First (this part)

– Conceptual and (some) technical/mathematical/computational background

Then (next part)

- **Molecular simulations** are one way to do statistical mechanics
  - Molecular Dynamics or MD
  - Monte Carlo or MC

We observe: people say: "The spectrum is the fingerprint of a molecule"

Is this true?

Always?

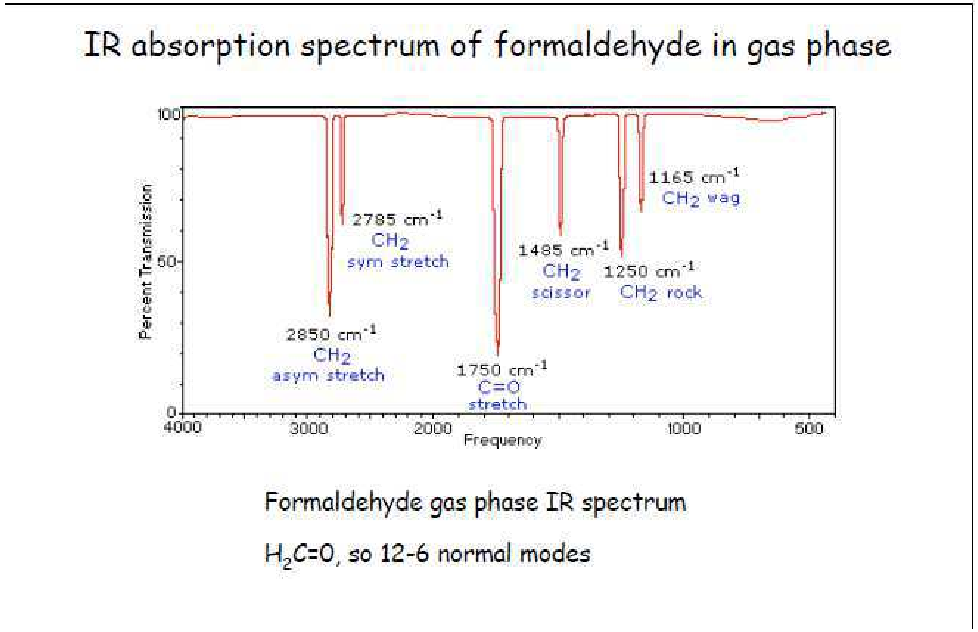
Under which conditions?

---

microscopic interpretation

MACROSCOPIC spectrum
(on a screen or a piece of paper)

CH_2 sym. stretching vibration
CH_2 asym. stretching vibration
C=O stretch
...
...
How can they know that?


IR absorption spectrum of formaldehyde in gas phase

Formaldehyde gas phase IR spectrum

$H_2C{=}O$, so 12-6 normal modes

1 molecule

some $\mathbf{10^{17}}$ molecules (10^{-6} N_A)

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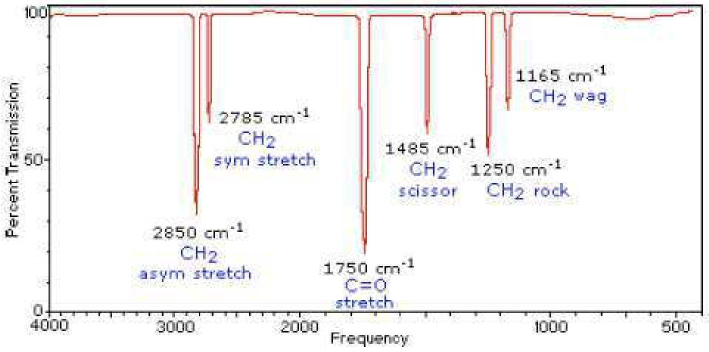

Formaldehyde gas phase IR spectrum

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They know it based on **assumptions** such as:

– All H_2CO molecules 'do the same thing' (vibrate, rotate, ...)

