Quantum Mechanical Pressure

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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.

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

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 converts it to its quantum mechanical equivalent.

$$KE = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2}$$

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 wave lengths,

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

quantizes kinetic energy.

$$KE(n) = \frac{n^2 h^2}{8ma^2}$$

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,

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

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

$$P = -\frac{d\,KE}{dV} = \frac{2}{3}\frac{A}{V^{5/3}}$$

Using equation (5) to eliminate A from equation (6) yields,

$$P = \frac{2}{3}\frac{KE}{V}$$

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