Equation of state and exclusion factor behaviour in multicomponent systems

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The recent theory of an equation of state of a fluid mixture is improved by choosing the exclusion factor in the gaseous region as dependent on the mixture composition.

The theory of an equation of state of an isotropic fluid system formulated recently[1] was based on a master equation, which can be generalised for a multicomponent mixture as

$$\tilde{p} = \int_0^{\varphi} \frac{d\varphi}{1 - f^{ex}\varphi} + \tilde{p}_{attr}, \tag{1}$$

where φ is the packing fraction of matter. The dimensionless pressure $\tilde{p}$ is defined as $\tilde{p} \equiv pv_0/k_BT$, where p is the pressure, $v_0 \equiv \sum_i x_i v_{i0}$ is the average particle (molecular or ionic) volume (x_i is the mole fraction and v_{i0} is the particle volume of the ith component), k_B is the Boltzmann constant, and T is the temperature. The exclusion factor $f^{ex} \equiv v^{ex}/v_0$ is defined as the ratio of the average excluded volume $v^{ex} \equiv \sum_i x_i v_i^{ex}$ (v_i^{ex} is the excluded volume of the ith component) and the average particle volume. The excluded volume of the ith component is defined as the partial volume of a particle of the ith component with resting centre of mass in the absence of attractive forces. Finally, $\tilde{p}_{attr}$ is a negative contribution to $\tilde{p}$ due to attractive forces, $\tilde{p}_{attr}$ looking differently for molecular and ionic systems.

The exclusion factor f^{ex} is a function of the packing fraction φ, and this function should be given for solving master equation (1). The solution of the master equation in the first approximation was based on the linear function $f^{ex} = 8 - k\varphi$, where 8 was the limiting exclusion factor value for a rarefied gas (k is a positive coefficient). This value is well known for a one-component system, and it should be replaced by a certain value of f_0^{ex} for a multicomponent system to give

$$f^{ex} = f_0^{ex} - k\varphi \tag{2}$$

and

$$\tilde{p} = \int_0^{\varphi} \frac{d\varphi}{1 - f_0^{ex}\varphi + k\varphi^2} + \tilde{p}_{attr}. \tag{3}$$

The solution of equation (3) depends on a value chosen for the coefficient k. The simplest solution corresponds to $k = (f_0^{ex}/2)^2$ and has the form

$$\tilde{p} = \frac{\varphi}{1 - b\varphi} + \tilde{p}_{attr}, \tag{4}$$

where $b \equiv f_0^{ex}/2$. With $f_0^{ex} = 8$ and $\tilde{p}_{attr} = -a'\varphi^2$ (a' is the attractive constant), equation (4) is the van der Waals equation of state.

The second approximation of the excluded volume theory[1] included the dependence

$$f^{ex} = \frac{f_0^{ex} - k_1\varphi}{1 + k_2\varphi} \tag{5}$$

with two positive constants k_1 and k_2. One additional positive constant K was introduced (numerically, but now as a symbol) from the limiting slope for the $f^{ex}(\varphi)$ function:

$$\left(\frac{df^{ex}}{d\varphi}\right)_{\varphi \to 0} = -K = 3b_3 - 4b_2^2 \tag{6}$$

As is shown in (6), the constant K can be easily calculated from the second (b_2) and third (b_3) virial coefficients for a system of hard particles. Using (5), we obtain the equation
relating coefficients k_1 and k_2 to each other, so that only one of them can be chosen independently.

$$k_1 + k_2 f_0^{ex} = K \tag{7}$$

Using (5), equation (1) becomes

$$\tilde{p} = \int_0^{\varphi} \frac{(1 - k_2\varphi)d\varphi}{1 - (f_0^{ex} - k_2)\varphi + k_1\varphi^2} + \tilde{p}_{attr}. \tag{8}$$

The solution of (8) depends on the values chosen for coefficients k_1 and k_2. The simplest solution corresponds to the condition

$$k_1^{1/2} = \frac{f_0^{ex} - k_2}{2} \equiv \beta, \tag{9}$$

which, together with (7), uniquely determines the coefficients k_1 and k_2:

$$k_1 = (f_0^{ex} - K^{1/2})^2,\ k_2 = 2K^{1/2} - f_0^{ex} \tag{10}$$

With these values of k_1 and k_2, (8) yields the equation of state

$$\tilde{p} = \left(1 + \frac{k_2}{\beta}\right)\frac{\varphi}{1 - \beta\varphi} + \frac{k_2}{\beta^2}\ln(1 - \beta\varphi) + \tilde{p}_{attr}, \tag{11}$$

where $\beta = f_0^{ex} - K^{1/2}$.