– They do it **independently** of each other
(i.e the vibration of molecule i does not change whether or not another molecule j is nearby)

'independent' means that the molecules do not interact, or, better,
that their interactions can be **neglected**
because (e.g.) the interaction energies involved are (very) **small compared to** some other
energies of interest,

e.g. the thermal energy $k_{\mathrm{B}}T$, k_{B} is Boltzmann's constant.

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What happens if these assumptions are not valid any more?

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More things to think about:

– Think e.g. of a typical property of a liquid like 'viscosity'. One molecule does not have a viscosity, two molecules don't have a viscosity, ... , and you could actually ask yourself:
How many molecules does it take so that something like viscosity arises?

– So we need a technique to treat many (enough) molecules.
(*If we are after something like "viscosity" (only an example!) we need not only to know 'on the average' where the molecules are (the 'structure', thermodynamics), but also how they move (the 'dynamics').*
We shall not deal much with this aspect here.

– And last but not least:
Nothing occurs at $T = 0$ K. We need also to understand the effect of **temperature**.

In other words

– The properties of matter (e.g. its structure, (e.g. phases in solids, but also in liquids), internal energy, viscosity, diffusion, ...)
cannot be related to the properties of a single molecule alone.
Such properties are properties of ensembles of many (how many?) molecules.
Such properties depend on the conditions e.g.:
temperatures T, density ρ, pressure p, ...

– Most methods in theoretical chemistry consider only the (potential) energies at T $=$ 0 K an thus neglect the influence of the kinetic energy (entropy).

– This is sufficient in many cases, e.g. when energy differences between educt and product in chemical reactions are large.

However, many reactions, e.g. in biology, are so fine-tuned that e.g. **temperature becomes a very important factor**

The solution
– Ludwig Boltzmann (1844-1906) and **statistical mechanics**

Statistical mechanics $\approx$ statistical thermodynamics
$\approx$ statistical physics $\approx$ many particle physics $\approx$

– **Analytical work**
Very simple models, gas phase ((almost) independent molecules),
some crystalline solids ($\rightarrow$ phonons]

– **Molecular simulations**
allow to go beyond simple (e.g. harmonic potentials)
and 'academic' cases, liquids, interfaces, inhomogeneous systems, ...

Here we shall briefly look at the **"partition function"**
and then study one simulation method: **Molecular Dynamics (MD)**
the other important one is (Metropolis) Monte Carlo (**MC**),
and there are several others (to be discussed if we have time)

Historic remark:

Numerical work (e.g. MD, MC) was not possible before computers
became generally available (1970ies with some precursors
(Edward Teller, Bernie Alder ...) since the 1940ies (Manhattan Project))

Theoreticians were used to search for 'analytical solutions'
(i.e. finding mathematical solutions of
(usually differential or integral) equations)

Simulations required a different way of thinking,
they were thus often called **computer experiments**

⟹ So we can say:

Statistical mechanics is a method to deal with systems
of many **interacting molecules** at **finite temperatures**.

microscopic

MACROSCOPIC

⇒ **Ludwig Boltzmann** and **Statistical Mechanics**

1844 -1906

Note: Ludwig Boltzmann probably knew nothing about quantum theory.
Max Planck's famous seminar
(introducing the 'quantum', Planck's constant (h or $\hbar$))
in Berlin was on Dec. 14, 1900.

WIKIPEDIA says it all:

It (i.e. statistical mechanics) provides a framework for relating the **microscopic** properties of individual atoms and molecules to the **macroscopic** or bulk properties of materials that can be observed in everyday life

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The basic tenet of statistical mechanics:

microscopic		**MACROSCOPIC**
microstates	$\Longleftrightarrow$	**MACROSTATE**
atoms, molecules		pressure, temperature ,
$\hat{H}\psi = E\psi$		viscosity, ...
$\hat{H}\psi = i\hbar\frac{\partial\psi}{\partial t}$		$p, V, T, Q, \Delta U, S, ...$
Schrödinger equation		observables
→ need to simplify		thermodynamics,
(coarse grain)		classical theories

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The problem is:

Under “normal“ conditions (i.e. at $T > 0$) there are, for any (physical/chemical) system*,

NOT ONLY ONE,
but **very, very, very many**
microscopic states (microstates)
that are **compatible with**

ONE given MACROSTATE of that system.

