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Accurate Effective Potentials and Virial Coefficients in Real Fluids. 1. Pure Noble Gases and Their Mixtures

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A new theory which accounts for the nonconformality of intermolecular potentials is used to obtain effective potentials which represent accurately the thermodynamic properties of simple and molecular fluids. This approximate nonconformal (ANC) theory introduces a constant softness (S) to incorporate deviations in conformality between the exact angle-averaged effective potential and a potential of reference. The softness S together with the molecular size and energy determine both the intermolecular potential and the thermodynamic properties of the fluid, i.e., the second virial coefficient, $B(T)$. The theory is applied here to the pure noble gases and their mixtures. The cross interactions in the binary mixtures are determined from suitable mixing rules. The effective potentials of these molecules and for their cross interactions are obtained and compared with accurate pair potentials available from the literature. The ANC potentials agree very well with known pair interactions, except for He, and the pure and cross virial coefficients give excellent agreement with experimental results.

1. Introduction

Intermolecular potentials are a fundamental ingredient of modern theories and computer simulations of the fluid state. Since the visionary work of van der Waals the importance of defining a suitable pair interaction in order to understand the thermodynamic properties of fluids has become clear. Many advances on the theory of classical fluids over the last few decades can be related to the development and test of relatively simple model interaction potentials which have proven to be very successful in explaining many properties of simple and complex fluids.^{1,2} As a result we have learned about the basic importance of several features of the intermolecular potential in determining the topology of the phase diagram of classical systems. In a parallel effort, researchers have been working on the determination of ever more exact interaction potential functions of real substances. This endeavour has produced detailed knowledge about pair interactions in many simple real systems and is based on two general types of approach: on one hand, ab initio quantum mechanical calculations of the potential function as those on the Ne-Ne and Ar-Ar potentials^{3,4} and, on the other hand, inversion of experimentally measured equilibrium and transport properties of gases complemented in some cases with differential scattering cross sections.^{5–8} It is thus that gas properties have been a leading source of information about pair interactions, and among them the inversion of the second virial coefficient $B(T)$ has been of particular importance due to the straightforward relation between the potential and $B(T)$ and to the relative abundance of experimental measurements of it.⁹ Knowledge of the second virial coefficient is also of practical importance because it is widely used in chemical engineering for the treatment of fluid phase and chemical reaction engineering.¹⁰

There are two traditional methods of inverting $B(T)$ to obtain information about the intermolecular potential. The first is to assume a given potential form which is a function of a few

parameters and then to determine these parameters by fitting the numerically predicted $B(T)$ to experimental data. This approach is usually hampered by being attached to a fixed mathematical form of the assumed intermolecular potential, such as the Lennard–Jones 12-6 potential (LJ/12-6), and such rigidity can lead to significant errors in the fit to $B(T)$ and hence in the final pair potential obtained. A second approach, not relying on an assumed functional form, is that of Smith and co-workers;^{11,12} this procedure nevertheless requires a large set of high quality experimental data and to our knowledge it has been applied only to argon¹² and methane.¹³ The main questions arising in the inversion of $B(T)$ have been critically reviewed by Knobler.¹⁴

An important and independent work on the theory of virial coefficients is due to Kestin and co-workers,¹⁵ who have produced explicit expressions for $B(T)$ for the noble gases on the assumption that these substances follow corresponding states, i.e., that their interaction potential functions are conformal. Furthermore, Kestin and co-workers have extended the theory to include other properties, such as viscosity coefficients, for the same noble gases. Nevertheless, Kestin's theory does not give explicit information about intermolecular potentials and is restricted to substances with conformal potentials. Lastly, given the practical importance of explicit expressions for $B(T)$ in chemical engineering applications, several empirical correlations have been proposed such as that due to Tsonopoulos which makes use of critical properties and the Pitzer acentric factor.¹⁶

