

Quadratic mixing rules for equations of state. Origins and relationships to the virial expansion

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ABSTRACT

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Quadratic mixing rules, originally proposed by van der Waals, are used extensively in mixture calculations involving equations of state. Several ways exist to derive such mixing rules from the principles of statistical mechanics or merely classical thermodynamic arguments. In this report we relate the quadratic mixing rules to the rigorous mixing rules for virial coefficients of mixtures.

The virial equation of state having a precise basis in statistical mechanics provides theoretical guidance for formulations of equations of state. In addition, the mixture combining rules for the virial coefficients are rigorous. The thesis of this paper is that, if multibody interactions occur in certain ways, the mixing rules for all virial coefficients become identical to the quadratic mixing rule for the second virial coefficient. This implies that quadratic mixing rules should be universal for coefficients (or their combinations) of equations of state.

Keywords: theory, equation of state, mixing rules, virial.

INTRODUCTION

Application of statistical mechanics is of central importance in the fundamental study of mixtures and prediction of mixture properties. It

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provides equations that enable, at least in principle, calculation of thermodynamic and transport properties of mixtures from a knowledge of quantities on the molecular level. The energy and pressure equations allow calculation of the internal energy and the compressibility factor from molecular distribution functions and intermolecular potentials of molecules in the mixture. Among all the theories of mixtures proposed, the mixture theory of imperfect gases is one of the few theories of mixtures that has the advantage of being applicable to all classes of mixtures although it is limited to low densities. The current work demonstrates that quadratic mixing rules are a general approximation for the imperfect gas theory of mixtures. We also show that imperfect gas theory provides mixing rules for equations of state, the simplest of which is the quadratic mixing rules of van der Waals.

When applying an equation of state (EOS) to mixtures it is necessary to specify mixing rules (MR) for the parameters of the EOS. As an empirical exercise, this would be a formidable task. However, the virial EOS which has a precise basis in statistical mechanics provides theoretical MR for the virial coefficients. Because practical and theoretical EOS can be expressed in density series form, the MR for virial coefficients suggest composition dependencies for the parameters (or their combinations) of the other EOS.

Unfortunately, this is not an entirely unambiguous exercise. Each virial coefficient has a different MR. Thus, for an equation of state with a finite number of parameters it is possible to select from many MR. The usual selection is the quadratic MR for the second virial coefficient. This is logical because the second virial term usually accounts for most of the deviations from ideality. Also from a historical perspective, the van der Waals EOS contains both of its parameters only in the second virial term.

The thesis of this paper is that the MR for all virial coefficients reduce to the quadratic form under certain assumptions. These assumptions appear to be reasonable and the implication is that quadratic MR are either valid or at least good approximations for all virial terms. This work extends earlier work of McGregor et al. (1987).

DERIVATION OF QUADRATIC MIXING RULES FOR VIRIAL COEFFICIENTS

The virial EOS is an infinite series in either pressure or density. This paper requires only the density form

$$Z - 1 = \sum_{k=1}^{\infty} B_{(k+1)} \rho^k \quad (1)$$

where Z is the compression factor, B_k are the virial coefficients and ρ is the density. The virial coefficients are functions of temperature and composition but not of density. The composition dependence is

$$B_{(z)} = \sum_{i=1}^c \sum_{j=1}^c \cdots \sum_{z=1}^c x_i x_j \cdots x_z B_{(z)ij \cdots z} \tag{2}$$

but the temperature dependence has no precisely determined form. In eqn. (2), c is the number of components in the mixture and x_i is the mole fraction of component i in the mixture. The z th virial coefficient is a function of irreducible clusters of z molecules. Thus, in the virial expansion, the N -body problem reduces to a series of one-body, two-body, three-body, etc. problems.

At this point, it is useful to define a tool which can simplify the extensive algebra required by the development

$$\sum_{i=1}^c \sum_{j=1}^c \cdots \sum_{z=1}^c X_i X_j \cdots X_z = \sum_{i=1}^c \sum_{j=1}^c \cdots \sum_{z=1}^c x_i x_j \cdots x_z B_{(z)ij \cdots z} \tag{3}$$

Note that one-to-one correspondence does not exist among the X variables and the x and B variables but only an overall equality of the multiple summations. In the light of eqn. (3), eqn. (2) becomes

$$B_{(z)} = \sum_{i=1}^c \sum_{j=1}^c \cdots \sum_{z=1}^c X_i X_j \cdots X_z = \left[\sum_{i=1}^c X_i \right]^z \tag{4}$$