* System: E.g. some **condensed phase**: A liquid, a supercritical fluid (vapor), a solution, a mixture, ...

Example

Take 1 mole of water.
Gibbs' rule (remember?) says you can specify (e.g.)
N (1 mole), the pressure (e.g. $p=$1 bar), and the temperature (e.g. $T=$298 K).
When you have specified these 3 quantities,
you **cannot** specify any 4th one (e.g. some volume ($V=n$ cm^3))
with these given values for N, p, T
the system will just 'have' the volume it wants.

This is one **MACROSTATE** of this system
and you can do classical (or phenomenological) thermodynamics
($\Delta U, \Delta G, \Delta S, c_p, c_V$, ... see part 2)

Example (in principle only, in reality it's much more complicated)

1	2	3	4	
vJn	v'J'n'	v''J''n''		microstate 1
vJn	v'J'n'	v''J''n''		microstate 2
vJn	v'J'n'	v''J''n''		microstate 3

(*different colors mean different values*)

All these (and many more) microstates can lead (be compatible with) the same MACROSTATE (N, p, T)
($\rightarrow$ principle of equal 'a-priori' probability)

Very important
At the conditions in chemistry ($T \approx 200, 300, 400...$ K,
and for 'heavy enough' molecules ($m > m_{\mathrm{H}_2}$))
the translational/rotational/(vibrational) microstates can be described by
classical (Newtonian) mechanics
instead of quantum mechanics (Quantum numbers → positions and velocities)

(remember the 'de Broglie wavelength' $\lambda = h/p = h/(mv)$, p momentum, v velocity)

⟹ Assuming that there is no electronic excitation
(we stay in the electronic ground state)
we can do classical (Boltzmann) statistical mechanics.

This also implies that we have many more **microstates** than particles, so
we can neglect spin (Pauli principle)
If not: → quantum statistics:
Fermi statistics (fermions), Bose-Einstein statistics (bosons)
example: electrons in metals (Fermi)

Summary of the introduction to stat.mech.

A MACROSTATE is completely described by only very few macroscopic variables, e.g. N_i, V, p, ... (→ Mr. Gibbs)

We can never (**really never never ever!**) hope to know all* microstates $\mathcal{P}_j$

Using, as just argued, classical mechanics, we can call:

$$\mathcal{P}_j = \{\vec{r}_1, \vec{r}_2, \vec{r}_3, ..., \vec{r}_{N_A}, \vec{v}_1, \vec{v}_2, \vec{v}_3, ..., \vec{v}_{N_A} \text{ at (say) some time } t_j\}$$

one (of many) **microstate**s of a chemical system compatible with one MACROSTATE.

* Roughly: There are more microstates in a glass of water than stars (possibly atoms) in the universe!

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Summarize the Simplifications

(**i**)(If the temperature is sufficiently high and/or the particles sufficiently heavy (i.e. the de Broglie wavelength $\lambda = h/p$ is small compared to the dimension of the particles) the atoms/molecules can be considered as 'classical' particles, subject to Newton's equation $M_i \cdot \frac{\partial^2 \vec{r}_i}{\partial t^2} = \vec{F}_i(........) \quad i = 1, ..., N$.
→ Exit Schrödinger's equation **(for the nuclei ONLY!)**

(**ii**) We can in some way 'pre-calculate' the interactions between the molecules and use these pre-calculated interactions (**the model**) in our study.
This 'removes' the electrons (which are at the origin of the interactions) from the problem (**The Born-Oppenheimer approximation**)