In spite of the large amount of information so far gathered by the above developments, they have not met the needs of fluid state theory and its applications in various respects. First, interaction potentials obtained from ab initio calculations are still unable to predict $B(T)$ within experimental error at low temperatures even for simple molecules such as neon.⁴ Second, the best available pair potentials, which are obtained by fitting a multiparameter empirical form to a wide range of gas proper-

ties, while able to account for the experimental data have again only been developed for simple substances such as the noble gases.^{5–8,17} For polyatomics and more complex molecules, the currently available potentials give results for $B(T)$ which in many cases are not in full agreement with experimental data. Also, the results available for complex molecules do not allow us to discern systematic changes in the intermolecular potentials when, for example, going from one substance to another within the same molecular family.

In a recent paper¹⁸ we have presented a theory for the virial coefficient of gases with nonconformal potentials, either spherical or nonspherical; we will refer to it as the approximate nonconformal (ANC) theory. In the ANC theory we propose a family of nonconformal potential functions which depend on the characteristic energy and size of the molecules, ϵ and r_m , and on two form parameters, S_R and S_A , which measure the average softness of the pair potential on its repulsive and attractive wings, respectively, relative to a spherical reference. In its first and simplest approximation, the ANC theory assumes a single softness (S) for both parts of the pair potential. S is an average of S_R and S_A . We showed also that $B(T)$ can then be written explicitly in terms of the same parameters ϵ , r_m , and S , and of the second virial coefficient of the reference system which corresponds to $S = 1$. These parameters, and in particular the softness S , are derived from a given true pair potential within well-prescribed approximations. In a second paper¹⁹ we widened the scope of the treatment to explicitly deal with gases comprising nonspherical, and particularly linear, model molecular systems. In these nonspherical cases, the effective parameters ϵ , r_m , and S are defined by the appropriate angle averages so that the potential reproducing $B(T)$ works as an “effective” spherical potential. In those papers we showed that the ANC theory gives excellent results for a wide variety of spherical and nonspherical model systems, thus providing us with (1) a robust tool for inverting $B(T)$ to obtain reliable angle averaged potentials, (2) a very simple model for expressing $B(T)$ in terms of the effective molecular parameters ϵ , r_m , and S , and (3) an insight into the dependence of these parameters on the nonsphericity and other basic features of the molecule.

In this paper we present the first results of applying the ANC theory to real substances: the noble gases and their binary mixtures. The cases of more complex molecules will be presented elsewhere. The application to real spherical molecules, for which accurate pair potentials are already available in the literature, is given not only because it constitutes the ideal testing ground of the ANC theory but also because it gives several pieces of interest as a bonus: First, the pair potentials for the cross interaction in noble gas mixtures are predicted by means of suitable combining rules. Next, we give very accurate and compact expressions for the virial coefficients of the pure gases and their mixtures. Lastly, the molecular parameters ϵ , r_m , and S for all the noble gases except He and Ne are shown to have, besides the not unexpected regularities with atomic number and critical temperature, a systematic behavior with critical volume.

In section 2 we review briefly the basic facts about the ANC theory and discuss the method employed in the fitting of the experimental $B(T)$ and discuss the method employed in the fitting of the experimental $B(T)$ data. In section 3, starting with the case of argon which we use here and elsewhere as our reference substance, we draw attention to the salient features of the results for each of the noble gases, including the extrapolation of the ANC model to radon. In section 4 we turn to mixtures introducing the combination rules that are found

best to describe the gas imperfection of mixtures. Lastly, in section 5 we summarize the main conclusions reached.

