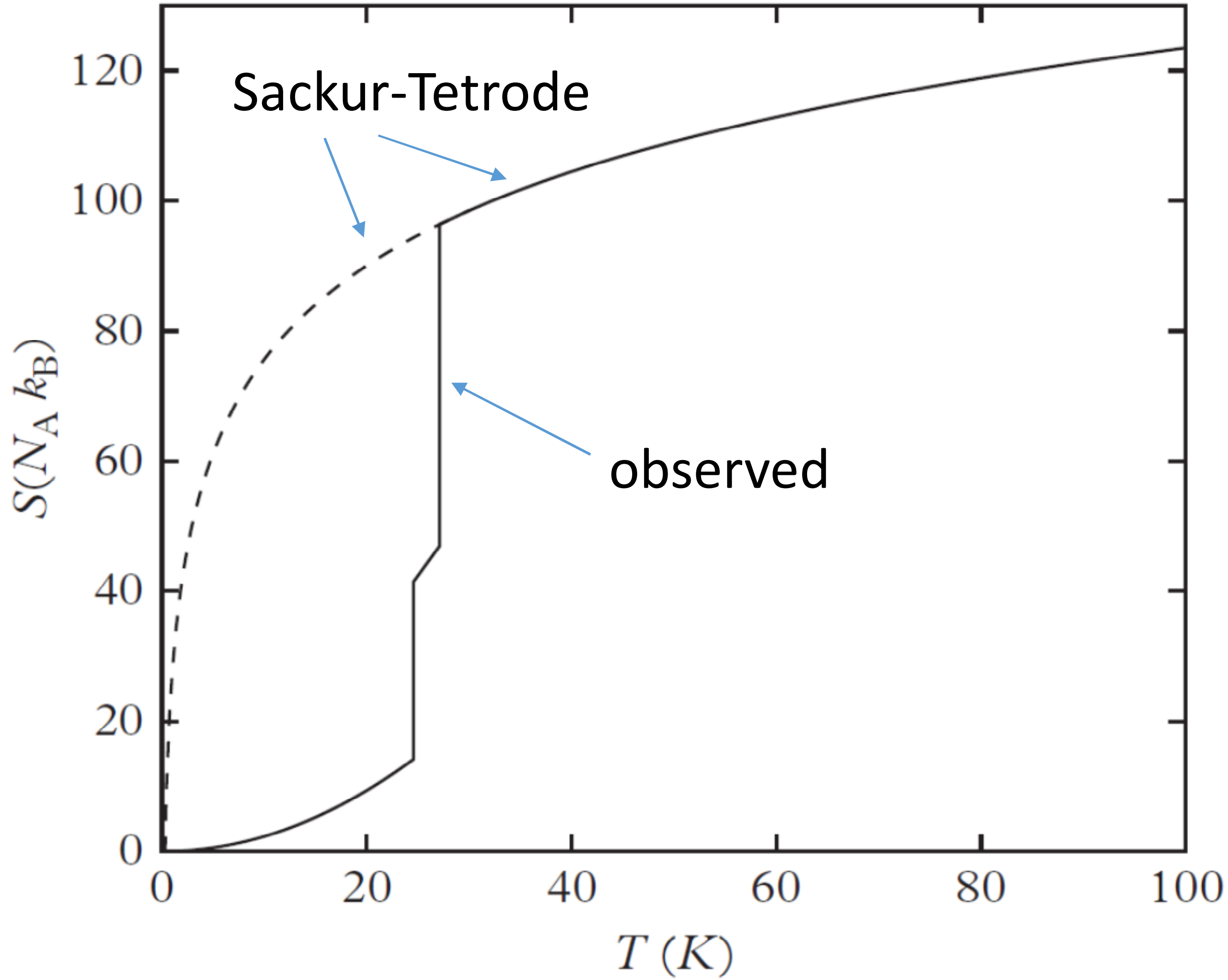
Statistical mechanics of a gas at high temperature