What to do about all this?

level of description of microstate		What can be done?
everything quantum mechanical	⇒	almost impossible except in very simple cases
classical mechanics highly simplified problems e.g. particle in the box, rigid rotor harmonic oscillator	⇒	analytical theory →**partition function** **Part 4**
classical mechanics, Born-Oppenheimer interaction models	⇒	**Computer simulations** MD or MC **Parts 5,6**
(some) electrons QM nuclei classical	⇒	special simulations

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Part 4

Statistical thermodynamics, a few analytical results

This is entirely taken from Mc.Quarrie, Statistical Mechanics
see Wilson, Decius & Cross for Normal Modes

We start from the assumptions just described (classical mechanics, forget about spin) and introduce Boltzmann's basic concepts (with a minimum of math, see textbooks for a rigorous treatment).

At the end, we will see that QM sneaks in again
– isotope exchange equilibria
– ortho-para hydrogen problem

Philosophy gets on my nerves. If we analyze the ultimate ground of everything, then everything finally falls into nothingness. But I have decided to resume my lectures again and look the Hydra of doubt straight into the eye, (Ludwig Boltzmann (1844-1906))

Boltzmann ($\dagger 1906$) did not know about quantum mechanics,
but firmly believed in the existence of 'molecules'

So the arguments leading to the correct
statistical mechanical expressions,
(essentially the '**partition functions**',
called $\Omega, Q = Z, \Xi$ ... , as the case may be)
where much more difficult for him (i.e. using classical mechanics)
than for us (since we **can** define **'state'**).

The basis idea is that there are an extremely large number of micro- (quantum-) states that all lead to the same macroscopic state, characterized e.g. by a certain number of molecules N in a certain volume V having a certain total energy E (thus (NVE))
(or (NpT) or (NVT) or (μpT) or $(N_1 N_2, V, E)$ or ...(Gibbs phase rule))

If one knows (or knows how to construct for a model)
all possible micro-states
one can (try to) compute the so-called '**partition function**'
(*German* **Zustandssumme = sum over states**)
by summing (integrating) over all (supposedly known) states compatible with the given conditions (e.g. NpT).

If one has this partition function (Ω, Q (Z) as the case (i.e. the external conditions) may be)
thermodynamic averages, i.e. the average value of observables under the given conditions, can be obtained.

under conditions of N, V, E constant,
the partition function is call **microcanonical** Ω (capital ω, o-mega)

under conditions of N, V, T constant,
the partition function is call **canonical** Q or Z
(*this is the one mostly used*)

under conditions of μ, V, T constant,
the partition function is call **grand canonical** Ξ (capital ξ, xi)

under conditions of .... constant,
the partition function is called **.......**

We shall deal, very little, only with Ω and Q

From the partition function $Q\left(Z, \Omega, ...\right)$ one can compute thermodynamic quantities like entropy, free energy, ..

From Ω

$$S = k_{\mathrm{B}} \ln \Omega \;\; (\textit{the most famous equation})$$

It says W, from German 'Wahrscheinlichkeit' (probability), because that is really what it is (as we shall shortly see)

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}, \text{ etc. etc.}$$

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From Q, the canonical partition function

$$\boxed{Q = \sum_{\textbf{all states } i} \exp(\frac{-E_i(N,V,T)}{k_\mathrm{B}T})}$$

$$S = k_\mathrm{B}T\;(\frac{\partial \ln Q}{\partial T})_{N,V} + k_\mathrm{B}\ln Q$$

$$\langle E\rangle = k_\mathrm{B}T^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

For an equilibrium

$$\nu_a A \;+\; \nu_b B \;\leftrightharpoons\; \nu_c C \;+\; \nu_d D$$

$$\mu_A = -k_\mathrm{B}T\left(\frac{\partial \ln Q}{\partial N_A}\right)_{N,V,T} \approx -k_\mathrm{B}T\;\ln\frac{q_A(V,T)}{N_A}$$

q is the **molecular partition function** (see later)