According to (6), the constant K can be found from the values of two virial coefficients for a system of hard particles (hard spheres). As is known, the van der Waals constant b coincides with b_2, and we may conclude that $b_2 = f_0^{ex}/2$. If the third virial coefficient b_3 is unknown for a mixture, we can approximately postulate b_3 to be in the same proportion with b_2 as in a system of hard spheres of equal size, where $b_2 = 4$, $b_3 = 10$, and $b_3 = 2.5b_2$. In this approximation,

$$K = (f_0^{ex})^2 - 3.75f_0^{ex}, \tag{12}$$

$$\beta = f_0^{ex} - [(f_0^{ex})^2 - 3.75f_0^{ex}]^{1/2}, \tag{13}$$

$$k_2 = 2[(f_0^{ex})^2 - 3.75f_0^{ex}]^{1/2} - f_0^{ex}. \tag{14}$$

For a one-component system, we have $f_0^{ex} = 8$, $K = 34$, $\beta \approx$ ≈ 2.169 and $k_2 \approx 3.662$, and equation (11) becomes

$$\tilde{p} = 2.688\,\frac{\varphi}{1 - 2.169\varphi} + 0.778\ln(1 - 2.169\varphi) + \tilde{p}_{attr}, \tag{15}$$

as was reported earlier[1] with $\tilde{p}_{attr} = -a'\varphi^2$.

Thus, the repulsive part of the equation of state can be formulated in terms of the only quantity, the initial value of the exclusion factor f_0^{ex}. That is why it is so important to study the behaviour of this quantity in a multicomponent system.

To analyse f_0^{ex}, we have to consider a rarified gaseous mixture, where all particles are capable of rotational motion and may be regarded as possessing a spherical shape. Since we consider a system without attractive forces, it is reasonable to turn to the model of hard spheres of various sizes. For moving particles of sort k with radius r_k, a single resting particle of sort i with radius r_i creates an excluded volume v_{ik}^{ex} as a sphere of radius $r_i + r_k$ (Figure 1). This makes the relationship

$$v_{ik}^{ex} = (v_{i0}^{1/3} + v_{k0}^{1/3})^3, \tag{16}$$

where $v_{i0} = 4\pi r_i^3/3$ and $v_{k0} = 4\pi r_k^3/3$ are the particle volumes of the ith and kth components.

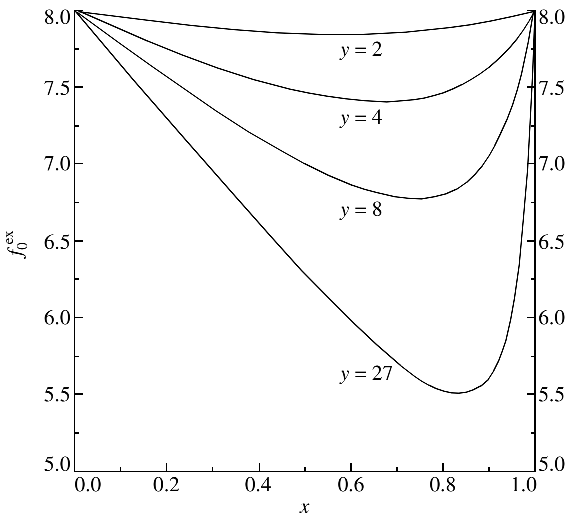

Figure 2 The dependence of the exclusion factor on the composition of a binary mixture of hard spheres at various volume ratios.