Statistical mechanics of a gas at “high” (i.e. not extremely low) temperature

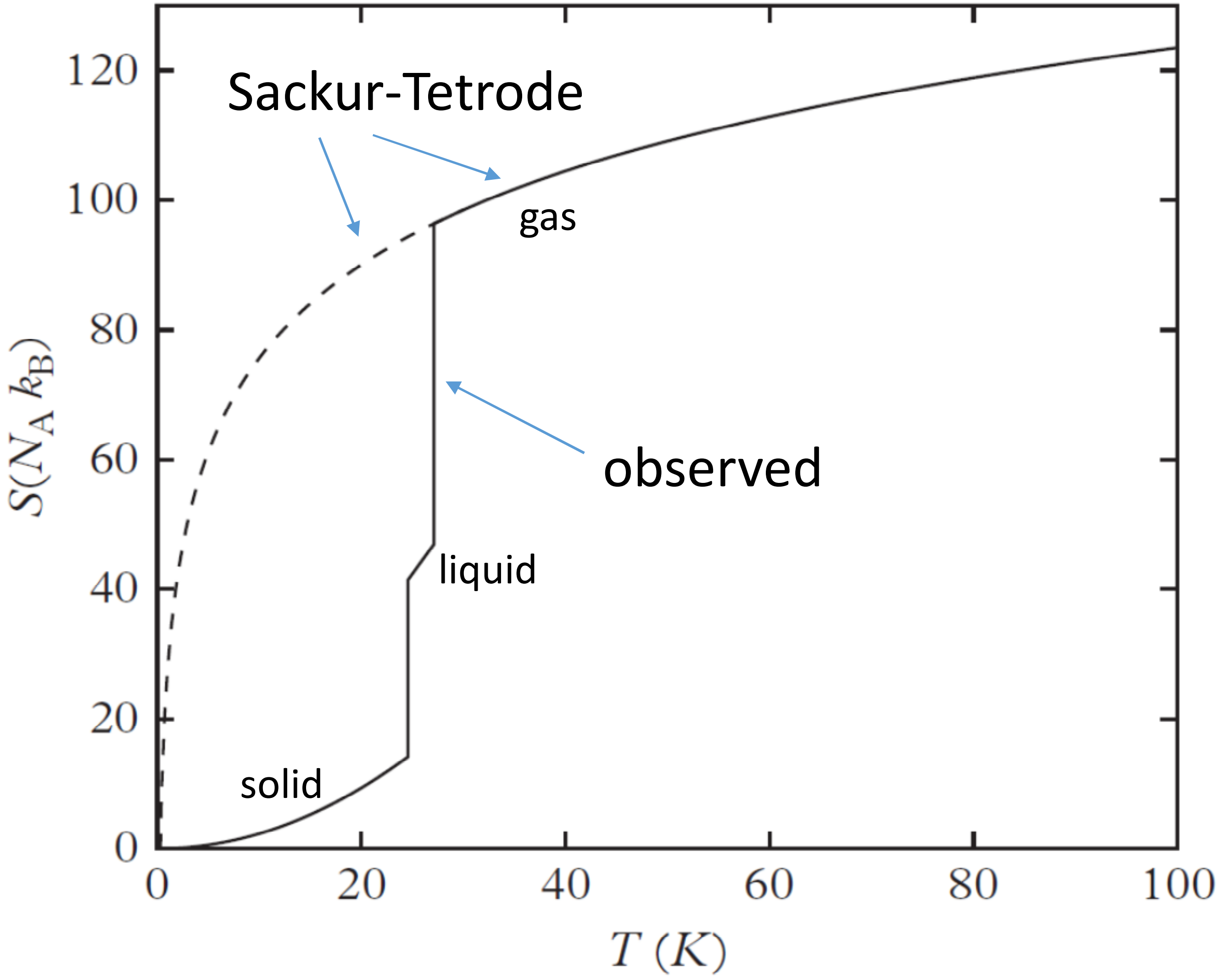
1. Obtain partition function for the translational motion of particles in a box
2. Hence obtain energy, heat capacity, **and entropy**
3. **The idea of k-space and density of states**
4. Bring in rotation and vibration