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The average value $\langle ... \rangle$ of any quantity (observable) A over the given ensemble (NVE, NVT , etc.) is given by (just two examples):

From Q (NVT)

$$\langle A \rangle_T = \frac{1}{Q} \int_{\text{all } p,q} A(p,q) \cdot \exp \frac{E(p,q)}{k_\mathrm{B}T} \,\mathrm{d}p\,\mathrm{d}q \qquad \text{(AvQ)}$$

From Ω (NVE)

$$\langle A \rangle_E = \frac{1}{\Omega} \int_{\text{all } p,q} A(p,q) \cdot \delta(E(p,q) - E_0) \,\mathrm{d}p\,\mathrm{d}q \qquad (\mathrm{Av}\Omega)$$

where q stands for all positions variables $(x_1, y_1, z_1, x_2.y_2, ..., z_N)$
and p for all velocity variables $(vx_1, vy_1, ..., vz_N)$

So the integrals are $6N$-fold integrals ($\int \int \int ...... \int$) over the (q,p)-space, which is called **phase space**

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$\Rightarrow$ not really doable (except in some very simple cases)!

We will look only at one case: "the diatomic ideal gas"
(see McQuarrie for details)
under NVT conditions → canonical partition function Q (Z)

Even though we will use classical statistical mechanics, it is simpler to argue with QM

The wavefunction for one molecule is assumed to be

$$\Psi = \psi_{\rm trans} \cdot \psi_{\rm rot} \cdot \psi_{\rm vib} \cdot \psi_{\rm elect}$$

(this is not always possible, nuclear spin is neglected)

We will use the following approximations:
$\psi_{\rm trans}$: particle in box states, continuum
$\psi_{\rm rot}$: rigid rotor states, almost classical
$\psi_{\rm trans}$: harmonic oscillator states, can be summed analytically
$\psi_{\rm elect}$: whatever you have computed quantum mechanically, ground state only

We can then compute a 'molecular partition function' q

$$q = q_{\text{trans}} \cdot q_{\text{rot}} \cdot q_{\text{vib}} \cdot q_{\text{elect}}$$

and since the molecules are assumed **not to interact** (ideal gas):

$$Q = \frac{q^N}{N!}$$

(It is with these approximations that most quantum chemistry programs propose values for such quantities)

All this is not easy, it takes one semester to derive the expressions,
and we have no time to do it here

$$q_{\mathrm{molec}} = q_{\mathrm{trans}} \cdot q_{\mathrm{rot}} \cdot q_{\mathrm{vib}} \cdot q_{\mathrm{elect}}$$

Approximations:
q_{elect}: Only electronic ground state

q_{trans}: Particle in box states
q_{rot}: Rigid rotor states
q_{vib} : Harmonic oscillator (normal mode) states

Remember?

Hamiltonian	Eigenvalues	Eigenfunctions
particle in box	$E_n = h^2/(8mL^2) \cdot n^2, n = 1, 2, 3...$	
harmonic oscillator	$E_v = \hbar\omega(v + 1/2) \quad , v = 0, 1, 2, ..$	
rigid rotor	$E_l = \hbar^2/(2I)l(l + 1), l = 0, 1, 2...$	

So, basically, we have to do sums like:

$$q_{\text{trans}} = \sum_{n=1}^{\infty} \exp \frac{-\mathcal{C}n^2}{k_{\text{B}}T} \quad \text{for the } x, y \text{ and } z \text{ directions}$$

$$q_{\text{rot}} = \sum_{l=1}^{\infty} \exp \frac{-\mathcal{D}l(l+1)}{k_{\text{B}}T} \quad \text{for the 3 axes of rotation (moments of inertia)}$$

$$q_{\text{vib}_\text{i}} = \sum_{v_i=0}^{\infty} \exp \frac{-\mathcal{E}_i(v_i+1/2)}{k_{\text{B}}T} \quad \text{for each mode } i \text{ (only 1 here)}$$

with $\mathcal{C}, \mathcal{D}, \mathcal{E}_i$ constants, see previous page

This can be done (maths), we'll only quickly look at the vibrational part

– The infinite sums can be carried out either exactly or to a very good approximation (see textbook)

