Light, Liquids & Interfaces
Micro-390

Lecture 2

Topic 1: Probability and thermodynamics

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Key concepts Lecture 1

Course Overview

General properties of liquids
Importance of interfaces

Energy and probability (P)
Boltzmann Distribution (BD)
Average Thermal Energy – importance of kT
states are occupied if E<kT

Material to study, Lecture 1 and 2
D. Ben-Amotz: Understanding Physical Chemistry:
Chapter 1: page 15 (start at section 1.2) – 50 (halfway section 1.5)

Energy and Probability

There exists a surprisingly simple relation between energy (ε), probability (P), and temperature:

Ludwig Boltzmann
1844-1906

$$P(\varepsilon) \propto e^{-\beta\varepsilon}$$

β=1/kT

Boltzmann Distribution

More precisely: $$\boxed{P(\varepsilon_i) = \frac{e^{-\beta\varepsilon_i}}{\sum_i e^{-\beta\varepsilon_i}}}$$ or $$\boxed{P(\varepsilon) = \frac{e^{-\beta\varepsilon}}{\int e^{-\beta\varepsilon} d\tau}}$$

For continuum of states

$$\sum_i P(\varepsilon_i) = 1$$

=the partition function q

and $$q \equiv \sum_{i}^{\text{all states}} e^{-\beta\varepsilon_i}$$

i: states

$$P(\varepsilon_j) = \frac{g_j e^{-\beta\varepsilon_j}}{\sum_i g_j e^{-\beta\varepsilon_i}} \qquad q \equiv \sum_{j}^{\text{all energies}} g_j e^{-\beta\varepsilon_j}$$

j: energy levels: g_j = number of states at given energy

Average & Expectation Value

Definition of expectation value for a physical property f that has a distribution P:

$$\langle f \rangle = \sum_i f_i P(f_i)$$

$$\langle f(x) \rangle = \int_{-\infty}^{+\infty} f(x) P(x) dx$$

Probability to find f for discrete values (e.g. spin)

Probability to find $f(x)$ for continuous values (e.g. speed)

Equivalent for the energy, using the Boltzmann distribution for P, we can ask **What is the average thermal energy** ?

$$\langle \varepsilon \rangle = \sum_i \varepsilon_i P(\varepsilon_i) = -\frac{1}{q}\frac{dq}{d\beta}$$

$$\langle \varepsilon(x) \rangle = \int_{-\infty}^{+\infty} \varepsilon(x) P(\varepsilon(x)) d\underset{\downarrow}{x}$$

Variable on which the energy depends

For discrete states

For a continuum of states

Example: Gasses

Have a continuum of energy levels

Kinetic energy relates velocity to energy $\varepsilon_x = \frac{1}{2} m v_x^2$

Ideal gas law (point atoms with no volume):

PV = NkT {molecular} PV = nRT {molar}

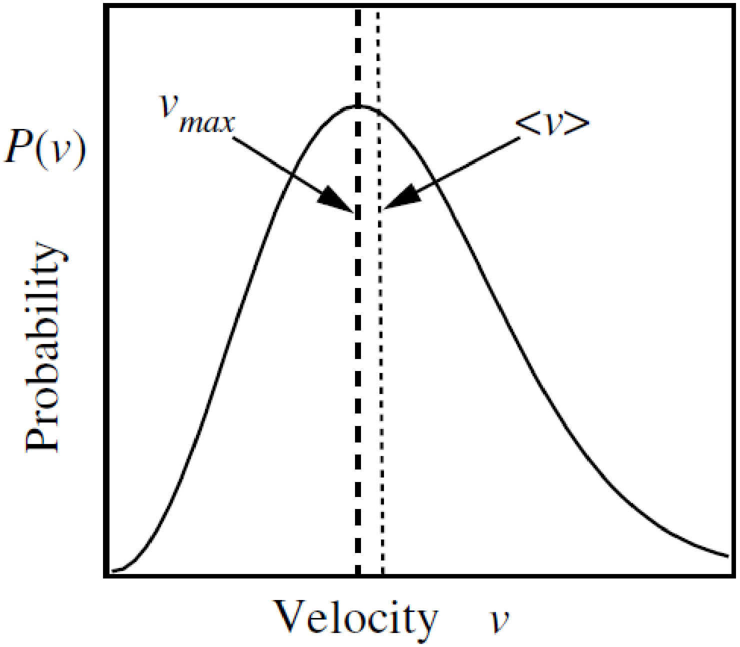
Maxwell-Boltzmann Distribution

Probability of speed / energy distribution in a gas:

$$P(v_i) = \sqrt{\frac{m}{2\pi kT}}\, e^{\frac{-mv_i^2}{2kT}}$$

$$P(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv^2}{2kT}} 4\pi v^2$$

$$\langle \varepsilon(v) \rangle = \int_{-\infty}^{+\infty} \varepsilon(\mathrm{v}) P(\varepsilon(v))\,dv = \frac{3}{2}kT$$