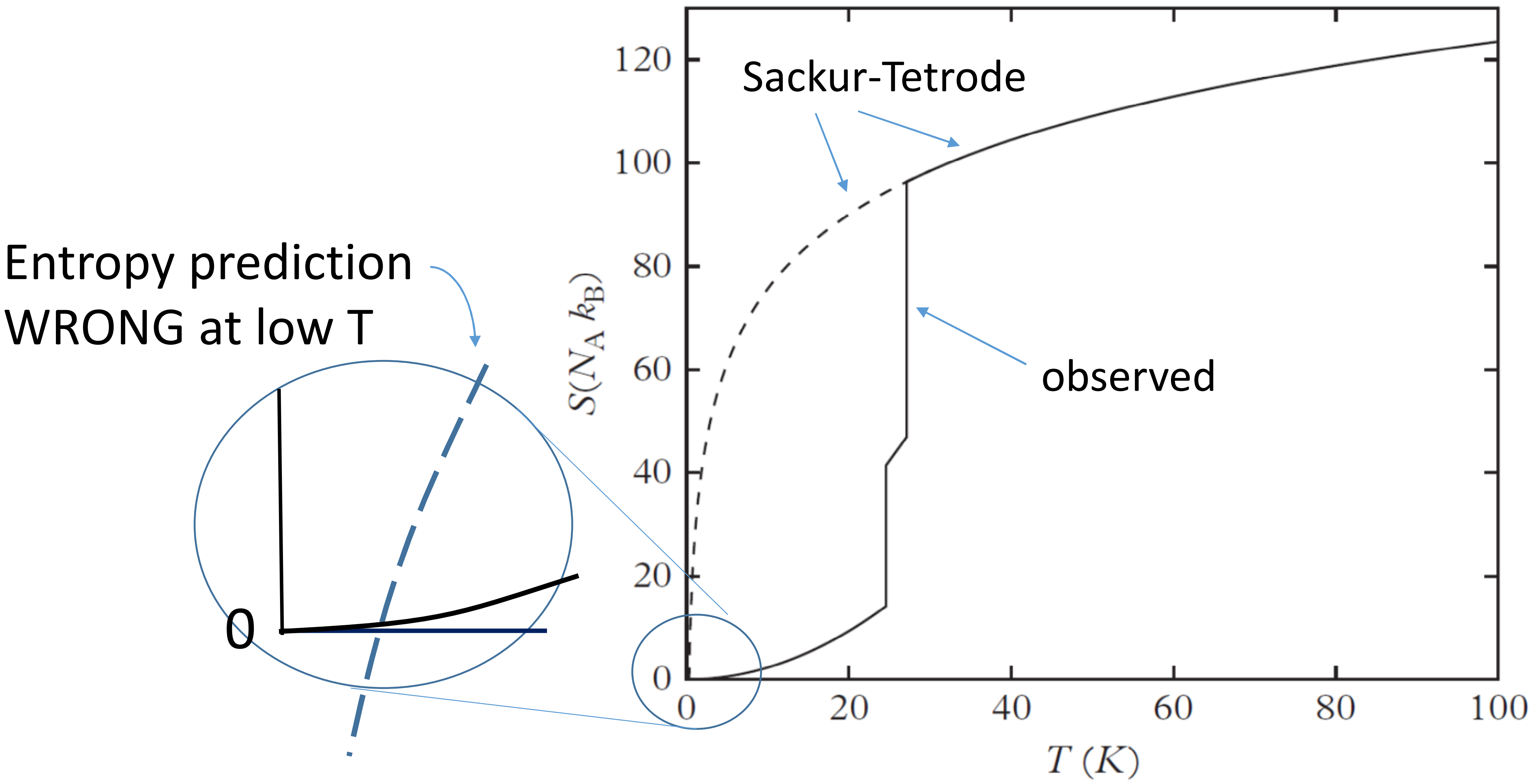
Sackur-Tetrode

observed

Entropy of neon as a function of temperature, with prediction of Sackur-Tetrode equation.



Entropy of neon as a function of temperature, with prediction of Sackur-Tetrode equation.