– So we need to find
the $\mathcal{C}$s, $\mathcal{D}$s and $\mathcal{E}$s

– For a molecule, (except for constants),
$\mathcal{C}$ contains the masses m,
$\mathcal{D}$ contains the moments of inertia I (from the masses and the geometry)
and $\mathcal{E}$ contains the vibrational frequencies

– This data is available in (from) quantum chemical programs (GAUSSIAN and such), so thermodynamic quantities can be computed with these approximations
(non-interacting molecules, rigid rotor, harmonic frequencies)

Example: Equilibria (see McQuarrie's book p.143)

$$\text{from the equilibrium condition : at } T, V = \text{const. : } \sum_i \nu_i \mu_i = 0$$

$$\nu_i = \frac{N_i}{\sum_i N_i} \quad \text{mole fraction}$$

$$A + B \rightleftarrows 2AB \quad , \quad K = \frac{N_{AB}^2}{N_A \cdot N_B} \quad = \quad ..... \quad = \quad \frac{q_{AB}^2}{q_A \cdot q_B}$$

So we need to find the individual qs for the molecules A, B and AB, combine them to get the Qs
(*which will be simple and only the qs survive, see above*),
and compute from them the ...., see equation .... above

In most chemical reactions, the main contribution to K comes from the q_{electr}-parts of the partition functions

Let's test this in a particular case:

$$\text{experimentally :} \quad \mathrm{H_2 + D_2 \rightleftarrows 2HD} \quad , \quad \mathrm{K} \neq \frac{2^2}{1 \cdot 1} = 4$$

K becomes $= 4$ only when $T \to \infty$. Why this?

It cannot be the q_{electr} since the electronic energies are **the same** for H_2, D_2 and HD (**Born-Oppenheimer approximation**)
So what is it?

Equilibrium constant, see e.g.
http://www4.ncsu.edu/~franzen/public_html/CH795N/lecture/XV/XV.html

---

We note in passing: The partition function contains no information about how the system gets from one state to the other, no time
(*like when you consider equilibria (say chemical potentials* μ*), you do not worry how you got there, how long it took to reach equilibrium*)

$$\mathrm{H_2 + D_2 \rightleftarrows 2HD} \quad , \quad \mathrm{K} \neq \frac{2^2}{1 \cdot 1} = 4$$

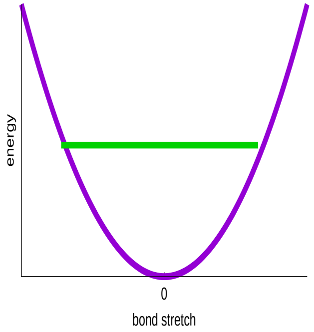
– q_elect is the same for H_2, D_2, HD

– One can check (not done here) that q_rot also does not contribute (even though the Is are not the same)

– this leaves q_vib
We go to a sufficiently low temperatures* so that the sum in q_vib can be approximated by the first term, $i = 0$, i.e. the zero point energy, ZPE

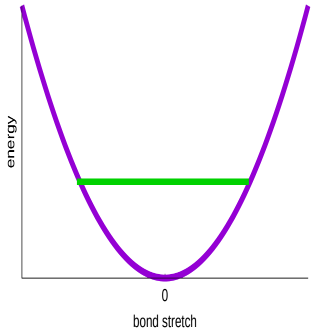
* but not too low, otherwise, in Hydrogen, other quantum effects (ortho- vs. para-hydrogen) have to be considered

