

Interaction between Unlike Nonpolar Molecules: Correction of the Geometric Mean Rule

Part 1. Basic Derivations

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It is proposed how to correct the geometric mean rule, which is widely used for calculating interactions (dispersion forces, potential functions, potential energies, unlike critical temperatures) between pairs of unlike molecules from those of the like molecules. The correction factors are expressed without further physical approximations than already appear in the equations (*e.g.* the Slater-Kirkwood theory for dispersion forces, and the Lennard-Jones (6- n) potential) on which the theory is based.

The usual way of estimating dispersion forces between two unlike nonpolar molecules is to calculate these as the geometric mean of the dispersion forces between the like molecules involved. Furthermore, this empirical geometric mean rule is used for molecular properties related to dispersion forces, for example the energy parameter ϵ of the pair potential function.

It is important, however, not to neglect small deviations from the geometric mean rule. Energies of mixing, for example, calculated from the solubility parameter equation, are typically increased by about 40 cal/mol for an equimolar mixture, when a 1 % decrease of the unlike interactions is introduced. Moreover, deviations up to 74 % between experimental and calculated second virial coefficients for nonpolar mixtures were demonstrated, when the simple geometric mean rule was used.¹

The purpose of this paper is to show how the geometric mean rule both for dispersion forces and for related properties can be expressed in a formally exact way, *i.e.* without more approximations than already appear in the well-established theories used.

The discussion of the numerical aspects are deferred to part 2 (dilute systems) and part 3 (dense systems) of this series.

DISPERSION FORCES

The attraction coefficient in the Slater-Kirkwood² theory for dispersion forces between two isolated unlike molecules 1 and 2 is

$$k_{12} = (3e\hbar/4\pi\sqrt{m}) \cdot \alpha_1\alpha_2 / [(\alpha_1/\kappa_1)^{\frac{1}{2}} + (\alpha_2/\kappa_2)^{\frac{1}{2}}] \quad (1)$$

where α is the polarisability and κ the number of electrons in the outer shells. e and m are the charge and mass of the electron, respectively, and \hbar is Planck's constant.

The attraction coefficients for two isolated like molecules are k_{ii}° (\circ indicates a pure substance), and after a slight rearrangement we have

$$1 = k_{ii}^{\circ} \cdot (8\pi\sqrt{m}/3e\hbar) \cdot (\alpha_i^{\circ}/\kappa_i)^{\frac{1}{2}} / (\alpha_i^{\circ})^2 \quad (i=1, 2) \quad (2)$$

By multiplying the right hand side of eqn. (1) with the geometric mean of eqn. (2), with $i=1$, and with $i=2$, one obtains

$$k_{12} = (k_{11}^{\circ} \cdot k_{22}^{\circ})^{\frac{1}{2}} \cdot f_1 \cdot f_2 \quad (3)$$

with the two correction factors defined

$$f_1 \equiv 2[\alpha_1^{\circ}\alpha_2^{\circ}/(\kappa_1\kappa_2)]^{1/4} / [(\alpha_1/\kappa_1)^{\frac{1}{2}} + (\alpha_2/\kappa_2)^{\frac{1}{2}}] \quad (4)$$

$$f_2 \equiv \alpha_1\alpha_2/\alpha_1^{\circ}\alpha_2^{\circ} \quad (5)$$

It should be stressed, however, that eqn. (3) is of little use until rules for calculating α_1 and α_2 are given (see part 2).

A similar treatment, based on the simpler London theory³ for dispersion forces, was presented by Reed.^{4,5}

POTENTIAL FUNCTION

Lennard-Jones and Cook⁶ proposed as the potential function between two spherical molecules

$$u(r) = j \cdot r^{-n} - k \cdot r^{-m} \quad (6)$$

where r is the distance between the molecular centers, and j and k are constants. Quantum theory⁷ requires $m=6$, but even though n often is assumed to be 12, it is evident⁸ that this might be a poor approximation, which will not be used here. This means that the two-parameter theorem of corresponding states is abandoned.

The parameters in eqn. (6) are not independent; let d_{12} be the value of r , for which $u_{12}(r)$ is minimum, then for two unlike molecules

$$u_{12}(r) = k_{12} [6n_{12}^{-1}d_{12}^{n_{12}-6} \cdot r^{-n_{12}} - r^{-6}] \quad (7)$$

An equivalent way to write this (6- n) potential function is

$$u_{12}(r) = [\varepsilon_{12}/(n_{12}-6)] [6(d_{12}/r)^{n_{12}} - n_{12}(d_{12}/r)^6] \quad (8)$$

where $u(d) = -\varepsilon$. By comparison of eqns. (7) and (8) one has

$$\varepsilon_{12} = k_{12} \cdot d_{12}^{-6} \cdot (n_{12}-6)/n_{12} \quad (9)$$

which for like molecules becomes

$$\varepsilon_{ii}^{\circ} = k_{ii}^{\circ} \cdot (d_{ii}^{\circ})^{-6} \cdot (n_{ii}^{\circ} - 6) / n_{ii}^{\circ} \quad (10)$$

Using eqn. (3) we see that the geometric mean rule for ε_{12} is

$$\varepsilon_{12} = (\varepsilon_{11}^{\circ} \cdot \varepsilon_{22}^{\circ})^{\frac{1}{2}} \cdot f_1 \cdot f_{\alpha} \cdot f_d^2 \cdot f_N \quad (11)$$

in which are defined

$$f_d = [(d_{11}^{\circ} \cdot d_{22}^{\circ})^{\frac{1}{2}} / d_{12}]^3 \quad (12)$$

$$f_N = (n_{11}^{\circ} \cdot n_{22}^{\circ})^{\frac{1}{2}} \cdot (n_{12} - 6) / (n_{12} [(n_{11}^{\circ} - 6)(n_{22}^{\circ} - 6)]^{\frac{1}{2}}) \quad (13)$$

It is normally accepted that the distance parameter (d_{12}) of the intermolecular potential function between unlike molecules should be calculated as an arithmetical mean of the distance parameters of the like molecules (d_{11}° and d_{22}°). This rule is exact for hard spheres, but even though its validity is not settled for more realistic potentials it is without doubt a good approximation⁹ and will be used here.

