Nonconformal Potentials and Second Virial Coefficients in Molecular Fluids. 1. Theory

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Nonconformal Potentials and Second Virial Coefficients in Molecular Fluids. 1. Theory

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The influence of the form of the interaction potential on the thermodynamic properties of fluids is investigated. Differences in the potential profile of nonconformal interactions are taken into account by the steepness of the potential functions and used to define a relative softness between interactions. In the dilute gaseous phase, the system of interest is characterized by a relative softness relating its virial coefficient $B(T)$ with respect to that of a reference system $B_0(T)$. For constant softness S, $B(T)$ is obtained directly from $B_0(T)$ by linear relations involving only S. The conditions on which S is exactly or approximately constant are analyzed and shown to hold in a wide range of cases. Furthermore, it is shown how to invert $B(T)$ to construct potentials whose form and parameters reproduce accurately the thermodynamic properties of the gas.

I. Introduction

The principal interest in second virial coefficients, $B(T)$, has been to correct ideal-gas behavior to represent the properties of real dilute gases and to estimate from sufficiently precise empirical $B(T)$ data the form and parameters of intermolecular pair potential energy functions. On the one hand, the practical use of experimental and theoretical $B(T)$ data is widespread in the treatment of fluid-phase and chemical reaction equilibria.[1,2] The needs of engineering have led to the development of explicit formulas to express B as a function of temperature T; these formulas are used to estimate the values of B beyond the measured range of T and for substances for which $B(T)$ has not been measured. The most successful of these formulas are those based on the principle of corresponding states and its empirical generalizations.[3−6] Also, expressions for $B(T)$ theoretically derived from assumed pair interactions have been developed for real molecules, spherical, quasispherical, and diatomics, notably by Kestin and co-workers.[7]

On the other hand, experimental $B(T)$ data have been one of the main sources of information about intermolecular pair potentials of real substances. The intermolecular potentials obtained by inversion of $B(T)$ are of value not only in studies of dilute fluids, but also in studies of various properties of dense fluids by statistical mechanical theories, simulations, and theoretical equations of state.[8] Nevertheless, in almost every case the inversion processes are hampered by the restriction of the procedure to potential functions of preselected mathematical form. An exceptional case is that of E. B. Smith and co-workers who developed an inversion technique which provides numerical values of the intermolecular potential $u(r)$ independent of any assumed potential function. This procedure has been applied to argon[9−11] and, using the second acoustic virial coefficient, to methane.[12] The main questions arising in the inversion of $B(T)$ have been reviewed by Knobler, with special mention of the problems introduced by errors in $B(T)$ at low temperatures, mainly due to gas adsorption, and by the limited range of the $B(T)$ data.[13]

It is worth remarking that on the experimental front reports continue to emerge both of new measurements of increasing precision and over ever wider ranges of temperature, e.g., those of Gilgen *et al.* on argon,[14] and of simulations of experimentally inaccessible systems, e.g., the square-well chain molecules described by Wichert and Hall.[15] These developments illustrate the new challenges to the theory of virial coefficients and intermolecular potentials. Therefore, for both theoretical and practical reasons, there is a need for procedures for inverting $B(T)$ data able to provide reliable information about the form and parameters of intermolecular potentials and applicable to a wide class of substances. In this paper we address this need by developing a reliable inversion method for $B(T)$ which provides explicitly and accurately the form of $u(r)$ and which also gives very compact expressions for $B(T)$ of model and real substances.

A recent approach to the statistical thermodynamics of fluids is based on the mean collision diameters for repulsive and attractive interactions.[16−18] These diameters, together with the average depth of the intermolecular potential, determine state-dependent core diameters $\sigma(T,\rho)$, ranges $\lambda(T,\rho)$, and a constant depth ϵ of a square well (SW) system which has the same pressure as the fluid of interest at temperature T and density ρ. The state dependence of σ and λ specify the particular system of interest: they are identical for fluids with potentials of the same form, i.e., conformal systems that follow corresponding states, but differ for nonconformal potentials. This approach has led to theoretical equations of state for systems with repulsive interactions and with Lennard-Jones $n/6$ and exp-6 potentials.[16,18]

More recently, the analysis of collision diameters in dilute gases has led to interesting applications and insights.[19,20] In the low-density limit, where σ and λ are functions of T only, the approach provides very simple expressions for the virial coefficients $B(T)$ of many gases of interest, both model and real. In a previous publication, we have shown that σ^3 and λ^3 of two nonconformal gases can be linearly related to each other by

means of two shape parameters S_R and S_A connected to the form of the potentials in their repulsive and attractive regions, respectively. These relations provide a simple expression for $B(T)$ of one gas in terms of $B_0(T)$ for the system taken as reference. Furthermore, they constitute a model for inverting $B(T)$ data to determine pair interaction parameters: a scale distance r_m, the energy ϵ, and the shape parameters S_R and S_A. For simple and not too complex real gases, these parameters and the model for $B(T)$ reproduce the available data within estimated experimental errors.[20] Nevertheless, in spite of their usefulness, the shape parameters were defined at the phenomenological level and thus their exact connection to the intermolecular potential was not known. Hence, the underlying reasons for the existence of simple regularities remained obscure so preventing the extension of the approach to more complex systems.

Spurred by the phenomenological regularities that we recently demonstrated, in this paper we derive from first principles simple relationships between collision diameters and virial coefficients for a wide class of pairs of nonconformal potentials. This derivation not only explains the regularities found previously but also defines the limits of their application. Furthermore, the theory offers a route to determine the form of the appropriate potential functions for molecular interactions for given substances in the gas phase. The theory is illustrated here by its application to spherically symmetric potentials. Application of the theory to nonspherical model and real molecules is the subject of forthcoming papers.