Each independent energy term (ε_x,ε_y, ε_z) contributes $\frac{1}{2}kT$ to the energy.

This turns out to be a general feature of quadratic terms in the Hamiltonian. For a linear diatomic molecule:

Translation: $\frac{1}{2}mv_x^2$, $\frac{1}{2}mv_y^2$, $\frac{1}{2}mv_z^2$

Rotation (z axis): $\frac{1}{2}I_x\omega^2$, $\frac{1}{2}I_y\omega^2$

Vibration: $\frac{1}{2}k\delta^2$, $\frac{1}{2}mv_\delta^2$ (displacement δ along normal coordiante)

$$\langle \varepsilon \rangle = \frac{7}{2}kT$$

Example: Gasses

Have a continuum of energy levels

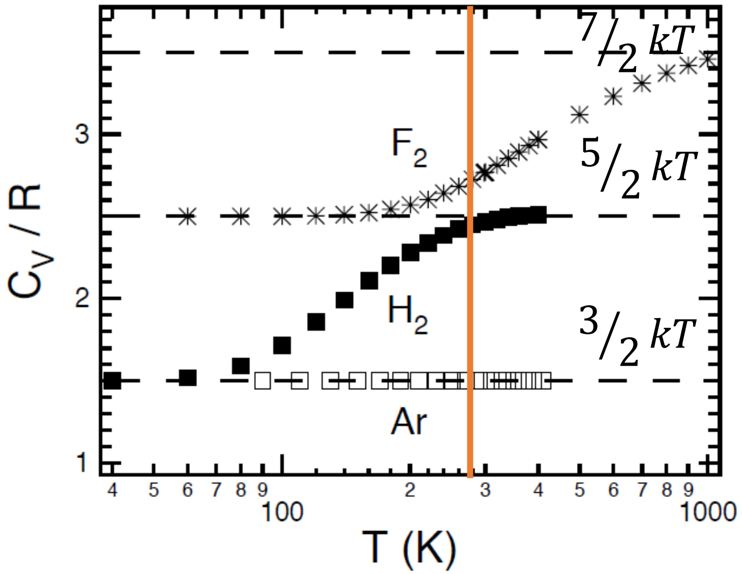
Kinetic energy relates velocity to energy $\varepsilon_x = \frac{1}{2} m v_x^2$

Total energy (U) is the sum of translational, rotational and vibrational energies

Quantization of Energy

For a monoatomic gas $\langle \varepsilon \rangle = \frac{3}{2}\mathrm{kT}$; $\mathrm{U} = \mathrm{N}\langle \varepsilon \rangle = \frac{3}{2}RT$

Calorimetry: $C_v = \left(\frac{\partial U}{\partial T}\right)_v = R\langle \varepsilon \rangle$ = Energy needed to heat a substance by 1 K



While Ar gas displayed the correct expectation H_2 and F_2 didn't ….

Why …. ?

kT = 209 cm^{-1}

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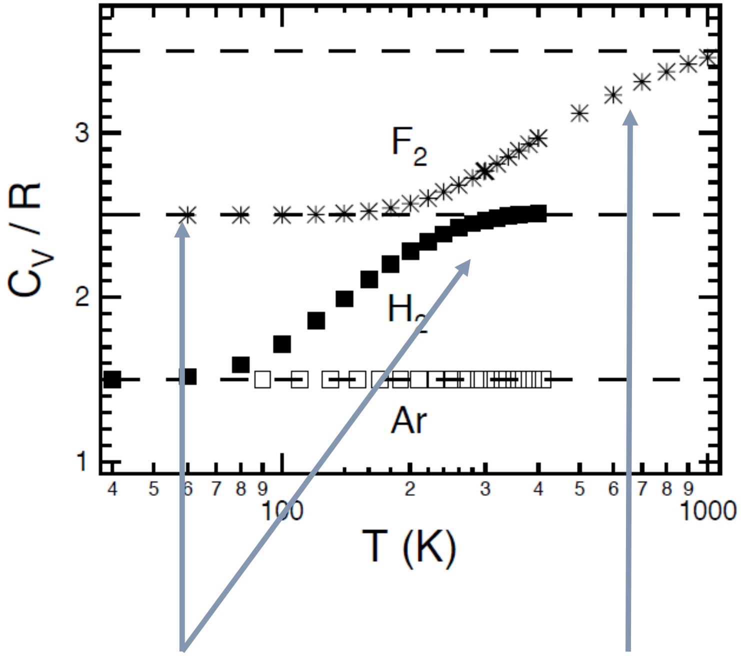


