1.98: Quantum Mechanical Pressure

Quantum mechanics is based on the concept of wave-particle duality, which for massive particles is expressed simply and succinctly by the de Broglie wave equation.

$$\lambda = \frac{h}{mv} = \frac{h}{p} \tag{1.98.1}$$

On the left side is the wave property, λ, and on the right the particle property, momentum. These incompatible concepts are united in a reciprocal relationship mediated by the ubiquitous Planck's constant. Using de Broglie's equation in the classical expression for kinetic energy, T converts it to its quantum mechanical equivalent.

$$T = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2} \tag{1.98.2}$$

Because objects with wave-like properties are subject to interference phenomena, quantum effects emerge when they are confined by some restricting potential energy function. For example, to avoid self-interference, a particle in an infinite one-dimensional square-well potential (PIB, particle in a box) of width a must form standing waves. The required restriction on the allowed wavelengths,

$$\lambda = \frac{2a}{n} \quad n = 1, 2, \ldots \tag{1.98.3}$$

quantizes the kinetic energy.

$$T(n) = \frac{n^2h^2}{8ma^2} \tag{1.98.4}$$

In addition to providing a simple explanation for the origin of energy quantization, the PIB model shows that reducing the size of the box **increases** the kinetic energy dramatically. This "repulsive" character of quantum mechanical kinetic energy is the ultimate basis for the stability of matter. It also provides, as we see now, a quantum interpretation for gas pressure. To show this we will consider a particle in the ground state of a three-dimensional box ($n_x = n_y = n_z = 1$) of width a and volume a^3. Its kinetic energy is,

$$T = \frac{3h^2}{8ma^2} = \frac{3h^2}{8mV^{2/3}} = \frac{A}{V^{2/3}} \tag{1.98.5}$$

According to thermodynamics, pressure is the negative of the derivative of energy with respect to volume.

$$P = -\frac{dT}{dV} = -\frac{2}{3}\frac{A}{V^{5/3}} \tag{1.98.6}$$

Using Equation 1.98.5 to eliminate A from Equation 1.98.6 yields,

$$P = \frac{2}{3}\frac{T}{V} \tag{1.98.7}$$

This result has the same form as that obtained by the kinetic theory of gases for an individual gas molecule.

Contributors and Attributions

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