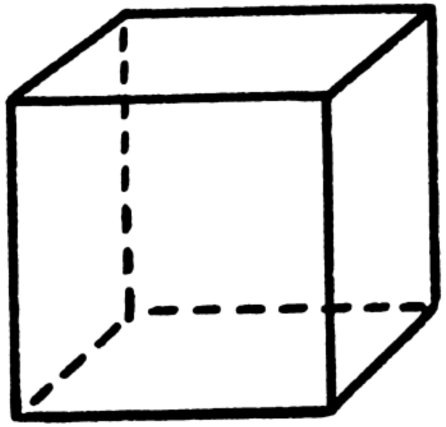


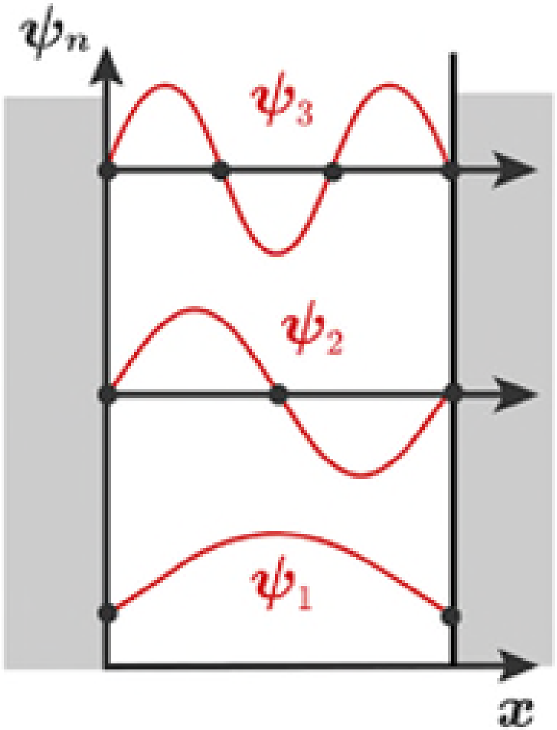
Entropy prediction WRONG at low T

At low T we have to take **indistinguishability** into account, which we have NOT done here.

Entropy of neon as a function of temperature, with prediction of Sackur-Tetrode equation.

Gas in a box

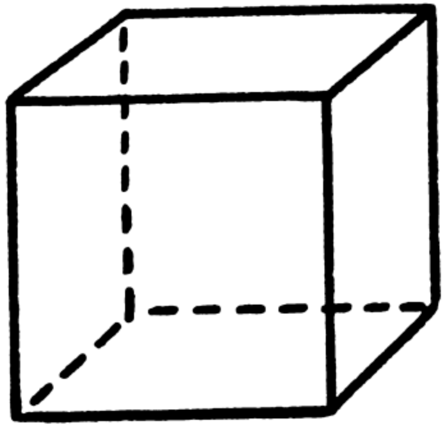


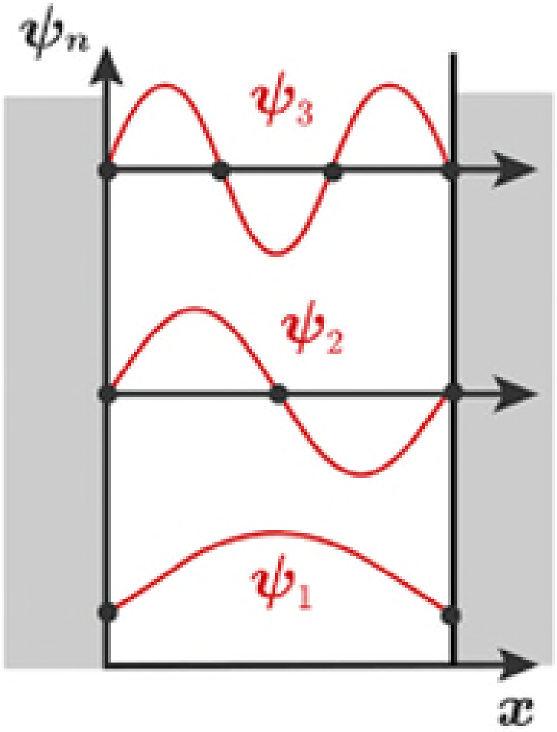


Potential well with

energy
eigenstates
(in one dimension)