2. Theory

The nonconformal theory considers a gas whose molecules interact through the pair potential $u(r, \Omega)$ which at fixed relative orientation Ω has a well-defined minimum at $r_{\min}(\Omega)$ of depth $\epsilon_m(\Omega)$. The properties of this gas are related to a reference system with spherical potential $u_0(r)$ and second virial coefficient $B_0(T)$. We have shown that the potentials $u(r, \Omega)$ and $u_0(r)$ may be related by introducing a relative measure of the difference between their profiles in a u vs r^3 plot. When the nonconformality between both potentials is such that it can be described by a constant parameter S , we have further shown that the virial coefficients $B(T)$ and $B_0(T)$ are explicitly and very simply related.^{18,20} Although there are pairs of potentials $u(r, \Omega)$ and $u_0(r)$ for which S is strictly constant and for them this NC theory is exact, the study of a great variety of widely used model systems, both spherical and nonspherical, has shown that assuming S to be constant leads to approximate results of high accuracy.¹⁹ We refer to this as the approximate nonconformal (ANC) theory, which in general allows us to use two values, S_R and S_A , of the softness parameter to describe the repulsive and attractive parts of the u vs r^3 profile, respectively.

It was also shown that when the whole profile is characterized by a unique softness $S = S_R = S_A$, the virial coefficient of the gas of interest may be written in reduced form as¹⁸

$$B^*(T^*) = \frac{B(T^*)}{4b_m} = 1 - S + SB_0^*(T^*) \quad (1)$$

where $T^* = kT/\epsilon = 1/\beta\epsilon$, $b_m = \pi r_m^3/6$, and S is the shape constant which measures the average softness of $u(r, \Omega)$ with respect to $u_0(r)$. Energies and distances are scaled with the constants ϵ and r_m , respectively, given by the angle averages

$$r_m^3 = \int d\Omega r_{\min}^3(\Omega) \quad (2)$$

and

$$\epsilon = \int d\Omega \epsilon_m(\Omega) \quad (3)$$

The angles Ω describing the intermolecular orientation are normalized so that $\int d\Omega = 1$.

From eq 1, the thermodynamics of the gas is determined by the scale constants ϵ and r_m and by the shape constant S . Equation 1 is exact when ϵ_m is angle independent and the ratio of slopes of $u(z, \Omega)$ and $u_0(z)$ against z^3 , where $z = r/r_m$, is constant. Nevertheless, eq 1 is a very good approximation when the ratio of slopes varies smoothly.

In this work we will use as reference the spherical Kihara potential²¹

$$u_0(z)/\epsilon_0 = \left[\frac{1-a}{z-a} \right]^{12} - 2 \left[\frac{1-a}{z-a} \right]^6 \quad (4)$$

where $z = r/r_{m0}$, r_{m0} is the position of the minimum, and a is the hard-core diameter in units of r_{m0} . We further take $a = 0.09574$ so that $u_0(z)$ is a good representation of the pair potential of argon. The virial coefficient $B_0^*(T^*)$ in eq 1 depends only on T^* and not on ϵ_0 and r_{m0} ;¹⁸ it is calculated numerically and is represented by polynomials in $\ln(T^*)$ given explicitly in the appendix for the range $0 \leq T^* \leq 250$ (ref 18 reports only the range $0.35 \leq T^* \leq 10$, which is insufficient for the purposes of this paper).

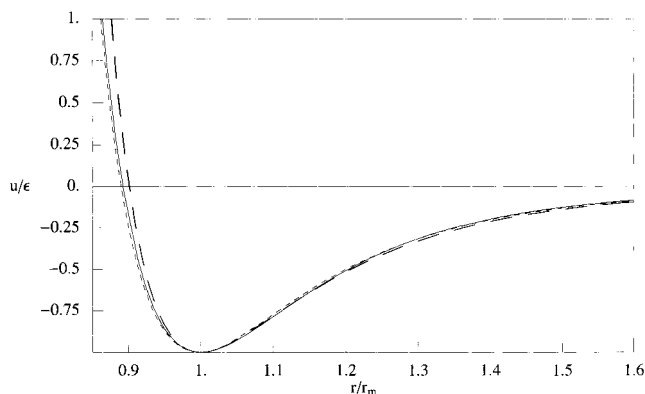


Figure 1. Comparison of the Aziz–Slaman pair potential for argon (solid line)⁷ with the ANC potential of this work: two- S approximation (short dashes) and one- S approximation (long dashes).