In section II we review briefly the principal concepts about collision diameters and their relation to $B(T)$. The main aspects of the new theory are developed in sections III and IV. We first investigate the effect of nonconformality between two potential functions $u(r)$ and $u_0(r)$ on the collision diameters and find a type of nonconformal transformation between $u(r)$ and $u_0(r)$ involving a well-defined parameter S which determines the profile of one potential with respect to the other. This parameter defines the ratio between the slopes of $u(r)$ and $u_0(r)$ against r^3. It is shown that such a transformation leads to an exact relation between the virial coefficients of both systems involving only the constant parameter S. In section IV we analyze the conditions under which the constant-S transformation is a good approximation for the nonconformality between $u(r)$ and $u_0(r)$. It is shown that there are many gases of interest, including those studied previously,[20] where the constant-S transformation provides an excellent approximation to the exact relation. In order to do so, many cases require separate values of S for the repulsive and attractive parts of the potential. Finally, we show that S is a measure of the difference in softness between the potentials and generalize the treatment to angle-dependent potentials. In section V we show that the theory provides a pathway to the inversion of $B(T)$ to obtain the potential parameters including the shape parameter S and then go on to generate potential functions having a constant slope ratio S with respect to a reference $u_0(r)$. These functions constitute accurate operationally effective potentials for systems satisfying the constant slope transformation. The class of potential functions used in this work is akin to the familiar Kihara potential with a spherical core and involves three parameters: an energy depth ϵ, a distance taken here as the position of the potential minimum r_m, and the softness S. Lastly, in section VI the principal conclusions of this work are summarized.

II. Collision Diameters and Effective Volumes

In order to simplify the presentation we will introduce the theory for spherical potentials and defer to section IV its generalization to angle-dependent potentials. Consider a system of particles interacting through the pair potential $u(r)$ with a well-defined minimum of depth $u(r_m) = -\epsilon$ at the point r_m separating the potential into a repulsive ($0 \leq r < r_m$) and an attractive ($r < r_m$) region. We also assume that $u(r) \to \infty$ when $r \to 0$ and $u(r) \to 0$ when $r \to \infty$. In the dilute gas the mean diameters in binary collisions are obtained from the low-density limit of the collision frequency.[20] Thus the mean collision diameter $\sigma(T)$ is given by

$$\sigma^3(T)\, e^{\beta\epsilon} = \int_0^{r_m} dr\, r^3 (\partial e^{-\beta u(r)}/\partial r) \qquad (1)$$

and the mean collision range $R(T)$ by

$$R^3(T)(e^{\beta\epsilon} - 1) = -\int_{r_m}^{\infty} dr\, r^3 (\partial e^{-\beta u(r)}/\partial r) \qquad (2)$$

The quantities ϵ, r_m, and $b_m = \pi r_m^3/6$ will be used as units of energy, distance, and volume. We denote the core and attractive volumes by $b = \pi\sigma^3/6$ and $\Lambda = \pi R^3/6$, respectively. In reduced units, $\sigma^* = \sigma/r_m$, $R^* = R/r_m$, $b^* = b/b_m = \sigma^{*3}$, and $\Lambda^* = \Lambda/b_m = R^{*3}$. Integrating by parts (1) and (2) we find

$$b^*(T^*) = 1 - 3e^{-\beta\epsilon} \int_0^1 dz\, z^2 e^{-\beta u(z)} \qquad (3)$$

$$\Lambda^*(T^*) = 1 + \frac{3}{e^{\beta\epsilon} - 1} \int_1^{\infty} dz\, z^2 [e^{-\beta u(z)} - 1] \qquad (4)$$

where $z = r/r_m$ and $T^* = kT/\epsilon = 1/\beta\epsilon$. The reduced second virial coefficient is then

$$B^*(T^*) = B(T^*)/4b_m = b^*(T^*)e^{\beta\epsilon} - \Lambda^*(T^*)(e^{\beta\epsilon} - 1) \qquad (5)$$

which equals $B_{sw}^*(T)$ of a spherical square well (SW) with diameter $\sigma(T^*)$, depth ϵ, and effective range λ_{ef} given by

$$\lambda_{ef}^3 = \Lambda^*(T^*)/b^*(T^*) \qquad (6)$$

From (5), the thermodynamics of the gas is determined by the scale constants ϵ and r_m and by the functions $b^*(T^*)$ and $\Lambda^*(T^*)$; the temperature dependence of $b^*(T^*)$ and $\Lambda^*(T^*)$ reflects the form of the potential profile, i.e., the variation of $u(z)$ with z.

It has been reported, although without proof, that b^* and Λ^* of various model and real gases obey very simple relations in terms of the volumes b_0^* and Λ_0^* of a reference fluid.[20] In the next section we derive these relations from first principles and prove that they follow from particular types of nonconformal relations between the system of interest and the reference.

III. Relative Softness of Nonconformal Interactions

We will explore the connection between the form of $u(r)$ and $b^*(T^*)$ and $\Lambda^*(T^*)$. We follow Frisch and Helfand[21] and Smith and co-workers[9-11] by introducing $\phi(z) = u(z)/\epsilon + 1$ and change the independent variable from z to ϕ. This transformation was
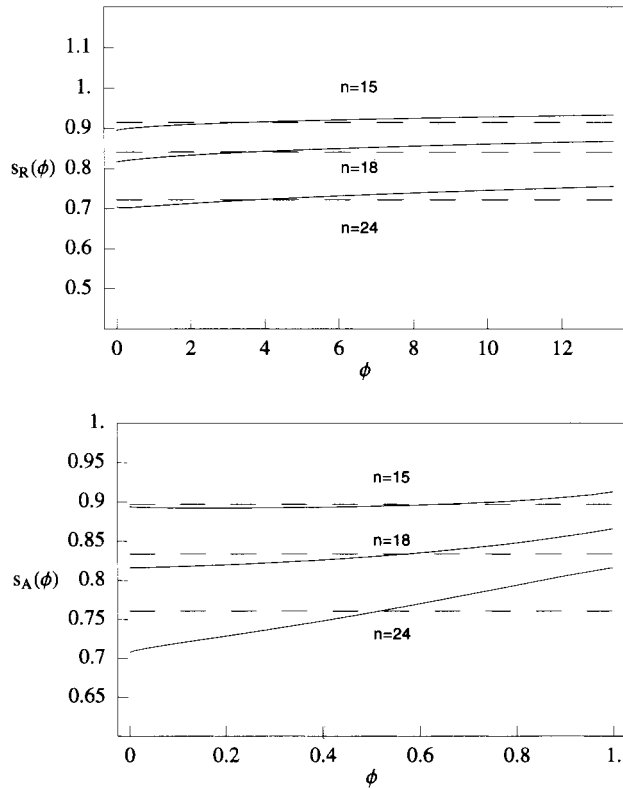
Figure 1. Ratio of slopes, $s(\phi)$ defined in eq 9, for Lennard-Jones $n/6$ potentials with $n = 15$, 18, and 24 with respect to the $n = 12$ interaction as the reference. The slope ratio varies slowly for a wide range of values of $\phi = u(z)/\epsilon + 1$. Repulsive (a, top) and attractive (b, bottom) regions. The continuous lines show $s(\phi)$ for the values of n as labeled. The dashed lines show the average values S_R and S_A in eqs 12 and 13.