In this equation, an individual X has no specific meaning. The sums of the products have specific meaning and the total RHS has specific meaning. At this point it is convenient to restrict the deviation to binary mixtures to reduce algebra, however the conclusions reached are valid for multicomponent mixtures. For a binary, eqn. (4) becomes

$$B_{(z)} = (X_1 + X_2)^z = \sum_{k=0}^z \binom{z}{k} X_1^k X_2^{z-k} \tag{5}$$

Now recasting the product of X variables into compositions and virial coefficients results in

$$B_{(z)} = x_1^z B_{(z)11 \cdots z} + x_2^z B_{(z)22 \cdots z} + \sum_{k=1}^{z-1} \binom{z}{k} x_1^k x_2^{z-k} B_{(z)11 \cdots k22 \cdots z-k} \tag{6}$$

where the z and k in the subscripts indicate the number of replications of 1 or 2. For example,

$$B_{(3)} = x_1^3 B_{(3)111} + x_2^3 B_{(3)222} + 3x_1 x_2^2 B_{(3)122} + 3x_1^2 x_2 B_{(3)112} \tag{7}$$

Rewriting eqn. (6) by factoring quadratic terms,

$$\begin{aligned} B_{(z)} &= x_1^z x_1^{z-2} B_{(z)11 \cdots z} + x_2^z x_2^{z-2} B_{(z)22 \cdots z} + \sum_{k=1}^{z-1} \binom{z}{k} x_1^k x_2^{z-k} B_{(z)11 \cdots k22 \cdots z-k} \\ &= x_1^2 (1 - x_2)^{z-2} B_{(z)11 \cdots z} + x_2^2 (1 - x_1)^{z-2} B_{(z)22 \cdots z} \\ &\quad + \sum_{k=1}^{z-1} \binom{z}{k} x_1^k x_2^{z-k} B_{(z)11 \cdots k22 \cdots z-k} \end{aligned} \tag{8}$$

Now, we note that

$$(1 - x_i)^{z-2} = \sum_{k=0}^{z-2} \binom{z-2}{k} (-1)^{z-2-k} x_i^{z-2-k} \quad (i = 1, 2) \quad (9)$$

which, when substituted into eqn. (8) produces

$$\begin{aligned} B_{(z)} &= B_{(z)11 \dots z} x_1^2 \sum_{k=0}^{z-2} \binom{z-2}{k} (-1)^{z-2-k} x_2^{z-2-k} \\ &\quad + B_{(z)22 \dots z} x_2^2 \sum_{k=0}^{z-2} \binom{z-2}{k} (-1)^{z-2-k} x_1^{z-2-k} \\ &\quad + \sum_{k=1}^{z-1} \binom{z}{k} x_1^k x_2^{z-k} B_{(z)11 \dots k22 \dots z-k} \\ &= x_1^2 B_{(z)11 \dots z} \left[1 + \binom{z-2}{0} (-1)^{z-2} x_2^{z-2} \right. \\ &\quad \left. + \sum_{k=1}^{z-3} \binom{z-2}{k} (-1)^{z-2-k} x_2^{z-2-k} \right] \\ &\quad + x_2^2 B_{(z)22 \dots z} \left[1 + \binom{z-2}{0} (-1)^{z-2} x_1^{z-2} \right. \\ &\quad \left. + \sum_{k=1}^{z-3} \binom{z-2}{k} (-1)^{z-2-k} x_1^{z-2-k} \right] \\ &\quad + \sum_{k=1}^{z-1} \binom{z}{k} x_1^k x_2^{z-k} B_{(z)11 \dots k22 \dots z-k} \end{aligned} \quad (10)$$

Because $x_1 + x_2$ is unity and by collecting quadratic terms, eqn. (10) becomes

$$\begin{aligned} B_{(z)} &= x_1^2 B_{(z)11 \dots z} + x_2^2 B_{(z)22 \dots z} + \left[\sum_{k=1}^{z-3} \binom{z-2}{k} (-1)^{z-2-k} \right. \\ &\quad \left. \times (x_1 + x_2) x_1^k x_2^{z-2-k} + (-1)^{z-2} x_1^2 x_2^{z-2} \right] B_{(z)11 \dots z} \\ &\quad + \left[\sum_{k=1}^{z-3} \binom{z-2}{k} (-1)^{z-2-k} (x_1 + x_2) x_2^k x_1^{z-2-k} \right. \\ &\quad \left. + (-1)^{z-2} x_2^2 x_1^{z-2} \right] B_{(z)22 \dots z} + \sum_{k=1}^{z-1} \binom{z}{k} x_1^k x_2^{z-k} \\ &\quad \times B_{(z)11 \dots k22 \dots z-k} = x_1^2 B_{(z)11 \dots z} + x_2^2 B_{(z)22 \dots z} \\ &\quad + \left[\sum_{k=1}^{z-3} \binom{z-2}{k} (-1)^{z-2-k} (x_1^3 x_2^{z-2-k} + x_1^2 x_2^{z-1-k}) \right. \end{aligned}$$