The probability of appearance of a particle of sort k near the resting particle of sort i is given by the mole fraction x_k, so that we can define the average excluded volume v_i^{ex} for a single particle of sort i as

$$v_i^{ex} = \sum_k x_k v_{ik}^{ex}. \tag{17}$$

Finally, the average excluded volume for all components is defined as

$$v^{ex} = \sum_i x_i v_i^{ex}, \tag{18}$$

or, putting (16) and (17) in (18),

$$v^{ex} = \sum_{i,k} x_i x_k (v_{i0}^{1/3} + v_{k0}^{1/3})^3. \tag{19}$$

Correspondingly, the exclusion factor in a rarified gaseous mixture is determined as

$$f_0^{ex} = \frac{v^{ex}}{v_0} = \frac{\sum_{i,k} x_i x_k (v_{i0}^{1/3} + v_{k0}^{1/3})^3}{\sum_i x_i v_{i0}}. \tag{20}$$

It is evident from (20) that $f_0^{ex} = 8$, irrespective of the mixture composition, provided the particles of all species are of the same size. Generally, however, f_0^{ex} does depend both on the particle size difference and on the mixture composition. We investigate this dependence by the example of a binary mixture by setting $x_1 \equiv x$, $x_2 \equiv 1 - x$, and introducing the particle volume ratio $y \equiv v_{20}/v_{10}$. For a binary mixture, equation (20) then takes the form

$$f_0^{ex} = \frac{8x^2 + 2x(1-x)(1+y^{1/3})^3 + 8(1-x)^2 y}{x + (1-x)y}. \tag{21}$$

Figure 2 represents a graphical illustration of equation (21). Since the deviation of f_0^{ex} from 8 is larger in the middle of the

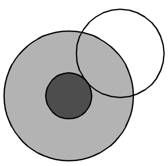

Figure 1 Excluded volume (shadowed) created by a resting particle (black) with respect to a moving particle of a different size.

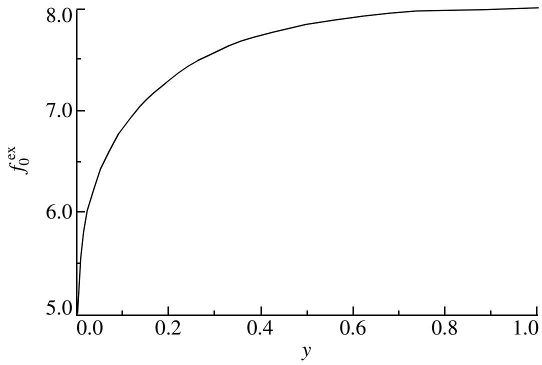

Figure 3 The influence of the particle volume ratio on the exclusion factor in a mixture of two sorts of hard spheres taken in equal amounts.

composition axis, it is of interest to estimate the dependence of f_0^{ex} on y at $x = 0.5$, when equation (21) becomes

$$f_0^{ex} = \frac{4 + (1+y^{1/3})^3 + 4y}{1 + y}. \tag{22}$$

This dependence is shown in Figure 3. The fact that the derivative $\mathrm{d}f_0^{ex}/\mathrm{d}y$ at $y = 1$ (when $f_0^{ex} = 8$) is zero secures the acceptability of the approximation $f_0^{ex} = 8$ within a certain range of volume ratios. The value $f_0^{ex} = 8$ still looks excellent at $y = 0.5$ (the deviation does not exceed 0.16). Even at $y = 0.3$, f_0^{ex} is greater than 7.5. However, the exclusion factor should be corrected at smaller particle volume ratios. As can be seen in Figure 3, f_0^{ex} decreases with y to the limiting value $f_0^{ex} = 5$ for $y = 0$ at $x = 0.5$.

Thus, we may conclude that the generalization of the theory of an equation of state with $f_0^{ex} = 8$ to multicomponent mixtures is acceptable if the size difference is not strongly pronounced (by a factor of no higher than 3). For mixtures with a strongly pronounced size difference of components, the limiting exclusion factor f_0^{ex} should be estimated according to equation (20).

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References

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