an important step of Smith's procedure for the inversion of the virial coefficient of argon.[9] Then, since $\phi(z \to 0) \to \infty$, $\phi(1) = 0$, $\phi(z \to \infty) = 1$, and $3dz\ z^2 = dz^3 = (\partial z^3/\partial\phi)\ d\phi$ we obtain from (3) and (4) the expressions

$$b^* = 1 + \int_0^\infty d\phi \left[\frac{\partial z^3(\phi)}{\partial\phi}\right]_R e^{-\beta\epsilon\phi} \tag{7}$$

$$\Lambda^* = 1 + \frac{1}{e^{\beta\epsilon} - 1} \int_0^1 d\phi \left[\frac{\partial z^3(\phi)}{\partial\phi}\right]_A (e^{-\beta\epsilon(\phi-1)} - 1) \tag{8}$$

where $z(\phi)$ is the inverse of $\phi(z)$ in the repulsive and attractive regions of $\phi(z)$ denoted here by the indexes R and A, respectively.

We take now a spherical reference potential $u_0(z)$ with depth $\epsilon_0 = \epsilon$ and introduce a function $s(\phi)$ to describe the difference in form between ϕ and ϕ_0 by

$$[\partial z^3(\phi)/\partial\phi]_\phi = s(\phi)[\partial z_0^3(\phi)/\partial\phi]_\phi \tag{9}$$

where $z_0(\phi)$ is the inverse of $\phi_0(z) = u_0(z)/\epsilon_0 + 1$ and both derivatives are calculated at the same value of ϕ. Hence $s(\phi)$ describes the nonconformality between $u(z)$ and $u_0(z)$. In general, within the potential well $\phi \in (0, 1)$, $s(\phi)$ has different values, denoted here by s_R and s_A, on the repulsive and attractive regions of $\phi(z)$, respectively. As an example, Figure 1 shows $s(\phi)$ for several pairs of Lennard-Jones (LJ) $n/6$ potentials with respect to the LJ 12/6 potential, this is one case for which regularities in B^*, b^*, and Λ^* have been reported.[20] The smooth behavior of $s(\phi)$ shown in these figures is typical of most model potentials commonly used in fluid theories.
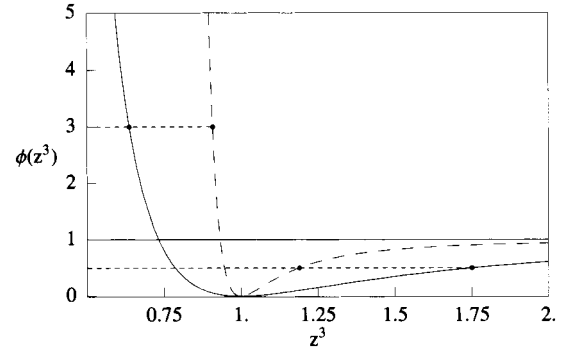
Figure 2. Potential function $\phi(z)$ (long dashed line) having a constant softness $S = 0.25$ with respect to the reference $\phi_0(z)$ (continuous line) plotted against z^3. The potential $u(z)$ has a slope 4 times larger than $u_0(z)$ at points of the same value of $\phi = u_0(z) + 1 = u(z) + 1$ as indicated by the two pairs of black circles.

The introduction of $s(\phi)$ allows us to relate the thermodynamic properties of both systems. Substituting (9) in (7) and (8), we obtain

$$b^* = 1 + \int_0^\infty d\phi\ s_R(\phi)[\partial z_0^3/\partial\phi]_R\ e^{-\beta\epsilon\phi} \tag{10}$$

and

$$\Lambda^* = 1 + \frac{1}{e^{\beta\epsilon} - 1} \int_0^1 d\phi\ s_A(\phi)[\partial z_0^3/\partial\phi]_A(e^{-\beta\epsilon(\phi-1)} - 1) \tag{11}$$

We also introduce the averages

$$S_R = \frac{1}{\phi_{max}} \int_0^{\phi_{max}} d\phi\ s_R(\phi) \tag{12}$$

with $\phi_{max} \simeq 10$, and

$$S_A = \int_0^1 d\phi\ s_A(\phi) \tag{13}$$

The simplest case is when both s_R and s_A are independent of ϕ so that $S_R = s_R$ and $S_A = s_A$. As an illustration, Figure 2 shows a reference potential $\phi_0(z)$ plotted against z^3 together with a potential $\phi(z)$ having $S_R = S_A = 0.25$; i.e., at equal values of ϕ the slope of $\phi(z)$ against z^3 is 4 times that of $\phi_0(z)$. In this case we obtain directly from (10) and (11) that

$$b^*(T^*) = 1 - S_R + S_R b_0^*(T^*) \tag{14}$$

$$\Lambda^*(T^*) = 1 - S_A + S_A \Lambda_0^*(T^*) \tag{15}$$

The volumes b_0^* and Λ_0^* are determined by (7) and (8) applied to $u_0(z)$ and give $B_0^*(T^*)$ through (5). Hence, when the slope ratio $s(\phi)$ between the nonconformal pair $\phi(z)$ and $\phi_0(z)$ is independent of ϕ and given by the constants S_R and S_A then the thermodynamic properties of the gas of interest are determined exactly by these two constants and the reference volumes $b_0^*(T^*)$ and $\Lambda_0^*(T)$.