H_2

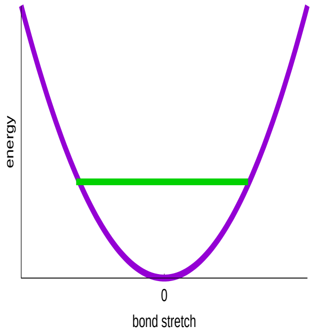


D_2

HD



HD



$$\mathrm{ZPE} = \frac{\hbar\omega}{2} = \frac{\hbar\sqrt{\frac{k}{\mu}}}{2} \quad , \quad \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \quad , \quad \text{we set } m_\mathrm{H} = 1\,,\; m_\mathrm{D} = 2\,,\; k = 1\,,$$

$$\hbar = 1 \qquad \Rightarrow \mu_{\mathrm{H}_2} = \frac{1}{2}\,,\; \mu_{\mathrm{D}_2} = 1\,,\; \mu_\mathrm{HD} = \frac{2}{3}$$

$$\mathrm{ZPE}_{\mathrm{H}_2} = \frac{\sqrt{2}}{2} \quad + \quad \mathrm{ZPE}_{\mathrm{D}_2} = \frac{1}{2} \qquad \mathrm{ZPE}_\mathrm{HD} = \frac{\sqrt{\frac{3}{2}}}{2} \quad (\cdot 2)$$

$$\text{Energy balance}: \qquad 1.207 \qquad < \qquad 1.225$$

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So the energy is a bit lower on the left hand side,
the partition function $(\exp(-....)$ thus a bit higher,
and K thus less than 4

Of course, the deviation of K from 4 will depend on temperature:
the higher T, the smaller the deviation
(as befits a quantum effect: when all vibrational levels become populated,
the effect goes away)

Excursion: Normal Modes (spectroscopy, computing simlified partition functions, ...)

In some cases, Newton's coupled differential equations:

$$m_i \frac{\partial^2 r_i}{\partial t^2} = \vec{\mathrm{grad}}_i V = \vec{F}_i \quad , \ i = 1, N$$

do have an analytical solution.

The most famous case are 'normal modes'
(*physicists talk about 'group coordinates'*),
which exist ONLY if the right hand side
(rhs, i.e. the potential V and forces $\vec{F}$)
have a very special form* and the motions are 'infinitesimally small' around an extremum (usually minimum, however, → transition states).

Normal modes are a generalization of the well-know
harmonic oscillator problem

* Otherwise, the equations cannot be solved analytically (Henri Poincaré)
$\Rightarrow$ numerical solutions = simulations

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Reminder:

$$\omega = \sqrt{\frac{k}{m}} \quad , \quad E_v = \hbar\,\omega\,(v + \frac{1}{2})$$

m: the mass; k: the force constant (2nd derivative of potential)
ω: frequency, v **vibrational quantum number**

(Note again the the frequency computed from classical mechanics is used in the expression for the quantum energies)

Classical solution:

$$\Delta x(t) = A \cdot \cos(\omega t) + B \cdot \sin(\omega t) = C \cdot \cos(\omega t + \delta)$$

$\Delta x(t) = x(t) - x_0$: a displacement with respect to an equilibrium position
A, B, C, δ from the initial conditions

for two masses m and M (and one 'spring') on has:

$$\omega = \sqrt{\frac{k}{\mu}} \quad , \quad \frac{1}{\mu} = \frac{1}{m} + \frac{1}{M} \quad , \quad \text{and } E_v = \hbar\, \omega\ (v + \frac{1}{2})$$

Spring: Hooke's law $V(x) = k \cdot (x - x_0)^2$
(often written as $V(x) = k/2 \cdot (x - x_0)^2$

For more masses and 'springs', we generalize the springs as:

$$V = \sum_{ij} k_{ij} \rho_i \rho_j \ \ (\textit{which can be expanded as } V = \sum_{kl} c_{kl}\ u_k^{x,y,z} u_l^{x,y,z} \ \ )$$

k_{ij} are (generalized) force constants (force field),
ρ internal (Wilson) coordinates (stretch, bend, torsion ...)
$u_k^{x,y,z}$ are (infinitesimally) small displacements
of particle k in x, y or z direction

Such a 'harmonic' potential can be obtained by expanding any potential around an extremum (minimum)
This is what the quantum chemistry codes do.