Gas in a box





Potential well with

energy
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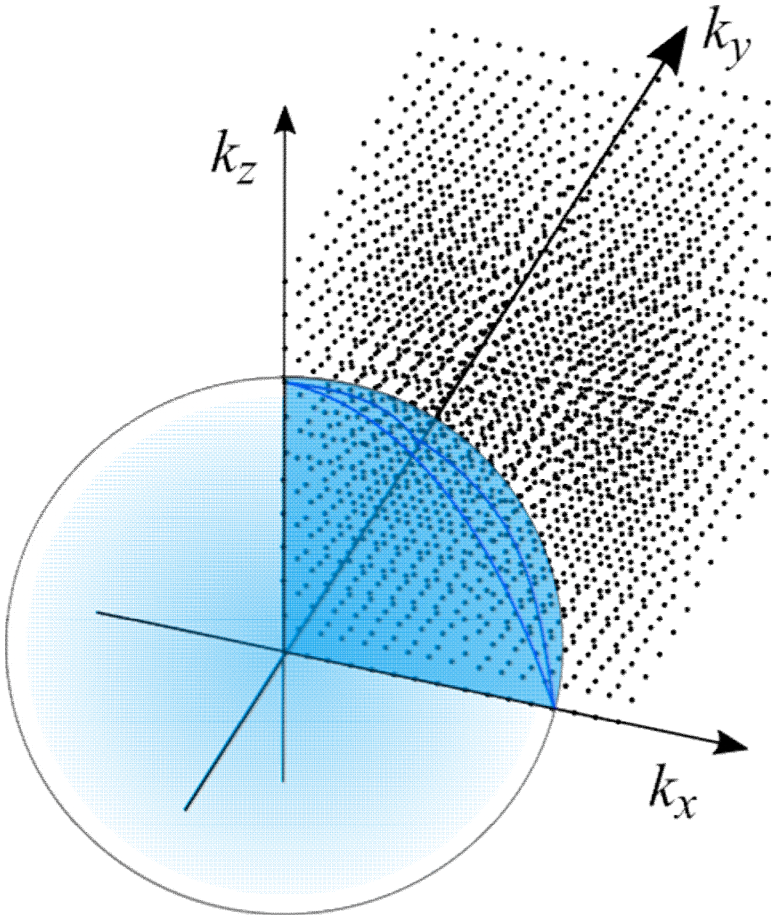
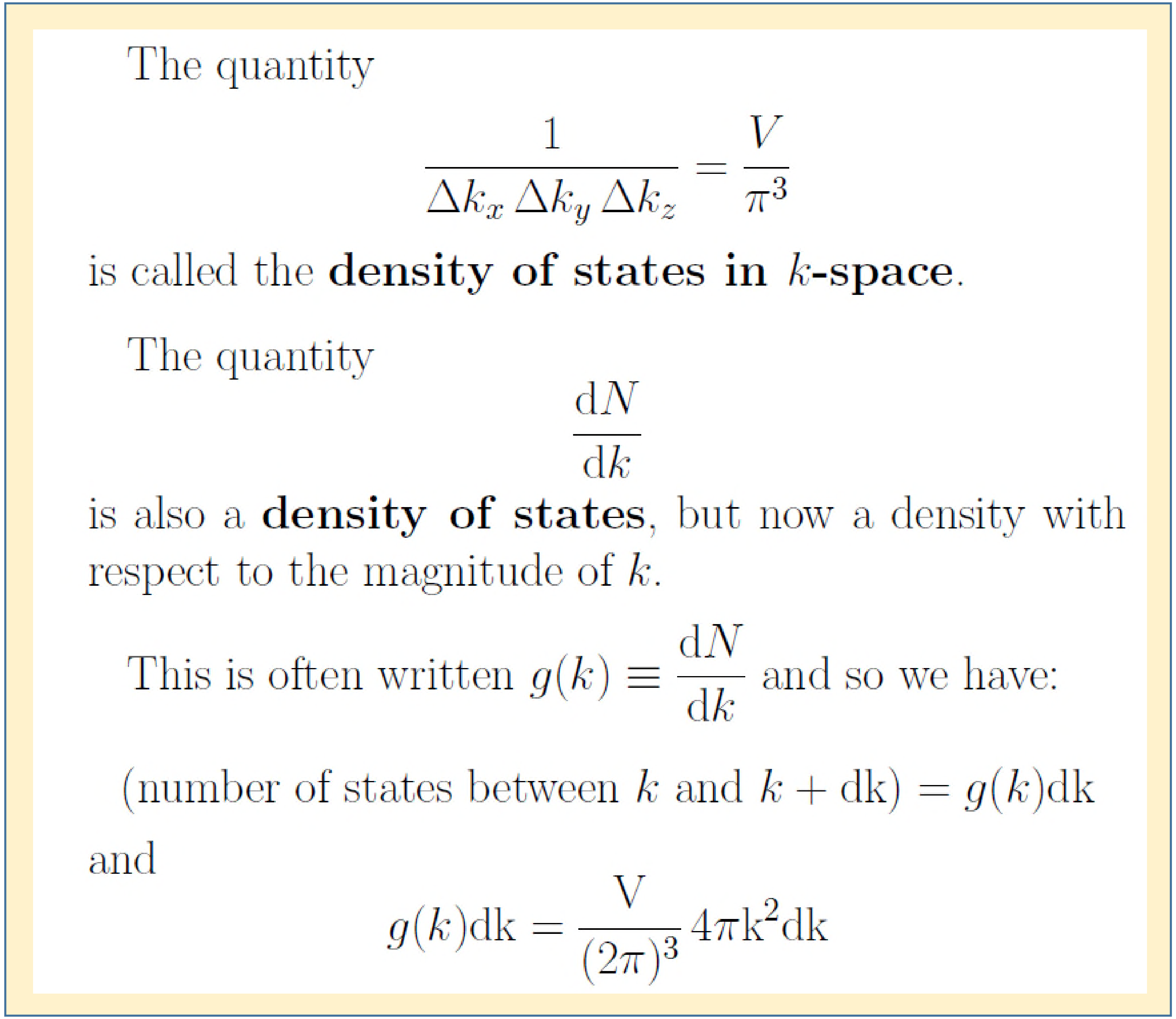