Equations 14 and 15 mean that the parametric plots of $b^*(T^*)$ against $b_0^*(T^*)$ and of $\Lambda^*(T)$ against $\Lambda_0^*(T^*)$ are straight lines with slopes S_R and S_A and common intercept at $1 - S_R$ and $1 - S_A$, respectively. Furthermore, the virial coefficient is obtained by substitution of (14) and (15) in (5). The final

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expression for $B^*(T^*)$ is particularly simple when $S_R = S_A = S$; then

$$B^*(T^*) = 1 - S + SB_0^*(T^*) \qquad (16)$$

so that the parametric plot of $B^*(T^*)$ against $B_0^*(T^*)$ is also a straight line.

The fact that the properties of nonconformal systems can be *exactly* related by the introduction of one or two shape constants represents a clear improvement to the principle of corresponding states in gases. Nevertheless, the conditions on which this improvement is exactly applicable, i.e., spherically symmetric $u(z)$ and constant slope ratio $s(\phi)$, seem too restrictive for the theory to have wide application. However, since linear parametric plots have been found in cases such as diatomics where these conditions are not strictly met,[20] these relations should be more widely valid as approximations. We consider now the basis for these approximations.

IV. Illustration and Generalizations

We show first that (14) and (15) hold approximately when $s(\phi)$ varies smoothly with ϕ. In this case we can expand $s_R(\phi)$ as

$$s_R(\phi) = \sum_{l=0}^{\infty} \kappa_l \phi^l \qquad (17)$$

so that the Laplace transform in (10) leads to

$$b^* = 1 - \kappa_0 + \kappa_0 b_0^* + \sum_{l=1}^{\infty} (-1)^l \kappa_l (\partial^l b_0^* / \partial \beta^{*l})$$

where $\beta^* = \beta\epsilon$. Neglecting all terms with $l \geq 1$ we recover (14) with $S_R = \kappa_0$. A similar result is obtained for Λ^* by introducing a series expansion for $s_A(\phi)$. Nevertheless, truncation after the $l = 0$ terms gives only a fair result for the desired virial coefficient and higher order terms must be taken into account. This can be accomplished in two ways while maintaining the validity of (14) and (15). The first way is to exploit the smooth behavior of b_0^* with β^* when the reference $u_0(z)$ is chosen as the Kihara potential specified below. Indeed, from the numerical evaluation of b_0^* and its derivatives it was found that to a good approximation

$$(-1)^l (\partial^l b_0^* / \partial \beta^{*l}) \simeq -\bar{\nu}_l + \bar{\nu}_l b_0^*$$

for $l \leq 4$ so that neglecting terms with $l \geq 5$ we arrive to (14) with

$$S_R = \kappa_0 + \sum_{l=1}^{4} \kappa_l \bar{\nu}_l \qquad (18)$$

A similar analysis can be made for S_A which leads again to (15).

The second and more direct approximation is obtained simply by substituting $s_{R,A}(\phi)$ by their averages $S_{R,A}$ given by (12) and (13) so that we arrive again at the desired relations (14) and (15). We illustrate this approximation for the LJ $n/6$ potentials for which $s(\phi)$ varies with ϕ and whose mean values S_R and S_A are shown by dashed lines in Figure 1, a and b. S_R was
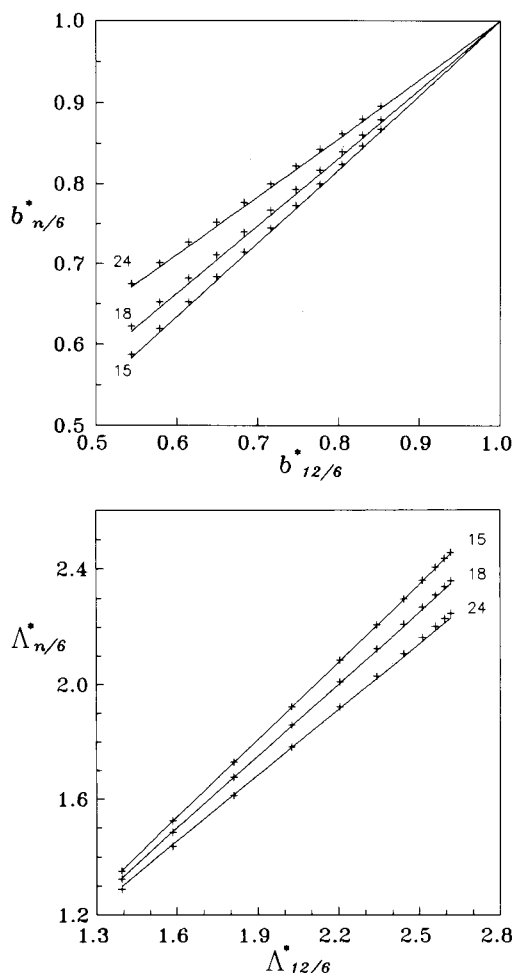
Figure 3. Parametric plots of the effective volumes b^* and Λ^* of Lennard-Jones $n/6$ potentials with respect to b_0^* and Λ_0^* of the $n = 12$ interaction for values of n as labeled. The crosses are the values obtained numerically from eqs 7 and 8. The solid lines are plots of eqs 14 and 15 with the average slopes S_R and S_A shown in Figure 1.

calculated with $\phi_{max} = 8.0$; the particular value of ϕ_{max} does not introduce a large error in (10) because when $\phi \gg 1$ the integrand is very small. Figure 3, a and b, shows the parametric plots of b^* and Λ^*, calculated directly from (7) and (8), against b_0^* and Λ_0^* for the same LJ potential pairs. Figure 3, a and b, shows also the straight lines with mean slopes S_R and S_A in (14) and (15) which are indeed very close to the parametric plots. This analysis provides the underlying justification for (14) and (15) to hold for LJ $n/6$, Kihara, and exp-6 potentials as reported previously.[20] A high-order approximation based on a truncated Taylor expansion as in (18) gives similar results.