$$\begin{aligned}
 &+ (-1)^{z-2} x_1^2 x_2^{z-2} \Big] B_{(z)11 \dots z} + \left[\sum_{k=1}^{z-3} \binom{z-2}{k} \right. \\
 &\times (-1)^{z-2-k} (x_1^{z-1-k} x_2^2 + x_1^{z-2-k} x_2^3) \\
 &\left. + (-1)^{z-2} x_1^{z-2} x_2^2 \right] B_{(z)22 \dots z} + \sum_{k=1}^{z-1} \binom{z}{k} x_1^k x_2^{z-k} B_{(z)11 \dots k22 \dots z-k} \quad (11)
 \end{aligned}$$

Now factoring $2x_1 x_2$ from the final summation of eqn. (11) gives

$$B_{(z)} = x_1^2 B_{(z)11 \dots z} + x_2^2 B_{(z)22 \dots z} + 2x_1 x_2 B_{(z)12}^* \quad (12)$$

where

$$\begin{aligned}
 B_{(z)12}^* = &\left[\frac{1}{2} \sum_{k=1}^{z-3} \binom{z-2}{k} (-1)^{z-2-k} (x_1^2 x_2^{z-3-k} + x_1 x_2^{z-2-k}) \right. \\
 &+ \frac{1}{2} (-1)^{z-2} x_1 x_2^{z-3} \Big] B_{(z)11 \dots z} + \left\{ \frac{1}{2} \sum_{k=1}^{z-3} \binom{z-2}{k} (-1)^{z-2-k} (x_1^{z-2-k} x_2 \right. \\
 &+ x_1^{z-3-k} x_2^2) + \frac{1}{2} (-1)^{z-2} x_1^{z-3} x_2 \Big\} B_{(z)22 \dots z} + \frac{1}{2} \sum_{k=1}^{z-1} \binom{z}{k} \\
 &\times x_1^{k-1} x_2^{z-k-1} B_{(z)11 \dots k22 \dots z-k} \quad (13)
 \end{aligned}$$

Equation (12) states that all virial coefficients have quadratic mixing rules if $B_{(z)12}^*$ is not a function of composition. However, eqn. (13) clearly contains composition dependence. McGregor et al. (1987) showed that the third virial coefficient has no composition dependence in eqn. (13) if certain relationships exist among the pure and cross third virial coefficients. In brief, their derivation is

$$\begin{aligned}
 B_{(3)} &= x_1^3 B_{(3)111} + x_2^3 B_{(3)222} + 2x_1 x_2 [(3/2)x_1 B_{(3)112} + (3/2)x_2 B_{(3)122}] \\
 &= x_1^2 B_{(3)111} + x_2^2 B_{(3)222} + 2x_1 x_2 \{ x_1 [(3/2)B_{(3)112} - (1/2)B_{(3)111}] \\
 &\quad + x_2 [(3/2)B_{(3)122} - (1/2)B_{(3)222}] \} \quad (14)
 \end{aligned}$$

Assuming that

$$B_{(3)12}^* = (3B_{(3)112} - B_{(3)111})/2 = (3B_{(3)122} - B_{(3)222})/2 \quad (15)$$

eqn. (14) reduces to

$$B_{(3)} = x_1^2 B_{(3)111} + x_2^2 B_{(3)222} + 2x_1 x_2 B_{(3)12}^* \quad (16)$$

which is the desired form. The recursive relationships which generalize the quadratic mixing rule for all virial coefficients are

$$\begin{aligned}
 B_{(z)12}^* &= [zB_{(z)11 \dots (z-1)2} - (z-2)B_{(z)11 \dots z}]/2 \\
 &= [zB_{(z)122 \dots z-1} - (z-2)B_{(z)22 \dots z}]/2 \\
 &= \left[\binom{z}{k} B_{(z)11 \dots k22 \dots z-k} - \binom{z-2}{z-k} B_{(z)11 \dots z} \right. \\
 &\quad \left. - \binom{z-2}{k} B_{(z)22 \dots z} \right] / (2(z-2)) \quad (17)
 \end{aligned}$$