While Ar gas displayed the correct expectation H_2 and F_2 didn't ….

Why …. ?

Rot. + Transl. states are populated

Vibr. + Rot. + Transl. states are populated

H_2: 4342 cm^{-1}: stretch mode
H_2: 354 cm^{-1}: rot mode
F_2: 1365 cm^{-1}: stretch mode
F_2: ~10 cm^{-1}: rot mode

Room temperature: 209 cm^{-1}

Probability relates to (chemical) transformation….

BD and Transformations

Transformations such as chemical reactions, shape changes, change of state, solubility, orientational distributions, partitioning, charging of an interface. (etc) can be computed using the Boltzmann distribution

$$A \rightleftarrows B \qquad K = \frac{[B]}{[A]} = \frac{X_B}{X_A}$$

$$\Delta\varepsilon = -kT \ln K$$

Knowing the initial and final states and their energy relations predictions can be made about interactions in liquids

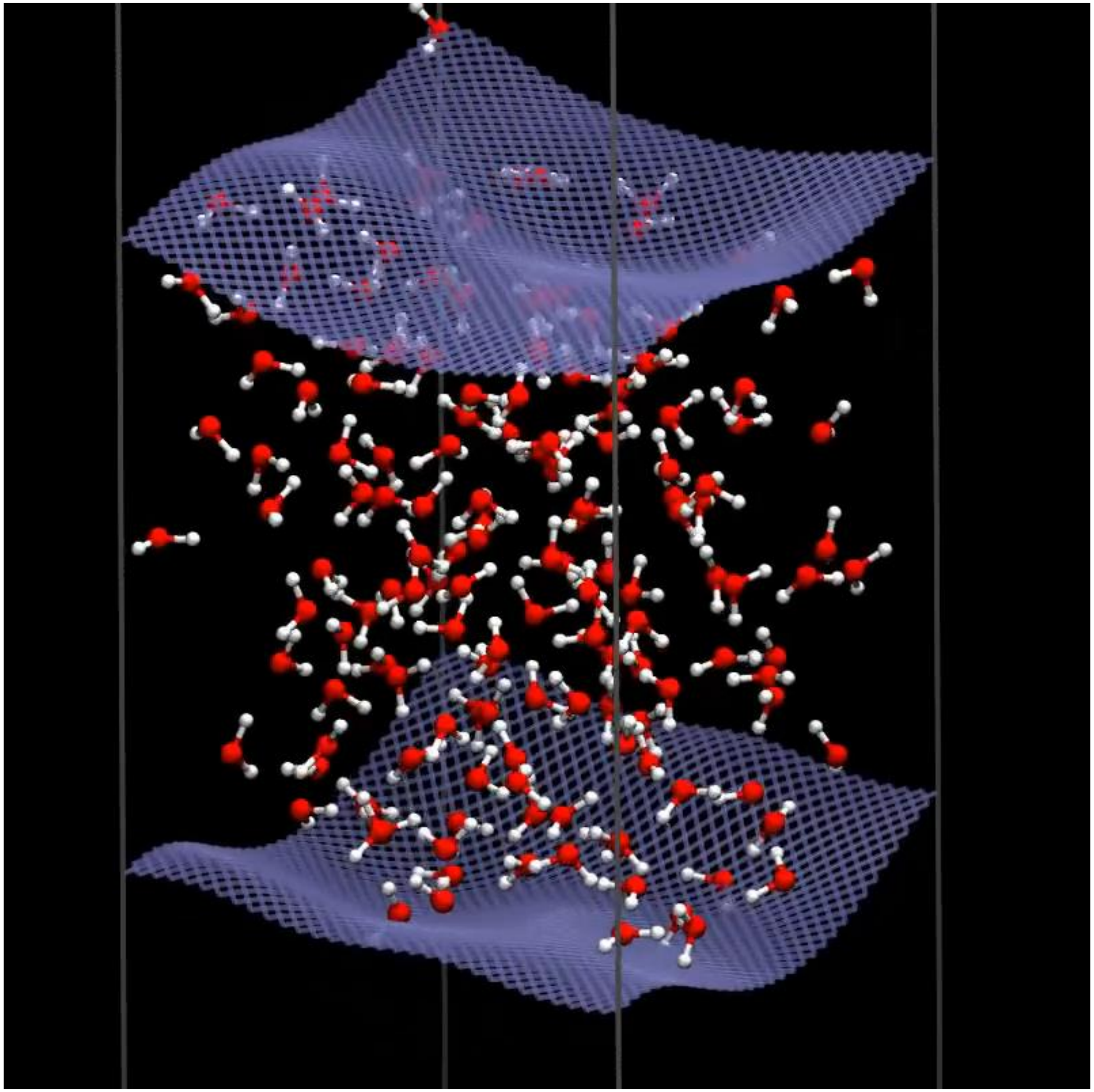
This is the same result that we have seen from thermodynamics and a very powerful tool that can be used in combination with the interaction energy (μ) and pair potential (w). [next ….]

