From quantum mechanics to statistical mechanics in a nutshell

– We want to study the statistical mechanics of a condensed phase
(a liquid at room temperature and $p = 1$ bar, say)

– We cannot study a macroscopic quantity, 1 mole, or 1 mmole, or 1 μmole, but we still need a big enough sample ($\approx$ 1000 molecules, say, $\approx 10^{-20}$ mole).

– So we happily write the Hamiltonian $\hat{H}(x, X)$ for the 1000 molecules, it contains $3 \cdot 3 \cdot 1000$ variables X for the nuclei (x, y, z, 3 atoms per molecule) and 10 times as many variable x for the electrons (and even more for the electronic spins)

– We use the Born-Oppenheimer approximation to separate $\hat{H}(x, X)$ into the sum of a nuclear $\hat{H}^{\text{nuc}}(X)$ and an electronic $H^{\text{ele}}(x)$ Hamiltonian, to be dealt with independently.

→ We first work on $H^{\text{ele}}(x)$. This is still much too big to be solved (and just one solution would not be useful anyhow).
So we separate $H^{\text{ele}}(x)$ into smaller Hamiltonians (building blocks) containing only (the electrons of) 1 or 2 (may be 3) molecules.

– These 'building block' Hamiltonians can be studied systematically. We need only the ground state energies E_0, but systematically for very many nuclear positions, not just close to the minimum (or minima).

– We tabulate the E_0 as a function of the (fixed) nuclear positions for which they were obtained.

– We try to express E_0 as a function of the positions by simple mathematical expressions (fits). Many approximations must be introduced here, in particular that the description must be 'modular'. ie that one should be able to construct the energies of large systems from the ones obtained for small systems.

→ We now deal with $H^{\text{nuc}}(X)$. First, we realize that at $T \approx 300$ K, the (thermal) de Broglie wavelength Λ for molecules, and even for atom heavier than Hydrogen, is small.
So we can replace the quantum mechanical equation (Schrödinger-eq) by the classical one,
ie. Newton's equation
This makes it (much much much) easier to study the time evolution of the system

– For Newton's equation $m \cdot \frac{\partial^2 x}{\partial t^2} = F$, we need the forces F acting on the masses m.
We realize that in the Born-Oppenheimer approximation the forces result only from the electrons. (The nucleus-nucleus repulsion is (as a constant for fixed positions) incorporated in $\hat{H}^{\text{nuc}}$)

– Forces $\vec{F}$ are (negative) derivatives (gradients) of potentials V: $\vec{F} = -\nabla V$
(for the force on one particle i : $\vec{F}_i = -\nabla_i V$)

– We now recognize that in the Born-Oppenheimer approximation our (fitted) E_0, the electronic ground state energy for the various nuclear positions, is this potential V that governs the nuclear motions.

– When we have understood the basis of statistical mechanics, we can start ⇒ CHE501