For the latter expression k ranges from 2 to $z-2$ and z is 3 or greater. For example, the expressions for the fourth and fifth virials are

$$\begin{aligned}
 B_{(4)12}^* &= 2B_{(4)1112} - B_{(4)1111} = 2B_{(4)1222} - B_{(4)2222} \\
 &= [3B_{(4)1122} - (1/2)B_{(4)1111} - (1/2)B_{(4)2222}]/2 \quad (18)
 \end{aligned}$$

$$\begin{aligned}
 B_{(5)12}^* &= [5B_{(5)11112} - 3B_{(5)11111}]/2 = [5B_{(5)12222} - 3B_{(5)22222}]/2 \\
 &= (5/3)B_{(5)11122} - (1/2)B_{(5)11111} - (1/6)B_{(5)22222} \\
 &= (5/3)B_{(5)11222} - (1/6)B_{(5)11111} - (1/2)B_{(5)22222} \quad (19)
 \end{aligned}$$

In general, $B_{(z)12}^*$ is not zero; it is only necessary that the multibody interactions underlying the virial coefficients occur in a manner such as to make eqn. (17) valid. Reasonable data exist to test eqn. (17) for third virial coefficients (eqn. (15)) but not for higher coefficients. McGregor et al. (1987) and Hamad et al. (1988) have demonstrated that eqn. (15) is a reasonable approximation for non-polar and weakly polar (reduced dipole moment less than 0.5) mixtures using both data and statistical mechanical models. Their arguments may be reasonably expected to propagate through the higher virial coefficients. As molecules become more polar and/or tend to associate, it is not possible to test the validity of either eqn. (15) or eqn. (17). If the species associate, the mole fraction is difficult to establish and thus the quadratic mixing rules may fail because eqn. (17) fails or because an incorrect value for mole fraction is available.

If we define

$$B_{(2)12}^* = B_{(2)12} \quad \text{and} \quad B_{(z)ii \dots z}^* = B_{(z)ii \dots z} \quad (20)$$

and substitute eqn. (17) into eqn. (13), then

$$B_{(z)} = x_1^2 B_{(z)11 \dots z}^* + x_2^2 B_{(z)22 \dots z}^* + 2x_1 x_2 B_{(z)12}^* \quad (21)$$

is a general expression for any virial coefficient and the quadratic mixing rule is generally valid. McGregor et al. (1987) showed that a recursive relationship exists in terms of eqn. (17) which makes eqn. (21) valid for multicomponent mixtures as well as binaries at least for the third virial

coefficient. While we do not present the general forms for such relationships, it is clear algebraically that they do exist.

It is interesting to note that given the form of eqn. (21) it is possible to use matrix algebra to express virial coefficients. Equation (1) becomes

$$Z - 1 = \sum_{k=1}^{\infty} [\mathbf{x}\mathbf{B}_{(k+1)}\mathbf{x}^T]\rho^k \tag{22}$$

where

$$\mathbf{B}_k = \begin{vmatrix} B_{(k)11}^* \cdots k & B_{(k)12}^* \\ B_{(k)12}^* & B_{(k)22}^* \cdots k \end{vmatrix} \tag{23}$$

(illustrated for binary)

$$\mathbf{x} = [x_1, x_2, \dots, x_c] \tag{24}$$

EXTENSION TO OTHER EQUATIONS OF STATE

The derivation of the virial equation is based on the assumption that the pressure can be expanded in powers of the absolute activity. The resulting series has a radius of convergence beyond which the series no longer represents the fluid pressure. Because the virial expansion diverges when used for liquids, the radius of convergence might be related to the gas–liquid phase transition. Nevertheless, this expansion is exact for mixtures of gases regardless of the relative differences in size, shape and nature of the molecules forming the gas.

Theoretical treatment of liquid mixtures has required new methods directed toward the many-body nature of liquids. However, to develop an analytic theory of mixtures which can take advantage of the versatility of imperfect gas theory of mixtures Hamad and Mansoori (1987) demonstrated that one can expand equations of state in virial equation form and utilize the virial coefficient mixing rules for parameters of the equations of state.