States in k space



The quantity

$$\frac{1}{\Delta k_x \, \Delta k_y \, \Delta k_z} = \frac{V}{\pi^3}$$

is called the **density of states in k-space**.

The quantity

$$\frac{\mathrm{d}N}{\mathrm{d}k}$$

is also a **density of states**, but now a density with respect to the magnitude of k.

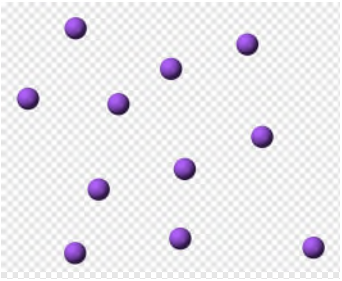
This is often written $g(k) \equiv \frac{\mathrm{d}N}{\mathrm{d}k}$ and so we have:

$$(\text{number of states between } k \text{ and } k + \mathrm{dk}) = g(k)\mathrm{dk}$$

and

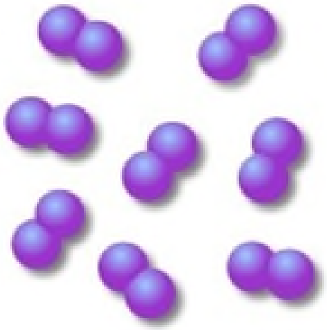
$$g(k)\mathrm{dk} = \frac{\mathrm{V}}{(2\pi)^3} 4\pi \mathrm{k}^2 \mathrm{dk}$$

So far, we have treated translational motion.

