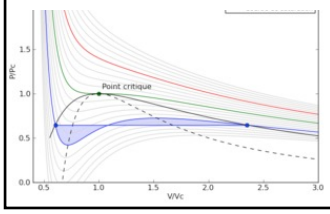
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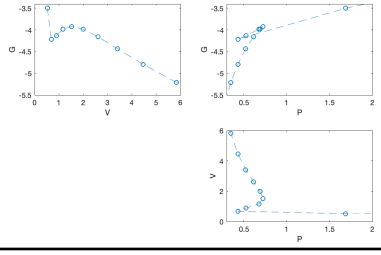
Equations of state

- **Model specific** relation between state variables beyond necessary thermodynamic relations:
- Ideal gas: $PV = NkT$
- van der Waals: $\left(p + \frac{N^2 a}{V^2}\right)(V - Nb) = NkT$
- Necessary to evaluate path dependent integrals

$$\int \delta W = -\int P dV$$

- Used to determine phase equilibria

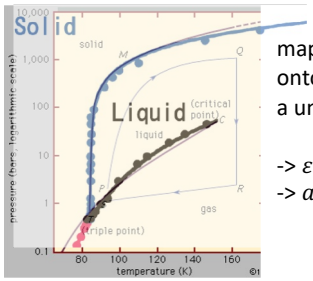




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Reduced state variables & corresponding states

- Non-dimensionalising equations
  - use characteristic quantities
  - LJ: ε, σ, m
  - Corresponding states: critical point T_c, P_c, V_c



map phase diagrams onto each other using a unique point

-> ε, σ, m for Ar
-> a, b for Ar

$$\left(p + \frac{N^2 a}{V^2}\right)(V - Nb) = NkT$$

$$\left(p' + \frac{3}{V'^2}\right)\left(V' - \frac{1}{3}\right) = \frac{8}{3}T'$$

$$T' = \frac{T}{T_c}, P' = \frac{P}{P_c}, V' = \frac{V}{V_c}$$

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Thermodynamic potentials

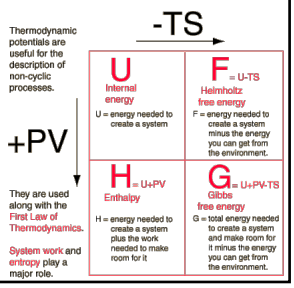
Energy	nat vars	TDI
Internal	$U(S,V,N)$	$dU = TdS - PdV + \mu dN$
Enthalpy	$H(S,P,N) = U + PV$	$dH = TdS + VdP + \mu dN$
Helmholtz	$F(T,V,N) = U - TS$	$dF = -SdT - PdV + \mu dN$
Gibbs	$G(T,P,N) = F + PV$	$dG = -SdT + VdP + \mu dN$
Grand	$\Phi(T,V,\mu) = F - \mu N$	$d\Phi = -SdT - PdV - Nd\mu$

Total differentials => $-S = \left(\frac{\partial \Phi}{\partial T}\right)_{V\mu} = \left(\frac{\partial G}{\partial T}\right)_{PN} = \left(\frac{\partial F}{\partial T}\right)_{VN}$, etc...

Derivatives of TDIs => Maxwell relations

$U(S,V)$: $\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S}$ => $-\left(\frac{\partial P}{\partial S}\right)_V = \left(\frac{\partial V}{\partial T}\right)_S$

etc...



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