Let us turn now to the interpretation of $s(\phi)$ and the parameter S. If we introduce the reduced potential $\omega = u/\epsilon$, the basic definition (9) becomes

$$s(\phi) = \frac{[\partial\omega_0(z)/\partial z^3]_{z_0(\phi)}}{[\partial\omega(z)/\partial z^3]_{z(\phi)}} \qquad (19)$$

The derivative $\partial\omega/\partial z^3$ is the slope of ω when plotted against z^3 and hence (19) means that the potential ω is $1/s(\phi)$ times steeper than ω_0 at the given value of ϕ. Consequently, S is the average inverse steepness. When $s = 1$, $\omega(z^3)$ has exactly the same slope as $\omega_0(z^3)$ and the two potentials are conformal. Now, since a very steep potential means a very "hard" molecule, S measures the softness or inverse "hardness" of $\omega(r)$ with respect

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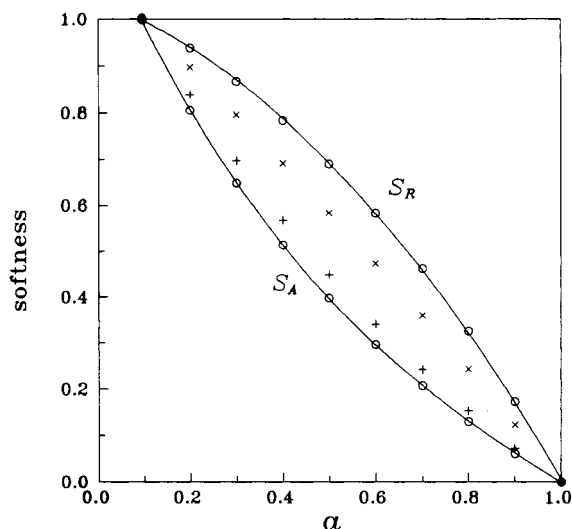
Figure 4. Softness parameters S_R and S_A of spherical Kihara molecules as a function of core diameter a. The circles represent the values obtained from the inversion of $B_K^*(T^*)$ in Table 1. The crosses stand for the values of S_R ($\times$) and S_A ($+$) obtained from parametric plots of b^* and Λ^*.

to $\omega_0(r)$. When $S < 1$, ω is on the average harder or steeper than ω_0 as in the example shown in Figure 2; but when $S > 1$, ω is softer. In particular, when the repulsive part of $\omega(z)$ is a hard core, then $S_R = 0$ and we find from (14) that $b^* = 1$ independently of T. On the other hand, $S_A = 0$ means an infinitely steep attractive potential of the square-well type and $\Lambda^* = 1$.

Based on this interpretation, in all cases for which (14), (15), or (16) hold, S will be called the softness of the potential. Any two systems with softnesses S_1 and S_2 with respect to the reference will follow corresponding states with each other whenever $S_1 = S_2$, so that $S_1 - S_2$ is a measure of the deviation from conformality between the potentials. Equations 14 and 15 mean that, once $b_0^*(T^*)$ and $\Lambda_0^*(T^*)$ are known, $B(T)$ for the gas of interest is determined by the four characteristic parameters ϵ, r_m, S_R, and S_A. In the simpler case when $S_R = S_A = S$ we have three parameters only and eq 16 holds.

As a useful illustration the softnesses S_R and S_A have been determined from the slopes of linear fits as in Figure 3 for the spherical Kihara functions

$$u_K(z;a)/\epsilon = \left[\frac{1-a}{z-a}\right]^{12} - 2\left[\frac{1-a}{z-a}\right]^6 \qquad (20)$$

where a is the hard-core diameter in units of r_m. Here we take $u_0(z) = u_K(z;a_0)$ with $a_0 = 0.095\ 738\ 9$ which makes $u_0(z)$ a good representation of the pair potential of argon.[20] The corresponding values of $b_0^*(T^*)$ and $\Lambda_0^*(T^*)$ are fitted by polynomials in $\ln(T^*)$ as detailed in Appendix A. Values of S_R and S_A for $a_0 \le a \le 1$ were approximated by straight-line fits to plots of $b^*(T^*)$ and $\Lambda^*(T^*)$ against $b_0^*(T^*)$ and $\Lambda_0^*(T^*)$ and are shown in Figure 4. As a grows, the potential becomes steeper in both its repulsive and attractive regions and thus S_R and S_A decrease as shown in Figure 4. Of course, for $a = a_0$ we find $S_R = S_A = 1$ whereas for $a = 1$ we obtain $S_R = S_A = 0$ so that the potential reduces to that for hard spheres.

The model $B_{theo}^*(T^*)$ is obtained from (14), (15), and (5) with the values of S_R and S_A. As a test of this model, B_{theo}^* was compared with $B_{num}^*(T^*)$ calculated numerically for $u_K(z;a)$ with $\epsilon = 1$, $r_m = 1$ and $a_0 \le a \le 1$. For each a and the

corresponding values of S_R and S_A shown in Figure 4 the rms deviation Q was calculated from

$$Q^2 = \frac{1}{n_p}\sum_{i=1}^{n_p}[B_{num}^*(T_i^*) - B_{theo}^*(T_i^*)]^2$$

over a set of n_p temperatures in the range $0.4 \le T^* \le 6.5$. The mean deviations were found to be of a few parts in 10^2 and are greater for $a \simeq 0.5$. For all a individual deviations $\delta B^* = B_{num}^*(T_i^*) - B_{theo}^*(T_i^*)$ are larger at the lowest T_i^*. The mean relative deviations $\delta B^*/B^*$ are smaller than 1% over most of the range and reach a few percent at $T^* \simeq 0.4$ (except, of course, very close to the Boyle temperature where B^* goes through zero). Hence the model provides an explicit and compact expression for $B_{num}^*(T^*)$ which is accurate at all but the lowest temperatures.