It has also been shown that when eq 1 is valid, $B(T)$ corresponds to a spherical potential $u_{\text{ANC}}(z)$, which has depth ϵ , a minimum at r_m , and a slope ratio S with respect to u_0 . This potential is given explicitly by

$$u_{\text{ANC}}(z)/\epsilon = \left[\frac{1-a}{(z^3/S + 1 - 1/S)^{1/3} - a} \right]^{12} - 2 \left[\frac{1-a}{(z^3/S + 1 - 1/S)^{1/3} - a} \right]^6 \quad (5)$$

In this equation $z = r/r_m$ and $u_{\text{ANC}}(z)$ has a hard-core diameter z_c

$$z_c^3 = (a^3 - 1 + 1/S)S$$

In the more general case, when $u_{\text{ANC}}(z)$ depends on two softnesses, S_A and S_R , $B^*(T^*)$ is still connected explicitly to the repulsive and attractive parts of $B_0^*(T^*)$ via the parameters ϵ , r_m , S_A , and S_R . In this case $u_{\text{ANC}}(z)$ is still given by eq 5 with the appropriate value of S for its attractive and repulsive parts. As illustration, Figure 1 shows the pair potential devised by Aziz and Slaman⁷ for argon. Inverting $B^*(T^*)$, calculated numerically from the Aziz–Slaman potential, we find that $S_R = 1.1030$ and $S_A = 0.9651$. The resulting $u_{\text{ANC}}(z)$ is compared with the original Aziz–Slaman potential in the same figure, showing that $u_{\text{ANC}}(z)$ is indeed very close to the true pair potential.

Nevertheless, we should emphasize that the applicability of the method is highly dependent on the quality of the $B(T)$ data available, a point of great importance when dealing with experimental data on real substances. These data are of very high precision when $B^*(T^*)$ is obtained by quadrature from an analytic expression for $u(z, \Omega)$, as in the example of the Aziz–Slaman potential quoted above. In these cases the virial coefficient is reproduced to high accuracy with very small deviations, which in the case of argon translate to deviations on the order of $0.01 \text{ cm}^3/\text{mol}$. But when dispersion of the experimental data is much higher than this value, as is the case for all volumetric virial coefficients measured, the use of different values S_A and S_R for the softness on both wings of the potential profile becomes meaningless. In this case the ANC theory can be used in a lower order approximation, assuming that the softness is the same for both parts of the potential; i.e., $S = S_R = S_A$. We call this the one- S approximation, and it leads to theoretical errors in $B(T)$ of about $0.2 \text{ cm}^3/\text{mol}$ in the case of argon. Since this last value is still smaller than even the best $B_{\text{exp}}(T)$ data, such as those of Gilgen et al. for argon²² with an

estimated error of $0.5 \text{ cm}^3/\text{mol}$, the one- S approximation should be good enough to account for current $B_{\text{exp}}(T)$ data on real gases. The unique value of S which gives the best characterization of the pair potential is an average of S_A and S_R and is obtained by inverting $B_{\text{exp}}(T)$ using eq 1. Figure 1 shows also the one- S potential $u_{\text{ANC}}(z)$ obtained from the $B^*(T^*)$ data for the Aziz–Slaman potential. Since $S_R > S_A$, the resulting $S = 1.0058$ produces an effective potential of the right overall shape but with a greater slope on the repulsive side and smaller on the attractive part; both effects tend to compensate and the resulting virial coefficient agrees with the original one within $0.2 \text{ cm}^3/\text{mol}$. The difference between the one- S $u_{\text{ANC}}(z)$ and the Aziz–Slaman potential in Figure 1 is typical of the agreement to be expected from the application of the ANC theory to real substances and in particular to the noble gases dealt with in this paper. The two- S ANC theory is at present only applicable to the acoustic virial coefficients of argon,^{23,24} which have experimental errors of about $0.1 \text{ cm}^3/\text{mol}$, small enough to yield meaningful values of S_A and S_R , but since accurate acoustic virial coefficients are not available for the other noble gases, this particular application is of little interest in a systematic discussion of their properties.