Topic 1: Probability and thermodynamics

Energy and probability
Boltzmann Distribution (BD)
Average Thermal Energy
Transformations and use of BD
Thermodynamics reminder
Free energy
Interaction energy & pair potential
Long & short ranged interactions

Material to study:
JN Israelachvilli: Intermolecular and surface forces:
Chapter 2

Useful background
D. Ben-Amotz: Understanding Physical Chemistry:
Chapter 2 & 3



Video: Michele Ceriotti, COSMO, EPFL

Interactions in liquids

In a liquid or at a liquid interface every molecule interacts with other molecules, changing partners and having sometimes multiple types of interactions. These many body interactions require three things to be understood:

Statistics

+

Thermodynamics

+

Molecular interactions

Thermodynamics: Reminder

Describe the equilibrium properties of a system
Quantitative statements about transformations between equilibrium states

But: no statements about structures or paths

Variables are **intensive** or **extensive**

independent on the size:

P, T, ρ

dependent on the size:

$U = \sum_i U_i$, S= $\sum_i S_i$, V= $\sum_i V_i$

Always define what is the <u>system</u>, the <u>surroundings</u> and the <u>process</u> of interest.

Thermodynamics: Definitions

Adiabatic process: a process that occurs under thermal isolation

Reversible process: A system interacting with its surroundings through a series of equilibrium states of system and surroundings. Change occurs through infinitesimal small steps

Entropy: Any form of energy that is not work $dS = \frac{\delta Q}{\mathrm{T}}$

also defined from statistical physics: $S = \mathrm{k}\ln\Omega$

Ω: Equivalent to the number of quantum mechanical states that are thermally accessible to a system

Thermodynamics: Laws

Thermodynamic laws:

1. The energy of the universe is constant, $dU = \overset{\substack{>0\text{, heat added} \\ \uparrow}}{\delta Q} + \overset{\substack{>0\text{, work done} \\ \uparrow}}{\delta W}$

2. The entropy of the universe seeks a maximum

3. $\lim_{T \to 0} S = 0$

Thermodynamics: State Functions

The energy U depends only on the initial and final state and not on the path taken. Q and W are not **state functions**

State functions that appear in reversible processes follow the laws of thermodynamics and are a set of exact [i.e. variables are independent] analytical differentiable functions that are single values.

State functions: U, H, G, A

State functions can be related by Legendre transforms

Thermodynamics: Free energy

U: internal energy
H: enthalpy: change in heat when (P,N) are constant

$H = U+PV$

A: (Helmholtz) free energy: the amount of work that can be exchanged in a reversible process with (T,N) constant

$A = U-TS$

G: (Gibbs) free energy: the amount of work that can be exchanged in a reversible process with (T,P) constant

$G = H-TS$

Free energy: the energy available to do work with.

Some notes on the Euler relation
State functions
Legendre transforms
Free energy

Key concepts Lecture 1 and 2

Energy and probability (P)
Boltzmann Distribution (BD)
Average Thermal Energy – importance of kT
Transformations and use of BD – predict likelihood of transformations
Thermodynamics reminder
Free energy = energy available to do work with

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