Characterization and Properties of Self-Assembled Materials

Part 2 Thermodynamics



Basics of statistical thermodynamics

- Classical equilibrium thermodynamics an 18th century applied science
 - developed primarily to design a more efficient steam engine
 - Clausius, Carnot, Maxwell ...
 - energy, free energy, entropy, volume extensive variables
 - temperature, pressure intensive variables
 - formalism worked well, mathematically consistent
 - but lacked fundamental understanding
- Physical understanding of thermodynamic functions and laws only possible after atomic and molecular theory of matter accepted – 19th century
 - Boltzmann, Gibbs

How is energy distributed among particles?

- Relatively closely spaced energy levels
- 1. System of 6 particles with a total energy of 6 units
- 2. " 6 particlestotal energy of 3 units



How is energy distributed among particles?

- Relatively closely spaced energy levels
- 1. System of 6 particles with a total energy of 6 units
- 2. " 6 particles total energy of <u>3 units</u>
- Normalize:



 $P = \exp(-E/kT)$

Boltzman distribution for boltzons (atoms, molecules)

Fermions (e.g.electrons) – max 2 can occupy same energy level → don't obey Boltzmann distribution.

What is temperature?

- Try to define temperature.
- Can absolute temperature be negative?

How do quantum effects modify Boltzmann distribution

- All particles (including atoms and molecules) are either bosons or fermions
- Bosons have integer net spin (0 or 1) most atoms and molecules and many elementary particles
- Fermions have half-integer spin (1/2, 3/2...) electrons
- Bosons obey Bose-Einstein statistics
 - interesting effects at low T e.g. superfluidity
- Fermions obey Fermi-Dirac statistics
 - Fermi gas "electron gas" in metals
 - must obey Pauli exclusion principle in conducting band orbitals filled with 1 electron only
 - at 0 K: E levels filled uniformly up to Fermi level (sharp cutoff in occupancy)
 - at finite T: occupancy cutoff rounded + high-energy tail

Compare solid (e.g. metal) and liquid (e.g. water) - Heat capacity

- a liquid, especially polyatomic, has more ways (modes) of storing energy
 - e.g. water: molecules translate, rotate, vibrate
 - atoms in metal crystal only vibrate
 - fewer energy levels, further apart
 - molar c_v per effective degree of freedom:

("Equipartition principle")

- translation: 1/2 R
- rotation: 1/2 R
- vibration: R (1/2 R potential e., 1/2 R kinetic e.)

Heat capacity for solid, liquid, gas

- Dulong-Petit rule:
 - all metals at high T have same molar $c_v = 3R$
- anomalies at low T (including room T):
 - c lower than expected

 $c \rightarrow 0 \text{ as } T \rightarrow 0$

- explained by quantum theory
- Einstein model simple (all atoms vibrate at same frequency)
- Debye model more advanced (coupled oscillators)
- Equipartition works only if energy levels are well populated. that is:
 - at high T
 - when levels close together
 - translational (also rotational) energy gas

C_v vs T for monatomic gases and a diatomic gas (oxygen)

- monatomic gases only translational energy
 - energy spectrum practically continuous
- diatomic has 3 transl + + 2 rot + 1 vibr. degrees of freedom
 - c_v should be 7/2 R
 - but vibr levels far apart – occupied scarcely at low T



Heat capacity across phases

• a typical pure substance



 corresponding DSC (differential scanning calorimetry) heating trace

Entropy

- Classical thermodynamics (Clausius):
 "Entropy = the function that remains constant after a *reversible* circular process"
- Reversible circular process

$$\oint \frac{dq}{T} = 0$$
$$\oint \frac{dq}{T} > 0$$

• Irreversible (real) process:



Carnot cycle

Entropy has absolute value

- Defect-free crystal of a pure substance at 0 K:
 - only 1 way of arranging

- $S = k \ln w \rightarrow S = 0$
- entropy has absolute value (unlike energy, enthalpy, free e.)
- 1 defect can be placed on N = 25 positions:

w = 25 S = k ln 25

- 2 defects on 25 x 24 positions
- n defects on N!/n! positions

C=O C=O

C=O C=O C=O C=O C=O C=O C=O C=O C=O C=O C=O C=O O=C C=O C=O

Orientationally disordered crystal - Configurational entropy

- CO crystal order-disorder phase transition
 - above T_{trans} equal probability of molecules facing right or left
 - We neglect the small defect energy.

