Statistical Molecular Thermodynamics

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Video 1.3

Quantization of Energy

Quantum Mechanics

Isn't this thermodynamics, not *quantum mechanics?*

Quantum mechanics provides the foundational principles for all molecular processes. Molecular statistical mechanics builds upon that foundation, and itself serves as the basis for thermodynamics.

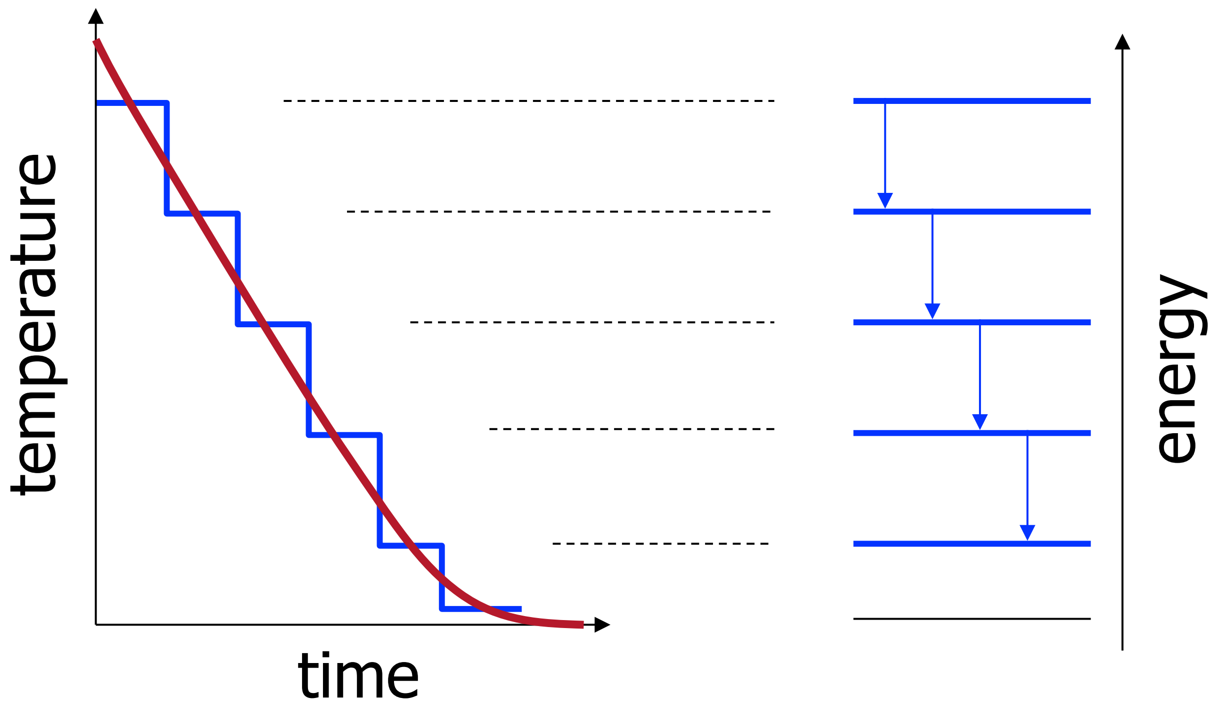
We will develop thermodynamics in a *molecular* context. Molecules behave quantum mechanically, so we *will* need to know some *results* that derive from quantum mechanics.

However, the study of molecular quantum mechanics is *not* a prerequisite for this course.

Energy Is Quantized

Imagine that your coffee could have only certain temperatures

Your coffee getting cold:

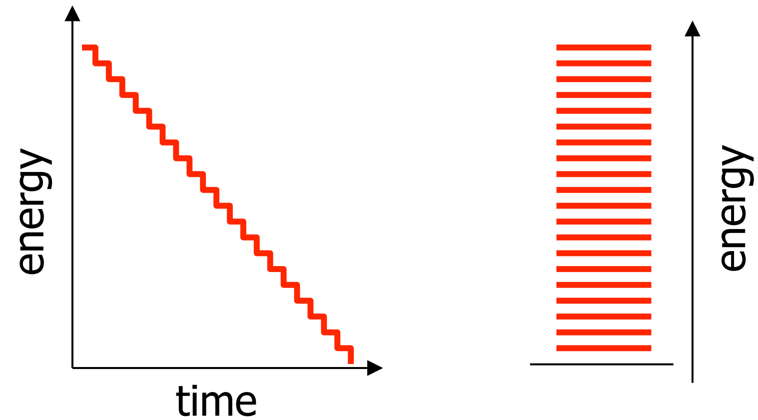


Relative Energy Spacing vs Size

Macroscopic

Big things have *small* relative energy spacing, look classical.

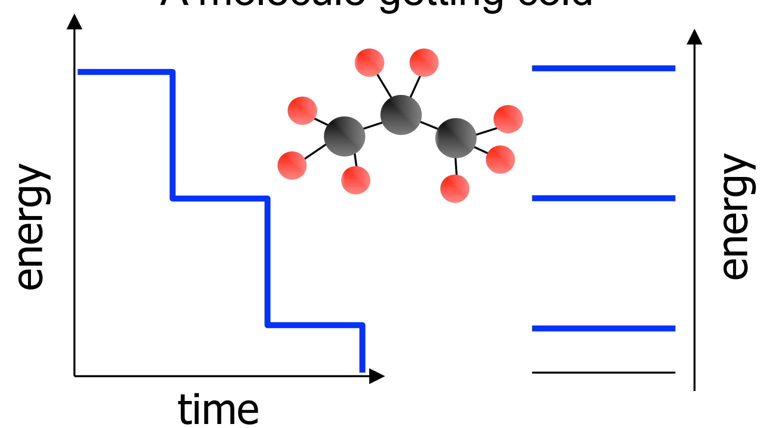
Your coffee getting cold



Microscopic

Small things (atoms, molecules) have *large* relative energy spacing, so we must consider quantized energy levels.

A molecule getting cold



Energy Is Quantized by h

Planck (1900)

Planck suggested that radiated energy can come only in quantized packets of size $h\nu$.

$$E = h\nu$$

Energy (J) → E

Planck's constant → $h = 6.626 \times 10^{-34}\ \mathbf{J \cdot s}$

The frequency (s^{-1}) → ν

We can thus specify the energy by *any one* of the following:

1. The frequency, ν (for example, Hz or s^{-1}): $E = h\nu$
2. The wavelength, λ (for example, m or nm): $E = h\dfrac{c}{\lambda}$ (c: speed of light in a vacuum)

   (using the relationship $\nu\lambda = c$)
3. The wavenumber, $\tilde{\nu}$ (for example, cm^{-1} or m^{-1}): $E = hc\tilde{\nu}$

   defined as $\tilde{\nu} = 1/\lambda$

The 1-D Schrödinger Equation

Erwin Schrödinger

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi_n(x) + V(x)\psi_n(x) = \varepsilon_n\psi_n(x) \qquad \hbar = \frac{h}{2\pi}$$

Kinetic energy — Potential energy — Allowed total energy

Solving the Schrödinger equation for a given (i) potential V and (ii) set of boundary conditions yields a set of wave functions, ψ_n, and a set of associated energies, ε_n, that are said to be “allowed”. The integer index n specifies the state.

$|\psi(x)|^2 dx$ is the **probability** that the system is located between x and $x+dx$. *In the absence of an experiment, there is no objective reality.*

Defining and solving relevant Schrödinger equations is the subject of quantum mechanics. Here, however, we need be familiar only with the *allowed energy levels* for the systems that we will encounter.