We close this section with a brief description of the fitting process used to determine the parameters in $u_{\text{ANC}}(z)$. For a given gas we determine ϵ , r_m , and S by minimizing the root-mean-square (rms) deviation of the values of $B_{\text{theo}}(T)$ predicted by the model, eq 1, from the experimental values. In straight fitting terms, it is important to recognize the need for $B_{\text{exp}}(T)$ results over very wide ranges of temperature. It is particularly important that the $B_{\text{exp}}(T)$ data be distributed reasonably well around the Boyle temperature, T_B , so that both the repulsive and the attractive parts of the potential can be well defined. In general terms, for heavy gases $B(T)$ is much better known for $T < T_B$ than for $T > T_B$, whereas for some of the very light gases the reverse is true. Given the wide range of magnitudes of $B(T)$ over the temperature range of interest, which in many cases includes T_B where $B(T)$ changes sign, we have used the absolute rms deviation Q given by

$$Q^2 = \sum_{i=1}^N [B_{\text{theo}}(T_i; S, \epsilon, r_m) - B_{\text{exp}}(T_i)]^2 / N \quad (6)$$

from the reported experimental values $B_{\text{exp}}(T_i)$ at the temperatures T_i measured. With this choice one avoids the very large relative deviations arising from those points very close to T_B .

Two points should be raised in connection with the application of the model. The first is practical and concerns the adequacy of the model in eq 1 to reproduce the experimental results of $B(T)$. An indicator of this adequacy is the value of Q in comparison to the scatter and estimated errors in $B_{\text{exp}}(T)$. This point is discussed below and exhibited by deviation plots for each particular type of substance. The second point, which is not totally independent from the first, concerns whether the model can give reliable values for the molecular parameters ϵ , r_m , and S and hence give a good “effective” potential. We have shown previously^{23,24} that when the range, accuracy, and precision of the input $B(T)$ data is very good, the errors intrinsic to the one- S model are on the order of a few percent for ϵ and r_m . These errors change systematically with the softness of the potential whose $B(T)$ is being inverted; the tendency being to produce potentials slightly deeper than the true pair potential.

3. Pure Noble Gases

For the heavier noble gases Ar, Kr, and Xe, which have spherical pair interactions and behave classically, the “effective”

TABLE 1: Results of the Fit to the Second Virial Coefficient of the Noble Gases^a

| substance (no. points) | model | Q (cm ³ /mol) | ΔT (K) | T_B (K) T_{JT} (K) | refs ^b |
|---------------------------|---------------------------------------|----------------------------|----------------|---------------------------|--|
| He (128) | this work | 0.5 | 15.50–1473 | 24.36 | DS: 1, 2, 3, 4, 6, 11, 13, 14 15, 16, 17, 18, 19, 20, 21, 22, 26, 27, 28, 29 |
| | Aziz et al. ⁵ | 4.1 | | 45.6 | |
| | LJ/12-6 ²¹ | 3.3 | | | |
| | Tsonopoulos ¹⁶ | 12.9 | | | |
| Ne (46) | Kestin et al. ¹⁵ | 25.4 | 55.64–973 | 123.97 | DS: 1, 2*, 3, 4, 5, 6 |
| | this work | 0.6 | | 233 | |
| | Kihara ²⁰ ($a = 0.0281$) | 0.6 | | | |
| | Slaman & Aziz ⁸ | 0.6 | | | |
| Ar (70) | LJ/12-6 ²¹ | 5.2 | 84.79–1024 | 407.75 | DS: 2*, 3*, 4*, 5*, 11*, 15*, 23*, 25*, 29*, 30* |
| | Tsonopoulos ¹⁶ | 0.9 | | 769 | |
| | Kestin et al. ¹⁵ | 7.0 | | | |
| | this work | 0.4 | | | |
| Kr (103) | BFW ¹⁷ | 2.1 | 128–873 | 566.87 | DS: 2, 3, 5, 7*, 8* |
| | Aziz & Slaman ⁷ | 0.8 | | 1069 | |
| | Kihara ²⁶ ($a = 0.0973$) | 0.4 | | | |
| | LJ/12-6 ²⁶ | 1.9 | | | |
| Xe (94) | Tsonopoulos ¹⁶ | 1.2 | 160.22–1079 | 784.28 | DS: 1, 2, 4, 6, 7, 8, 9 |
| | Kestin et al. ¹⁵ | 2.7 | | 1479 | |
| | this work | 3.0 | | | |
| | Kihara ²⁶ ($a = 0.1335$) | 3.0 | | | |
| Rn | Barker ¹⁷ | 3.0 | | 1020.02 | 25 |
| | LJ/12-6 ²⁶ | 7.8 | | 1923 | |
| | Tsonopoulos ¹⁶ | 3.6 | | | |
| | Kestin et al. ¹⁵ | 3.8 | | | |