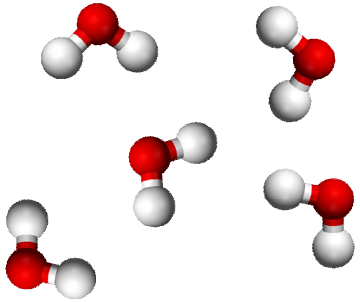


For MONATOMIC gas that's the whole story

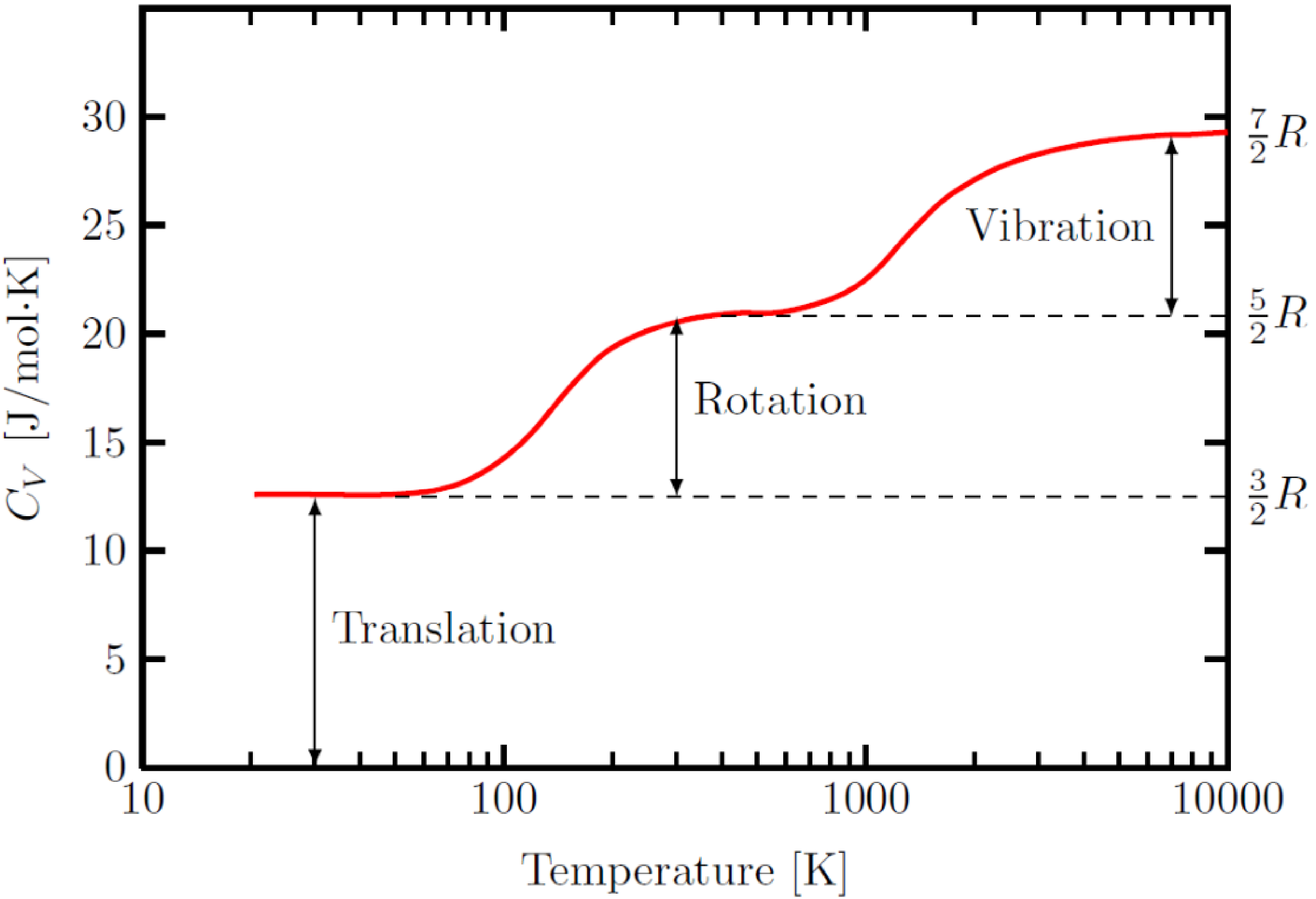
(except there can be fine structure in the internal electronic energy levels … see notes)



For DIATOMIC gas we have also rotation and vibration.



For POLYATOMIC gas there is even more rotation and vibration.



Heat capacity of a typical diatomic gas as a function of temperature.

Most gases have rotation but not vibration excited at room temperature.