With this potential (bilinear form) Newton's equations of motion can be solved analytically
(*see Wilson, Decius and Cross*)
and one gets for the motions of particle i:

$$\vec{r}_i(t) - \vec{r}_i^{\,0} = \sum_{J=1}^{\mathcal{N}} A_J \cdot \vec{Q}_i^J \cdot \cos\left(\Omega_J \cdot t + \delta_J\right)$$

There are (if ....) $\mathcal{N} = 3N - 6$ normal modes for a system (molecule) of N masses, $\mathcal{N} = 3N - 5$ for linear systems (molecules)

A_j and δ_J are arbitrary amplitude and phase factors
(which depend on the initial conditions)

$\vec{Q}_i^J$ are vectors (the normal modes) describing the relative motion of atom i under mode J.

Properties of normal modes, look at the equation:

- All atoms i in a normal mode J move 'in phase' (or anti-phase), the A and δ depend only on J, not on i

- Normal modes are 'orthogonal' (or adiabatic) to each other,
this means a mode J will not transfer vibrational energy to another mode
(*you know that e.g. in molecules this is not entirely true*)

- Normal modes are the main tool to assign and interpret
vibrational spectra (IR, Raman)
the symmetry of the normal modes is related to the selection rules

We can uses the frequencies Ω from the classical normal mode calculations to obtain the QM energy levels
The quantum energies are, since the modes are independent:

$$E_{v_1,v_2,v_3,\ldots,v_{\mathcal{N}}} = \hbar\Big(\Omega_1(v_1+\frac{1}{2})+\Omega_2(v_2+\frac{1}{2})+\Omega_3(v_3+\frac{1}{2})+\ldots+\Omega_{\mathcal{N}}(v_{\mathcal{N}}+\frac{1}{2})\Big)$$

$$(\ \mathcal{N} \text{ independent modes} \quad \Rightarrow \quad \mathcal{N} \text{ quantum numbers } \nu\ )$$

Some words of caution:

Since normal modes are independent, i.e. do not exchange energy, a normal mode system will not evolve toward thermodynamic equilibrium!

Refer to:

→ Your spectroscopy class (IR, Raman)

→ Statistical mechanics (the Ωs for the vibrational partition function)

What have we missed up to now? Mostly intermolecular interactions
(real gas, fluids, liquid, solid ... condensed phases)

Let's go back to Ludwig Boltzmann
(who could not know quantum mechanics)

–He thought about N classical particles (beads) interacting in some way through potentials.
–He would then get the 'states' by solving Newton's equations for the N particles (numerically or otherwise)
and write down the positions and velocities at regular time intervals.
The total energy would stay constant due to the properties of these equations (see above).
–Summing over the so-defined 'states'
(and there is a difficulty here that only quantum mechanics could resolve)
he got a slightly different partition function (called microcanonical, Ω)

Reminder:

Statistics where the spin contributions can be neglected (e.g. molecules) are called **'Boltzmann statistics'**
If the spin cannot be neglected
(symmetry of wave function, Pauli principle)
we have either **'Fermi statistics'**
(e.g. 'free' electrons in solids, spin $= 1/2$, fermions)
or **'Bose.Einstein statistics'** (spin 1,2,3, ..., bosons)

'Fermi statistics': electrons in solids, Fermi surface,
Fermi energy (which is usually $>> k_{\mathrm{B}}T$), ...

'Bose statistics', e.g.: ^{3}He-^{4}He mixtures below 4 K