 $w = 2^{N}$

- Entropy of disordered state:

S = N k ln2

- "configurational" entropy (depends on arrangement, doesn't include energy or volume)
- molar heat of order disorder transition:

 $\Delta H = RT_t \ln 2$

Entropy of mixing

• If we have a binary alloy, or generally a mixture of 1 and 1:

$$N_1 + N_2 = N$$

$$\Rightarrow w = N! / (N_1! N_2!)$$

to calculate entropy, use Stirling approximation:

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\ln n! = n \ln n - n
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Thus:
$$S = k \text{ Inw} = k (\text{InN!} - \text{InN}_1! - \text{In N}_2)$$

= $k (N \text{InN} - N_1 \text{InN}_1 - N_2 \text{InN}_2 - N + N_1 + N_2)$
But since $N_1/N = X_1$, and $N_2/N = X_2$ = mole fractions
 $\rightarrow S = -k (N_1 \text{InX}_1 + N_2 \text{In } X_2)$
or, per mole $(N = N_A)$:

$$\mathbf{S}_{mol} = -\mathbf{R} \left(\mathbf{X}_1 \ln \mathbf{X}_1 + \mathbf{X}_2 \ln \mathbf{X}_2 \right)$$

a function with a maximum

Ways to increase entropy



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From C. Kittel, "Thermal Physics"

Energy and free energy

- constant volume:
 - change in energy = change in internal energy dE = dU $dU/dT = c_v$
 - Helmholtz free energy:

A = U - TS

- constant pressure:
 - change in energy = change in enthalpy
 - $dE = dH dH/dT = c_p$ H = U + PV
 - Gibbs free energy (free enthalpy)

$$G = H - TS = U + PV - TS$$

Maxwell daemon

A very useful expression

- G = H TS = U + PV TS
- differentiate:

dG = dU + PdV + VdP - TdS - SdT

but since

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-dU = PdV - TdS
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(1st law of thermodynamics: change in internal energy U at constant P and T equals work given out PdV minus heat taken in TdS)

SO

$\underline{dG = VdP - SdT}$

- Free energy always decreases with increasing T. (S always >0)
- Free energy always increases with increasing P. (V always >0)

Free enthalpy vs T for a pure substance undergoing a 1st order transition (e.g. melting)



Free enthalpy of a •small crystal •strained crystal •crystal with other non-equilibrium defects (per unit volume)

A small crystal has • large surface • large surface free energy $G_c = G_{bulk} + G_{surface} = G_C^0 + \Delta G$

What is ΔG ?

$$\begin{split} \Delta G = \sum A_i \sigma_i \quad (A_i = \text{surface area of i-th crystal face}) \\ (\sigma_i = \text{its surface free energy}) \end{split}$$

 T_m^0 = melting point of perfect infinite crystal T'_m = depressed melting point of a real crystal



Temperature

Partition function and free energy

What is the connection with statistical thermodynamics?