Total heat capacity when rotation is fully excited

$$\begin{aligned} C_V &= C_V^{(t)} + C_V^{(r)} + C_V^{(v)} \\ &= \frac{3}{2}Nk_B + \begin{cases} Nk_B & \text{(linear molecule)} \\ \frac{3}{2}Nk_B & \text{(non} - \text{linear molecule)} \end{cases} + Nk_B \sum_{i=1}^{q_v} \frac{\left(T_{v,i}/(2T)\right)^2}{\sinh^2\left(T_{v,i}/(2T)\right)} \end{aligned}$$

Translational

rotational

Vibrational
(simple harmonic motion
for each normal mode)

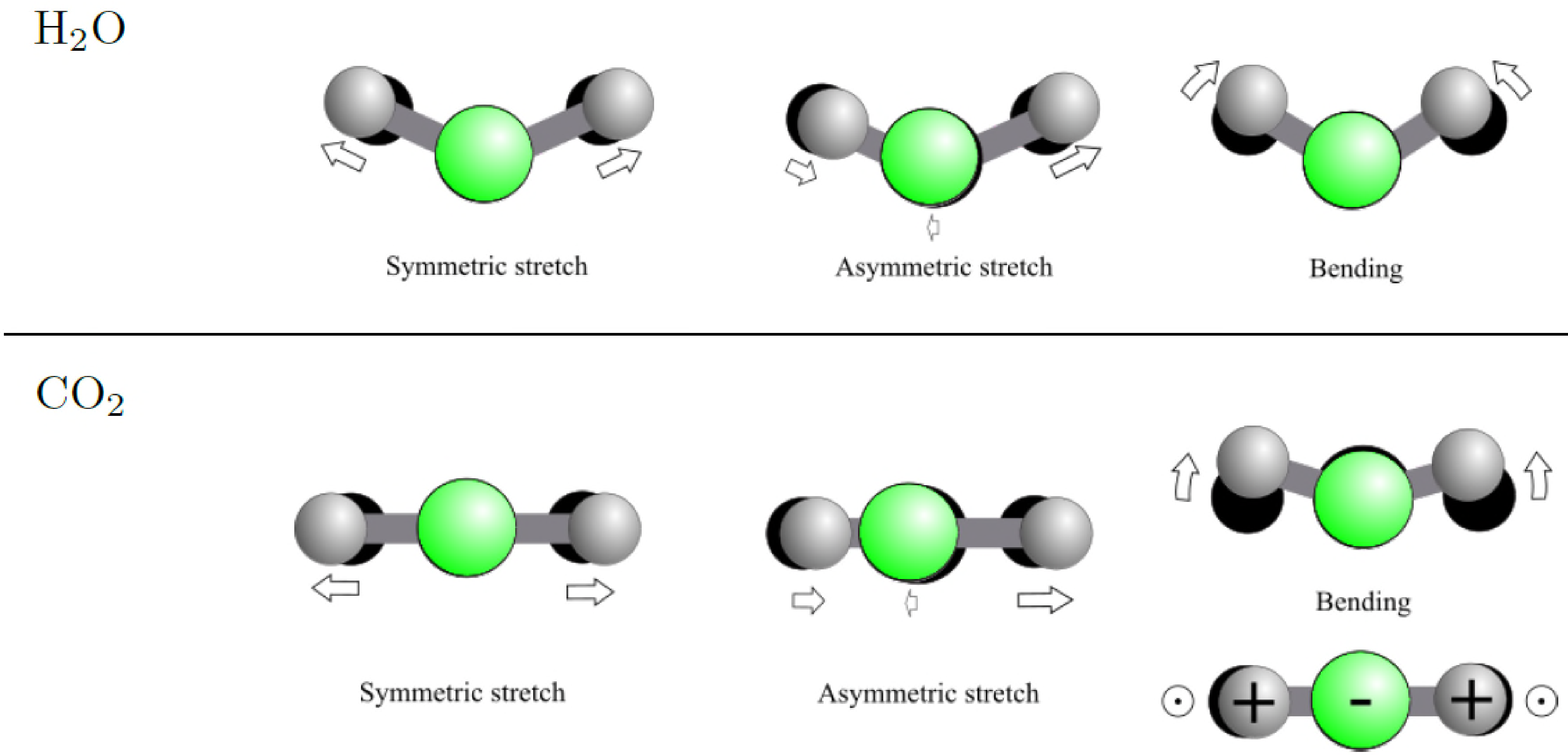


Fig. E.1 Normal modes of H_2O and CO_2 molecules. The arrows indicate the motion during one half of any given oscillation. The second bending mode for CO_2 is in the direction perpendicular to the plane of the diagram.