^a Q is the absolute rms deviation of the models from the experimental results; T_B and T_{JT} are the Boyle and Joule–Thompson temperatures, respectively. ^b DS refers to Dymond & Smith compilation⁹ with numbers to the corresponding references therein. The asterisk marks sets of data from which some straneous points were removed for the $B(T)$ fit.

potentials derived from the ANC theory should be equal to the true pair interactions except for the approximations involved in assuming a unique and constant softness S . Hence, since there are several accurate pair potentials for these gases available in the literature, comparison of these pair potentials with our results for Ar, Kr, and Xe provides an important test of the approximation involved in the ANC theory.

A second important feature of the ANC theory, besides giving reliable pair potentials, is that it expresses explicitly $B(T)$ in terms of the same set of parameters used in the potential. This is a great advantage over the simpler LJ or Kihara potentials for which a quadrature to obtain $B(T)$ is still required.

Radon gas, which also behaves classically, was not included initially in this analysis due to the unavailability of virial coefficient data. Of course, application of the ANC theory to the lighter noble gas molecules He and Ne is not expected to give accurate pair interactions because their exact treatment should be quantum mechanical; nevertheless, these gases have also been considered here in order to test the extent of applicability of the theory.

Most of the experimental data on $B_{\text{exp}}(T)$ were obtained from the exhaustive compilation of Dymond and Smith.⁹ Relevant additional sources of $B_{\text{exp}}(T)$ data are those of Gilgen et al. for argon²² and of Hohm and Truemper for xenon.²⁵ For each gas, Table 1 shows the number of experimental points selected, their temperature range, and the corresponding references. Most of the data correspond to class I of Dymond and Smith, which have an estimated error of at least 1 cm³/mol; the argon data of Gilgen et al. have a smaller error, of 0.5 cm³/mol, and the xenon

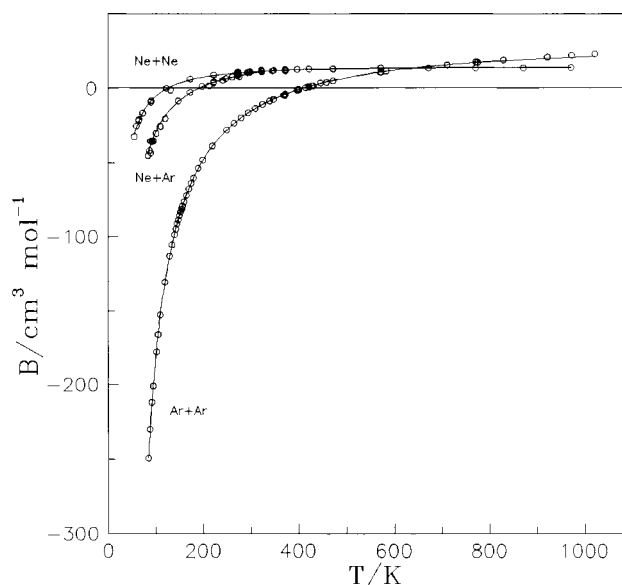


Figure 2. Second virial coefficients $B(T)$ from top to bottom for Ne + Ne, Ne + Ar, and Ar + Ar: solid lines, $B_{\text{theo}}(T)$ from ANC theory; circles, experimental data from references in Table 1.^{9,33}