The generalization of the theory to angle-dependent potentials is straightforward although somewhat involved. The procedure is detailed in Appendix B and here we describe only the leading results. In this case $u(z,\Omega)$ is also a function of the angles Ω needed to specify the orientation between a pair of molecules and is assumed to have a well-defined minimum of depth ϵ_Ω at distance r_Ω for fixed orientation Ω. For $u(z,\Omega)$ the softness $s(\phi,\Omega)$ with respect to $u_0(z)$ depends on the angles and the mean softnesses are now given by the double averages

$$S_R = \frac{1}{\phi_{max}}\int d\Omega \int_0^{\phi_{max}} d\phi\ s_R(\phi,\Omega) \qquad (21)$$

$$S_A = \int d\Omega \int_0^1 d\phi\ s_A(\phi,\Omega) \qquad (22)$$

where the angles are normalized so that $\int d\Omega = 1$. The distance and energy parameters are now the angle averages

$$r_m^3 = \int d\Omega\ r_\Omega^3 \qquad (23)$$

$$\epsilon = \int d\Omega\ \epsilon_\Omega \qquad (24)$$

The main steps in the generalization are as follows. The desired virial coefficient $B^*(T^*)$ is expressed first as an angle average of $B_0^*(T_\Omega^*)$, where $T_\Omega^* = kT/\epsilon_\Omega$. $B_0^*(T_\Omega^*)$ is then expanded in a Taylor series about $\epsilon = \langle\epsilon_\Omega\rangle_\Omega$. We then find that eq 16 is again a valid approximation but with the final values of b_m and S affected by $\langle s\epsilon_\Omega\rangle_\Omega$ and $\langle s\epsilon_\Omega^2\rangle_\Omega$. Details are found in Appendix B.

We have shown in this section that the second virial coefficient $B^*(T)$ of a wide class of potentials can be simply and accurately written in terms of a spherical reference potential $u_0(z)$. The differences in form and molecular geometry are accounted for by the relative softnesses S_R and S_A of the given potential with respect to the reference.

## V. Effective Potentials and Inversion of $B(T)$

Finally, in this section we show the adequacy of the theory to invert $B(T)$ to determine the potential function. First, we show that the parameters ϵ, r_m, S_R, and S_A can be obtained reliably if numerical data of $B(T)$ are available. Second, we will show how to construct an operationally effective potential with these parameters. This will be of importance in applications to real gases where the intermolecular potential is not known beforehand.

We illustrate the first of these points in reference to the spherical Kihara potentials $u_K(z;a)$ for which the virial coef-

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TABLE 1: Effective Potential Parameters for Spherical Kihara Interactions[a]

a	ϵ	r_m	S_R	S_A	$10^4 Q$
0.1	1.000	1.000 78	0.9997	0.9900	0.32
0.2	1.004	1.008 06	0.9385	0.8054	1.86
0.3	1.007	1.013 17	0.8666	0.6485	3.19
0.4	1.011	1.016 26	0.7837	0.5139	3.90
0.5	1.013	1.017 66	0.6899	0.3975	4.14
0.6	1.016	1.017 24	0.5830	0.2963	3.97
0.7	1.018	1.015 15	0.4621	0.2078	3.38
0.8	1.020	1.011 53	0.3258	0.1300	2.49
0.9	1.021	1.006 49	0.1727	0.0612	1.44

[a] The parameters reported are the result of inverting the numerical values of $B_K^*(T^*)$. The last column shows the rms deviation of the resulting model from the input data.
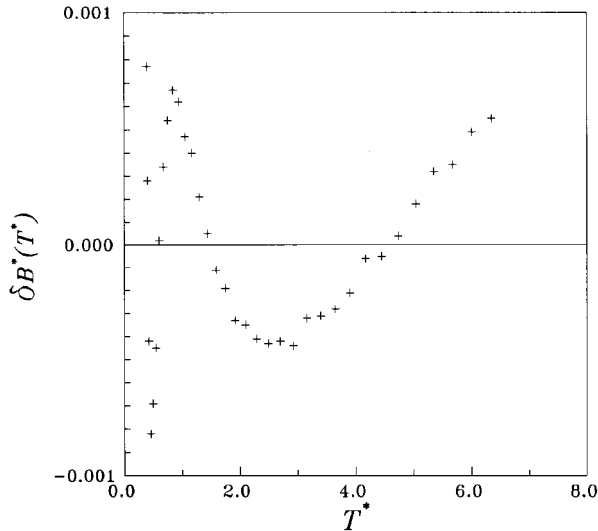
Figure 5. Plot of the deviations $\delta B^* = B_{num}^* - B_{theo}^*$ for the virial coefficient of a Kihara gas with spherical core of diameter $a = 0.5$. The parameters S_R and S_A used were those obtained from the inversion of $B_K^*(T^*)$.

ficient $B(T)$ is obtained by simple integration. The input test values are $\epsilon = 1$ and $r_m = 1$ and the Kihara diameter a has the values shown in Table 1. Then new values of ϵ, r_m, S_R, and S_A were obtained from $B(T)$ by assuming that the model holds; i.e., by a least-squares fit of eqs 5, 14, and 15 to the numerical $B(T)$ data; the results are shown in Table 1. We first point out that the small number of parameters and the simplicity of the model make the inversion procedure very robust and convergence is achieved easily. Second, we notice that the rms deviations of the fit to $B(T)$ in the last column of the table are very small for all cases considered, thus demonstrating the strength of the model to represent the virial coefficient. These deviations are 2 orders of magnitude smaller than those obtained when S_R and S_A are determined from the parametric plots of b^* and Λ^*. Figure 5 shows the deviations δB^* for $u_K(z;a)$ with $a = 0.5$ where $Q \simeq 4 \times 10^{-4}$ is maximum. The comparison is similar for other spherical potentials such as LJ $n/6$ and exp-6. From this figure we see that δB^* is uniformly small except at the lower temperatures.

Nevertheless, the real test is whether the potential parameters obtained from the inversion are close to the correct values. The values of ϵ and r_m obtained from the inversion are shown also in Table 1. They are very close to the assumed input values, with maximum errors of 2% for ϵ at $a = 0.9$ and for r_m at $a = 0.5$. The values of S_R and S_A obtained from the inversion are also shown in Figure 4. It is seen that the inversion reduces

most of the deviations in the parametric approximations at the price of slight changes in ϵ, r_m, S_R, and S_A.

Therefore, the inversion of $B^*(T^*)$ with this model is very reliable and gives accurate values of the potential parameters. If the potential of interest is spherically symmetric, a spherical potential constructed with the given parameters should be very close to the true pair potential. However, if the potential of interest $u(z,\Omega)$ has an angular dependence, the inversion gives only a spherical *effective* potential $u_{ef}(z,S_R,S_A)$ with $S_R = \langle S_R(\Omega)\rangle$, $S_A = \langle S_A(\Omega)\rangle$, $\epsilon = \langle\epsilon_\Omega\rangle$, and $r_m^3 = \langle r_\Omega^3\rangle$. Indeed, different potentials $u(z,\Omega)$ having the same values of ϵ, r_m, S_R, and S_A will have exactly the same second virial coefficients.