The van der Waals, Berthelot, and Redlich–Kwong equations are three examples of two-parameter equations of state. These equations have the following general form:

$$Z = 1/(1 - b\rho) - a\rho/RT^q(1 + \delta\rho) \tag{25}$$

where *a* and *b* are constant for a specific substance and

EOS	<i>q</i>	δ
van der Waals	1	0
Redlich–Kwong	3/2	<i>b</i>
Berthelot	2	0

The majority of other cubic equations of state are actually modifications of these equations. As a result, the present discussion and conclusions are valid as well for such other cubic equations.

Virial expansion of eqn. (25) results in the following equation:

$$Z - 1 = [b - a/RT^q]\rho + [b^2 + a\delta/RT^q]\rho^2 + [b^3 - a\delta^2/RT^q]\rho^3 + [b^4 + a\delta^3/RT^q]\rho^4 + \dots \quad (26)$$

Since eqn. (26) is a two-parameter equation (parameters a and b) two mixture expressions (based on the second and third virial coefficients) are needed. Comparison of eqn. (26) with eqn. (1) indicates the following expressions for the second and third virial coefficients

$$B_{(2)} = b - a/RT^q \quad (27)$$

$$B_{(3)} = b^2 + a\delta/RT^q \quad (28)$$

Following eqn. (21), the mixture parameters (a_m and b_m) then can be calculated from the following two equations:

$$b_m - a_m/RT^q = \sum \sum x_i x_j (b_{ij} - a_{ij}/RT^q) \quad (29)$$

$$b_m^2 + a_m \delta / RT^q = \sum \sum x_i x_j (b_{ij}^2 + a_{ij} \delta / RT^q) \quad (30)$$

The general solution for a_m and b_m from the above two equations is

$$a_m = (b_m - S_1)RT^q \quad (31)$$

$$b_m = -\delta + [\delta^2 + 4(\delta S_1 + S_2)]^{1/2}/2 \quad (32)$$

where

$$S_1 = \sum \sum x_i x_j (b_{ij} - a_{ij}/RT^q) \quad (33)$$

and

$$S_2 = \sum \sum x_i x_j (b_{ij}^2 + a_{ij} \delta / RT^q) \quad (34)$$

The general solution MR for a_m and b_m as given by eqns. (31) and (32) is temperature-dependent and varies for different equations of state. If we assume a_m and b_m to be independent of one another and use the following combining rule for b_{ij}

$$b_{ij} = (b_{ii} + b_{jj})/2 \quad (35)$$

eqn. (31) produces the following simple mixing rules:

$$a_m = \sum \sum x_i x_j a_{ij} \quad (36)$$

$$b_m = \sum x_i b_{ii} \quad (37)$$

Equations (36) and (37) are the quadratic van der Waals MR which are widely used in the literature or equations of state, as discussed by Kwak and Mansoori (1986). It should also be pointed out that these mixing rules are independent of the thermodynamic state conditions and the equations of state for which they are used.

For the case of the van der Waals and Berthelot EOS (when $\delta = 0$) eqns. (31) and (32) assume the following forms:

$$a_m = \sum \sum x_i x_j a_{ij} - RT^q \left[b_m - \sum \sum x_i x_j b_{ij} \right] \quad (38)$$

$$b_m = \left[\sum \sum x_i x_j b_{ij}^2 \right]^{1/2} \quad (39)$$

Again, by assuming combining rule (35) for b_{ij} these two equations simplify to the following mixing rules:

$$a_m = \sum \sum x_i x_j a_{ij} + RT^q \left[b_m - \sum x_i b_{ii} \right] \quad (40)$$

$$b_m = \left[\left(\sum x_i b_{ii} \right)^2 + \sum x_i b_{ii}^2 \right]^{1/2} \quad (41)$$

Equations (40) and (41) were originally proposed by Hamad and Mansoori (1987). The derivations reported above for cubic equations of state can be applied to other equations of state, whether empirical or statistical mechanical.

CONCLUSIONS

Within reasonable assumptions reflecting multibody interactions, the quadratic mixing rule is generally applicable to all virial coefficients. Because nearly all equations of state reduce to a virial form, this observation indicates rational mixing rules for the parameters of such equations of state. We have illustrated this approach for three common equations of state. The quadratic relation also permits a matrix notation for the virial equation of state.

Embodied within the multibody interaction assumptions which lead to the general quadratic mixing rule for virial coefficients is an implicit

assumption which relates $B_{(z)ij}$ to $B_{(z)ij}^*$, $B_{(z)iz}^*$, $B_{(z)jz}^*$, etc. This is tantamount to saying that the multicomponent values are functions of only binary values. Thus, the underlying assumptions for this paper enable calculation of multicomponent properties from binary properties.

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