Repulsion Phenomena and Shape Factors in Equations of State

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Monte Carlo and molecular dynamics results for a variety of nonattractive rigid bodies, such as rigid sphere enmers and spherocylinders, reveal useful characteristics of "shape factor" parameters of simple equation of state models.

The present work focuses on a generalization of the repulsion term, P_R, of the van der Waals concept of the equation of state for real fluids.

$$P = P_R + P_A$$

The repulsion term, for nonattracting rigid spheres, can be expressed, in terms of the classical equation, as

$$(PV/NkT)_o = 1 - \frac{2\pi N}{3VkT}\int_0^\infty r^3 g_0^{(12)}(r)\left(\frac{dU}{dr}\right)_0 dr \approx 1 + \frac{4y - 2y^2}{(1-y)^3} = \frac{1 + y + y^2 - y^3}{(1-y)^3}$$

For nonspherical rigid bodies, a shape factor (ζ) can be introduced into the simple model,

$$(PV/NkT)_o = 1 - \frac{2\pi N}{3VkT}\int_0^\infty r^3 g_0^{(12)}(r)\left(\frac{dU}{dr}\right) dr \approx 1 - \frac{2\pi N}{3VkT}\int_0^\infty \varsigma(r) r^3 g_0(r)\left(\frac{dU}{dr}\right)_0 dr$$

$$\approx 1 - \frac{2\pi N}{3VkT}\langle\zeta\rangle\int_0^\infty r^3 g_0(r)\left(\frac{dU}{dr}\right)_0 dr$$

and,

$$(PV/NkT) \approx \frac{1 + (4\zeta - 3)y + (3 - 2\zeta)y^2 - y^3}{(1-y)^3}$$

This shape factor, ζ, as defined above, can be regarded as a first-order perturbation parameter for nonspherical bodies relative to the spherical shape, resulting in some degree of generalization of the repulsion term of the van der Waals model of the equation of state for real fluids.