We now proceed to the final stage and construct potentials having a given softness S with respect to the reference. These potentials will prove to be useful as effective interactions for real gases. We will use reduced potentials $\omega_{ef} = u_{ef}/\epsilon$ and $\omega_0 = u_0/\epsilon_0$. We start from the potential $\omega_0(z)$ and construct $\omega_{ef}(z)$ such that (19) will hold with $s(\phi) = S = $ constant. The case with $S_R \neq S_A$ can be obtained easily from this. From (19) and setting $y = z^3$ the desired relation is

$$S\frac{\partial\omega_{ef}(y,S)}{\partial y}\bigg|_{y(\phi)} = \frac{\partial\omega_0(y)}{\partial y}\bigg|_{y_0(\phi)} \qquad (25)$$

This equation requires both derivatives to be taken at the same value ϕ, i.e.

$$\omega_{ef}(y) = \omega_0(y_0) = \phi - 1$$

In order to determine ω_{ef} we absorb the constant S into the left-hand side of (25) by changing variable from y to $\bar{y} = y/S + K$, where K is an arbitrary constant. Hence $d\bar{y} = dy/S$ and we can write

$$\frac{\partial\omega_{ef}}{\partial\bar{y}}\bigg|_{\bar{y}(\phi)} = \frac{\partial\omega_0}{\partial y}\bigg|_{y_0(\phi)}$$

Thus the desired new potential ω_{ef} is obtained from ω_0 by substituting in the latter

$$z^3 \rightarrow z^3/S + K \qquad (26)$$

This transformation can be applied to any continuous potential used as reference. A case of particular interest is the spherical $n/6$ Kihara potential with hard-core diameter a in units of r_m given by

$$\omega_K(z;n,a) = C_n\left[\frac{1-a}{z-a}\right]^n - (1+C_n)\left[\frac{1-a}{z-a}\right]^6 \qquad (27)$$

where $C_n = 6/(n-6)$ and $z = r/r_m$. For $a = 0$, $\omega_K(z;n,a)$ reduces to the LJ $n/6$; for $n = 12$ and $a = a_0$, ω_K gives the reference (20). Using (26) in (27) we obtain a new potential ω_M which depends on S and K. This constant shifts the position of the potential minimum from $z_m = 1$, to $z_m^3 = (1-K)S$. In order to keep $z_m = 1$ we choose $K = 1 - 1/S$ and thus find the modified potential

$$\omega_M(z;n,a,S) = C_n\left[\frac{1-a}{(z^3/S + 1 - 1/S)^{1/3} - a}\right]^n -$$

$$(1+C_n)\left[\frac{1-a}{(z^3/S + 1 - 1/S)^{1/3} - a}\right]^6 \qquad (28)$$
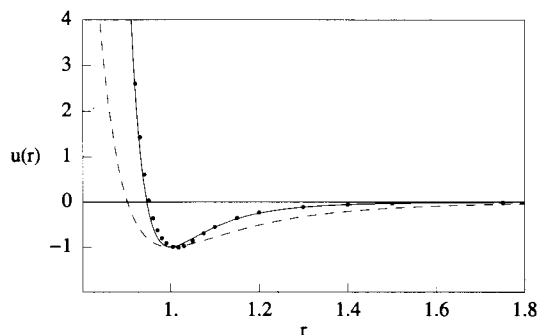
Figure 6. Kihara potential $u_K(z)$ with core diameter $a = 0.5$ (solid line) compared with the corresponding potential $u_{ef}(z)$ (black circles) which has $\epsilon = 1.013$, $r_m = 1.01766$, $S_R = 0.6899$, and $S_A = 0.3975$ obtained from the inversion of $B_K^*(T^*)$. The reference potential $u_0(z)$ with $S = 1$ is shown by the dashed line.

This potential has a hard-core diameter

$$z_0^{\,3} = (a^3 - 1 + 1/S)S$$

and resembles the Smith–Thakkar potential.[22] It is straightforward to show that any pair of potentials (28) with the same values of n and a but with different softnesses S_1 and S_2 satisfy (19) with $S = S_1/S_2$. The transformation (26) forms a group, so that any potential (28) with specified values of a and n can be used as reference. This procedure can be applied easily to other reference potentials.

The potential $\omega_M(z;12,a,S)$ can be used as the effective potential for systems adequately described by a single softness S. Systems which require different softnesses S_R and S_A have as effective potential

$$\omega_{ef}(z;a,S_R,S_A) = \omega_M(z;12,a,S_R), \quad z < 1$$
$$= \omega_M(z;12,a,S_A), \quad z > 1 \tag{29}$$

which is continuous and has a continuous first derivative at $z = 1$.

In order to illustrate the adequacy of the effective potential obtained by this inversion procedure, Figure 6 compares the potential $u_K(r;12,a=0.5)$ with the corresponding effective potential (29) $\omega_{ef}(z;a_0,S_R,S_A)$ with parameters taken from the inversion procedure and shown in Table 1. The black circles in the figure show u_{ef} and are indeed very close to the solid line showing u_K. The only notable deviations between u_K and u_{ef} are those at the very bottom of the well. It is interesting that the big difference in the hard-core diameters ($a = 0.5$ in u_K, $z_0 = 0.735$ in u_{ef}) matters only at extremely short distances.

VI. Conclusions

We have extended the principle of corresponding states in gases to account for the nonconformality between two potentials; deviations from conformality are accounted for by the introduction of the slope ratio s between the two potential functions. Then $B(T)$ of one system is simply expressed in terms of $B_0(T)$ of the second (reference) system by introducing softness constants S_R and S_A. The theory is exact for constant softness and gives a good approximation when $s(\phi)$ varies smoothly with ϕ and also when the potential depth is angle dependent.

The theory can be applied to determine the explicit form of the pair potential by inversion of known $B(T)$ data including the interaction parameters.

The application of the theory here developed to more complex molecules, both model and real with especial consideration of linear and chain molecules, will be covered in forthcoming papers.