POTENTIAL ENERGIES

The potential energy of one mole 1-fluid with molal volume v_1 is, assuming that potential energies are additive,

$$e_1 = \frac{2\pi N_0^2}{v_1} \int_0^{\infty} g_{11}(r) \cdot u_{11}(r) \cdot r^2 \cdot dr \equiv \frac{2\pi N_0^2}{v_1} \int 11^{\circ} \quad (14)$$

where $g(r)$ is the radial distribution function, and N_0 is Avogadro's number. The integral cannot be calculated immediately; it is therefore factorized into an integral which is easy to calculate, and the function ψ which depends on the radial distribution function ($u(\sigma) = 0$):

$$e = \frac{2\pi N_0^2}{v} \cdot \psi \cdot \int_{\sigma}^{\infty} u(r) \cdot r^2 \cdot dr \quad (15)$$

Using a Lennard-Jones (6-n) potential, the integration yields

$$e = -2\pi N_0^2 \cdot \psi \cdot \varepsilon \cdot d^3 \cdot q / 3v \quad (16)$$

with

$$q \equiv [n / (n - 3)] \cdot (n/6)^{3/(n-6)} \quad (17)$$

In the classical solubility parameter theory^{10,11} it is assumed that

$$\int 12 + \int 21 = -2(|\int 11^{\circ}| \cdot |\int 22^{\circ}|)^{\frac{1}{2}} \quad (18)$$

in which the symbols represent integrals of the same kind as in eqn. (14). 12, 21, 11, and 22 are the indices on $g(r)$ and $u(r)$. The correct form of eqn. (18) is found to be (using the same procedure as previously in this paper)

$$\int 12 + \int 21 = -2(|\int 11^{\circ}| \cdot |\int 22^{\circ}|)^{\frac{1}{2}} \cdot f_1 \cdot f_{\alpha} \cdot f_d \cdot f_n \cdot f_v \quad (19)$$

in which are defined ($f_1 \cdot f_{\alpha} \cdot f_d$ was introduced by Reed^{4,5})

$$f_v \equiv \frac{1}{2} \cdot (\psi_{12} + \psi_{21}) / (\psi_{11} \cdot \psi_{22})^{\frac{1}{2}} \quad (20)$$

$$f_n \equiv f_N \cdot q_{12} / (q_{11} \cdot q_{22})^{\frac{1}{2}} \quad (21)$$

CRITICAL TEMPERATURES

Chueh and Prausnitz¹² and Brewer¹³ report deviations (which will be utilized in part 2) from the geometric mean rule in terms of critical temperatures, T^c .

Using the Lennard-Jones (6- n) potential, eqn. (8), and the dilute-gas approximation⁷ for the radial distribution function

$$g(r) = \exp\{-u(r)/kT\} \quad (22)$$

the integral of eqn. (14) is evaluated numerically in the range $9 < n < 30$ and $0.8 < \tilde{T} \equiv kT/\varepsilon < 1.6$. The results are fitted into

$$-f_{ij}/(\varepsilon_{ij} \cdot d_{ij}^3) = a/\tilde{T}_{ij}^2 + b/\tilde{T}_{ij} + q_{ij}/3 \quad (23)$$

$$a \equiv 0.0756 + 2.5856/(n_{ij} + 4.6528) \quad (24)$$

$$b \equiv 0.0988 + 1.6228/(2n_{ij} - 4.6528) \quad (25)$$

with an average numerical deviation of ± 0.14 %.

Let us at a given temperature, say T^c , assume that $ev/(2\pi N_0^2 \cdot d^3 \cdot kT)$ is independent of ε and n , so that eqn. (23) can be written (including the normalisation $\tilde{T}^c \equiv kT^c/\varepsilon = 1.3$ for $n = 12$)

$$a/(\tilde{T}_{ij}^c)^3 + b/(\tilde{T}_{ij}^c)^2 + q_{ij}/(3 \cdot \tilde{T}_{ij}^c) = 0.6967 \quad (26)$$

Finally, eqn. (11) and the relationship between \tilde{T}^c and ε give

$$T_{12}^c = (T_{11}^c \cdot T_{22}^c)^{\frac{1}{2}} \cdot f_I \cdot f_\alpha \cdot f_d^2 \cdot f_N \cdot f_c \quad (27)$$

$$f_c \equiv \tilde{T}_{12}^c / (\tilde{T}_{11}^c \cdot \tilde{T}_{22}^c)^{\frac{1}{2}} \quad (28)$$

in which \tilde{T}_{11}^c , \tilde{T}_{22}^c , and \tilde{T}_{12}^c are solutions to eqn. (26) for $n_{ij} = n_{11}^c = n_{22}^c$ and n_{12}^c , respectively.

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