• Probability that system has energy E_i is:

$$P_{Ei} = \frac{g_i \exp(-E_i / kT)}{\sum_{E_0}^{E_{\infty}} g_i \exp(-E_i / kT)} = \frac{g_i \exp(-E_i / kT)}{Z}$$

- Z is the partition function
 - (German: Zustandsumme = sum of states)
 - g_i = "degeneracy" of level *i* (number of states with energy E_i

Partition function and free energy

average energy of the system (U = internal energy):

$$\left\langle E\right\rangle = U = \frac{\sum_{E_0}^{E_\infty} E_i g_i \exp(-E_i / kT)}{\sum_{E_0}^{E_\infty} g_i \exp(-E_i / kT)} = \frac{\sum_{E_0}^{E_\infty} E_i g_i \exp(-E_i / kT)}{Z} = kT^2 \frac{d \ln Z}{dT}$$

- But, most importantly, (Helmholtz) free energy :
 A = kT ln Z This one you should remember!
- $Z \rightarrow$ maximum, hence A (and G) \rightarrow minimum
- Also, since TS = U A: $S = \frac{U}{T} + k \ln Z$

Partition function of crystal and liquid

- "density of states" *g* is much larger in melt than in crystal
- (liquid has many more ways of storing energy in an energy interval *dE* compared to crystal) - crystal only vibrations

$$Z = \int_{E.\min}^{\infty} g(E) \exp(-E/kT) dE$$

- But energy states in liquid start at higher *E* (atoms further apart).
- So at low T most liquid states inaccessible (low Boltzman factor)





Partition function gives molecular interpretation of free energy

- at high T both Z_C and Z_L increase
 - but Z_L increases more because the large number of liquid states become accessible
 - "Entropy wins over energy at high temperatures"
- *Z* = weighted sum of states (weighted by Boltzman factor)
- Z always tends to maximum
 - since

 $A = -k \ln Z$

 \rightarrow free energy (A or G) tends to minimum

Problem: Give a qualitative interpretation of the temperature-induced transition between the regular helical and random coil conformation (helix-coil transition) in biological macromolecules, such as collagen. Remember that helix is stabilized by intramolecular H-bonds.

Binary mixtures

Entropy of mixing: $S_{mol} = -R (X_1 \ln X_1 + X_2 \ln X_2)$



Binary mixtures

Example: binary alloy

- G_C has small maximum mild incompatibility between atoms 1 and 2
- All G's decrease with incr. T but we take G_C as reference
- When G on tie line is lower than G of pure components system is biphasic
- Tangent points of tie lines define composition of phases in equilibrium
- Phase diagram on the right:
 "eutectic" -
- "Lever rule":

$$R_{C} f_{C} = R_{L} f_{L}$$

 $f_{C} , f_{L} = crystal, liquid fractions$



Binary mixtures

- In previous slide G_C and G_C had fixed shapes
 - only shifted with temperature
- However G can change shape with temperature, because:

a) G = H - TS TS changes with T

b) Solubility parameter χ (chi) changes with T

 $\chi = A + B/T$ B positive or negative Entropy of mixing: $S_{mol} = -R (X_1 \ln X_1 + X_2 \ln X_2)$

Free enthalpy of mixing:

$$G_{mol} = H_{mol} - TS_{mol} = RT (X_1 X_2 \chi + X_1 InX_1 + X_2 In X_2)$$

(This comes from interaction energy)



Note: Since all free energies decrease with incr. T, the order of Gcurves should in fact be revcersed.

from: I.W. Hamley, "Introduction to Soft Matter"

Morphology of phase separation

Spinodal decomposition: -As concentration fluctuations grow G increases less and less.

 → bicontinuous morphology
 Length scale of phase separation increases with time Nucleation and growth (binodal): -As concentration fluctuations grow G increases more steeply.

- \rightarrow discrete droplets
- Droplets grow and merge with time ("Ostwald ripening")



Example: compatible polymer blends

- Polymers generally immiscible
 - reason: low entropy of mixing
- Only a few miscible polymer pairs are known:

polystyrene	poly(2,6-dimethylphenylene oxide)
polystyrene	poly(vinylmethylether)
poly(vinyl chloride)	poly(butylene terephtalate)
poly(methylmethacrylate)	poly(vinylydene fluoride)
poly(ethylene oxide)	polyacrylic acid

• miscibility due to favourable interaction between **1** and **2**.