Problem 1.18

Very roughly speaking, quantum mechanics is relevant when the de Broglie wavelength of the particle in question (h/p) is greater than the characteristic size of the system (d). In thermal equilibrium at (Kelvin) temperature T, the average kinetic energy of a particle is

$$\frac{p^2}{2m} = \frac{3}{2}k_B T$$

(where k_B is Boltzmann's constant), so the typical de Broglie wavelength is

$$\lambda = \frac{h}{\sqrt{3mk_B T}}. \tag{1.45}$$

The purpose of this problem is to determine which systems will have to be treated quantum mechanically, and which can safely be described classically.

(a) **Solids.** The lattice spacing in a typical solid is around $d = 0.3$ nm. Find the temperature below which the unbound[23] *electrons* in a solid are quantum mechanical. Below what temperature are the *nuclei* in a solid quantum mechanical? (Use silicon as an example.) *Moral:* The free electrons in a solid are *always* quantum mechanical; the nuclei are generally *not* quantum mechanical. The same goes for liquids (for which the interatomic spacing is roughly the same), with the exception of helium below 4 K.

(b) **Gases.** For what temperatures are the atoms in an ideal gas at pressure P quantum mechanical? *Hint:* Use the ideal gas law ($PV = Nk_B T$) to deduce the interatomic spacing. *Answer:* $T < (1/k_B)(h^2/3m)^{3/5}P^{2/5}$. Obviously (for the gas to show quantum behavior) we want m to be as *small* as possible, and P as *large* as possible. Put in the numbers for helium at atmospheric pressure. Is hydrogen in outer space (where the interatomic spacing is about 1 cm and the temperature is 3 K) quantum mechanical? (Assume it's monatomic hydrogen, not H_2.)

Solution

The following constants are needed for this problem.

Planck's constant:	$h \approx 6.62606 \times 10^{-34}\ \mathrm{J \cdot s}$
Electron Mass:	$m_e \approx 9.10938 \times 10^{-31}$ kg
Proton Mass:	$m_p \approx 1.67262 \times 10^{-27}$ kg
Boltzmann's constant:	$k_B \approx 1.38065 \times 10^{-23}\ \dfrac{\mathrm{J}}{\mathrm{K}}$

[23] In a solid the inner electrons are attached to a particular nucleus, and for them the relevant size would be the radius of the atom. But the outer-most electrons are not attached, and for them the relevant distance is the lattice spacing. This problem pertains to the *outer* electrons.

Part (a)

Quantum mechanics is relevant when the de Broglie wavelength is greater than the characteristic size of the particle.

$$\lambda = \frac{h}{\sqrt{3mk_BT}} > d$$

Solve this inequality for T.

$$\frac{h^2}{3mk_BT} > d^2$$

$$T < \frac{h^2}{3mk_Bd^2}$$

For an unbound electron, use the mass of an electron for m and use the lattice spacing for d: $m = m_e$ and $d = 0.3 \times 10^{-9}$ m.

$$T < 1.29 \times 10^5 \text{ K}$$

From the periodic table, note that the average atomic mass of silicon isotopes is 28.086 amu. Protons and neutrons have roughly the same mass and electrons are negligible in comparison, so use $m = 28.086m_p$. Also, use the lattice spacing for d: $d = 0.3 \times 10^{-9}$ m.

$$T < 2.51 \text{ K}$$

Part (b)

The ideal gas law is commonly known as $PV = nRT$, but it can also be written as

$$PV = Nk_BT,$$

where N is the number of gas molecules in the volume V. Assume that all the gas molecules in a sample are equally spaced, each within its own cubic box and forming a lattice altogether. The characteristic length of the system d will then be the length of a cube's side, which also happens to be the intermolecular distance. Within one of these cubic boxes, $N = 1$ and $V = d^3$.

$$Pd^3 = k_BT$$

Solve for d.

$$d = \sqrt[3]{\frac{k_BT}{P}}$$

For quantum mechanics to be necessary, the de Broglie wavelength λ must be greater than d.

$$\lambda = \frac{h}{\sqrt{3mk_BT}} > d$$

$$\frac{h}{\sqrt{3mk_BT}} > \sqrt[3]{\frac{k_BT}{P}}$$

$$\frac{h}{3^{1/2}m^{1/2}k_B^{1/2}T^{1/2}} > \frac{k_B^{1/3}T^{1/3}}{P^{1/3}}$$

Solve for T.

$$T^{5/6} < \frac{hP^{1/3}}{3^{1/2}m^{1/2}k_B^{5/6}}$$

$$T < \left(\frac{hP^{1/3}}{3^{1/2}m^{1/2}k_B^{5/6}}\right)^{6/5}$$

$$T < \frac{h^{6/5}P^{2/5}}{3^{3/5}m^{3/5}k_B}$$

From the periodic table, note that the average atomic mass of helium isotopes is 4.003 amu. Protons and neutrons have roughly the same mass and electrons are negligible in comparison, so use $m = 4.003m_p$. Also, use $P = 1$ atm $= 101\,325$ Pa.

$$T < 2.92 \text{ K}$$

From the periodic table, note that the average atomic mass of hydrogen isotopes is 1.008 amu. Protons and neutrons have roughly the same mass and electrons are negligible in comparison, so use $m = 1.008m_p$. Also, use the interatomic distance for d: $d = 1$ cm $= 0.01$ m.

$$\lambda = \frac{h}{\sqrt{3mk_BT}} > d$$

$$T < \frac{h^2}{3mk_Bd^2}$$

$$T < 6.29 \times 10^{-14} \text{ K}$$

Therefore, monatomic hydrogen in outer space can be treated classically at 3 K.