Appendix A

Reference System. The effective volumes of the reference potential (20) with $a = 0.095\,738\,9$ were calculated numerically and fitted to obtain

$$b_0^* = \sum_{m=0}^{4} c_m (\ln T^*)^m \tag{30}$$

$$\Lambda_0^* = b_0^* \sum_{m=0}^{10} l_m (\ln T^*)^m \tag{31}$$

the coefficients c_m and l_m are given in Table 2. The number of significant figures in a, c_m, and l_m, as well as the order of the polynomials in (30) and (31), were chosen such as to ensure a reproducibility of the calculated $B(T)$ at least an order of magnitude better than the best available experimental results for argon.

Appendix B

Angle-Dependent Potentials. We consider here the more general case when $u(z,\Omega)$ is angle dependent so that both the position of the minimum r_Ω and the depth ϵ_Ω depend on the intermolecular orientation. The effective ϵ and r_m are now given by (24) and (23). It is simpler to work with the full virial coefficient

$$B^*(T^*) = \sigma^{*3} e^{\beta\epsilon} - R^{*3}(e^{\beta\epsilon} - 1)$$

which can be written as

$$B^*(T^*) = 1 + I_R + I_A$$

where

$$I_R = -3 \int d\Omega \int_0^{z_\Omega} dz\, z^2 e^{-\beta u(z,\Omega)} \tag{32}$$

$$I_A = 3 \int d\Omega \int_{z_\Omega}^{\infty} dz\, z^2 [e^{-\beta u(z,\Omega)} - 1] \tag{33}$$

We define now $\phi(z,\Omega) = u(z,\Omega)/\epsilon_\Omega + 1$ and change again the independent variable in (32) and (33) from z to ϕ. We then introduce $s(\phi,\Omega)$, $S_R(\Omega)$, and $S_A(\Omega)$ by generalizing (9), (12), and (13) for a given Ω. Assuming for simplicity that $S_R = S_A = S(\Omega)$, we find after some manipulation that

$$B^*(T^*) = 1 + \int d\Omega\, S(\Omega)[B_0^*(T_\Omega^*) - 1] \tag{34}$$

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TABLE 2: Parameters in the Fit of the Reference Effective Volumes

m	c_m	l_m	m	l_m
0	$7.663\ 230\ 5 \times 10^{-1}$	$2.679\ 786\ 56$	6	$1.682\ 855\ 86 \times 10^{-3}$
1	$-7.247\ 001\ 68 \times 10^{-2}$	$6.843\ 877\ 82 \times 10^{-1}$	7	$5.884\ 159\ 73 \times 10^{-4}$
2	$-5.656\ 659\ 11 \times 10^{-3}$	$-7.144\ 487\ 40 \times 10^{-2}$	8	$-4.426\ 438\ 88 \times 10^{-4}$
3	$6.161\ 108\ 54 \times 10^{-4}$	$7.788\ 581\ 73 \times 10^{-3}$	9	$8.633\ 160\ 56 \times 10^{-5}$
4	$7.577\ 863\ 85 \times 10^{-5}$	$1.644\ 211\ 69 \times 10^{-2}$	10	$-4.761\ 344\ 07 \times 10^{-6}$
5		$-8.736\ 312\ 67 \times 10^{-3}$		

where $B_0^*(T_\Omega^*)$ is the virial coefficient of the reference calculated at the temperature

$$T_\Omega^* = kT/\epsilon_\Omega$$

Using the fact that the effective depth ϵ is the average of ϵ_Ω, (24), we now write $\delta\epsilon = \epsilon - \epsilon_\Omega$ and expand $B_0^*(T_\Omega^*)$ in a Taylor series about ϵ to get

$$B_0^*(T_\Omega^*) = B_0^*(T^*) + \delta\epsilon(\Omega)\left[\frac{\partial B_0^*(T^*)}{\partial\epsilon}\right] + \frac{1}{2}[\delta\epsilon(\Omega)]^2\left[\frac{\partial^2 B_0^*(T^*)}{\partial\epsilon^2}\right] + \ldots$$

Substituting this in (34), we find

$$B^*(T^*) = 1 - \hat{S} + \hat{S}B_0^*(T^*) + \gamma(T^*) \tag{35}$$

with $\hat{S}$ given by

$$\hat{S} = \int d\Omega\, S(\Omega)$$

and

$$\gamma = \langle S\delta\epsilon\rangle_\Omega\left[\frac{\partial B_0^*(T^*)}{\partial\epsilon}\right] + \langle S\delta\epsilon^2\rangle_\Omega\left[\frac{\partial^2 B_0^*(T^*)}{\partial\epsilon^2}\right] + \ldots \tag{36}$$

In a first-order approximation γ is neglected to recover (16) with $\hat{S} = S$. However, numerical calculations with a realistic $u(z,\Omega)$ shows that this approximation gives only a fair prediction of $B^*(T^*)$. To second order $\langle S\delta\epsilon\rangle_\Omega$ is small and when $B_0^*(T^*)$ is taken as (20), the second-order term in (36) is approximately proportional to $B_0^*(T^*)$, so that to a good approximation

$$\gamma \simeq c_1 + c_2 B_0^*(T^*) \tag{37}$$

where c_1 and c_2 are constants approximately proportional to $\langle S\delta\epsilon\rangle_\Omega$ and $\langle S\delta\epsilon^2\rangle_\Omega$, respectively. In particular, when S is independent of Ω then $\langle S\delta\epsilon\rangle_\Omega = 0$ and c_1 vanishes. Using this result in (35) we find again eq 16 by making

$$S = \frac{c_2 + \hat{S}}{1 + c_1 + c_2}$$

and

$$b_m = \pi(1 + c_1 + c_2)r_m^3/6$$

so that the effective softness and size are both affected by $\langle S\delta\epsilon\rangle_\Omega$ and $\langle S\delta\epsilon^2\rangle_\Omega$.

So eq 16 holds again to a very good approximation, but the values of b_m and S are affected by the angular dependence of the potential through $\langle S\delta\epsilon\rangle_\Omega$ and $\langle S\delta\epsilon^2\rangle_\Omega$. This means that even if r_Ω and s were constant, the angle dependency of ϵ_Ω would make $r_m \neq r_\Omega$ and $S \neq s$.

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