data of Hohm and Truemper have an error between 0.3 and 1.0 cm³/mol. As an illustration, Figures 2–4 show the comparison of $B_{\text{theo}}(T)$ with the set of $B_{\text{exp}}(T)$ for Ar, Kr, and Xe; in all three cases the agreement is excellent. The figures include results for mixtures of these gases, which will be discussed in the next section. For the pure gases the ranges of temperatures covered

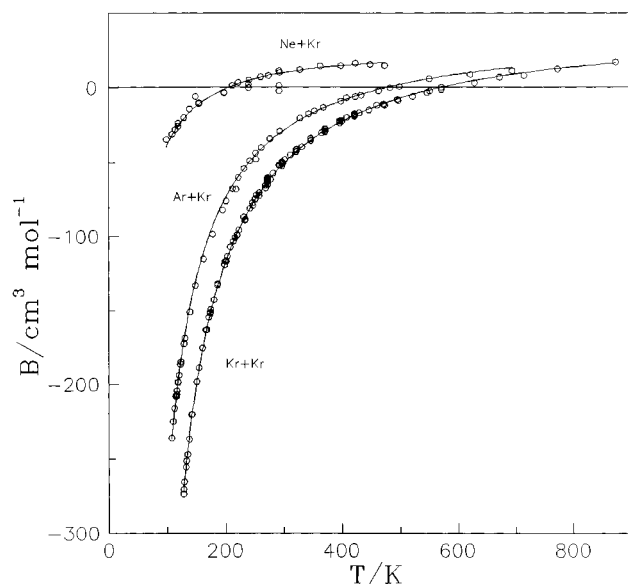


Figure 3. Second virial coefficients $B(T)$ from top to bottom for Ne + Kr, Ar + Kr, and Kr + Kr. Symbols as in Figure 2.

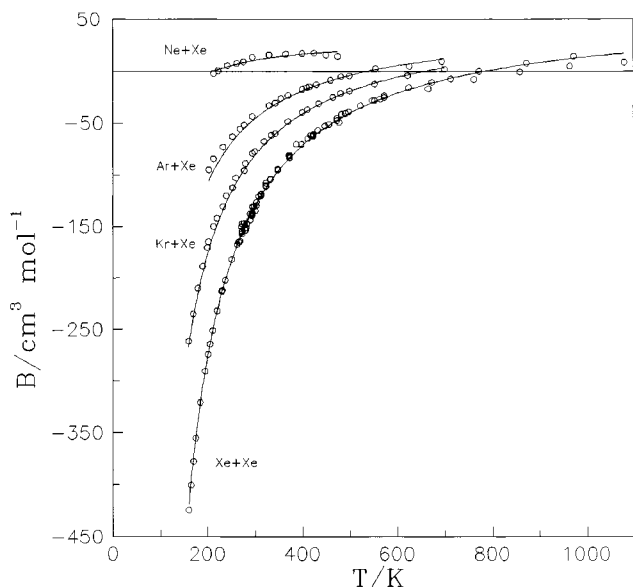


Figure 4. Second virial coefficients $B(T)$ from top to bottom for Ne + Xe, Ar + Xe, Kr + Xe, and Xe + Xe. Symbols as in Figure 2.

by $B_{\text{exp}}(T)$ are wide and encompass the Boyle temperature. The application of the model 1 for $B_{\text{theo}}(T)$ individually to each gas gives Q between 0.4 and 3 cm³/mol, so it gives an excellent fit of the whole set of $B_{\text{exp}}(T)$. We now consider the individual results for all six noble gases.

3.1. Argon. Values of ϵ , r_m , and S for argon were obtained from reported $B_{\text{exp}}(T)$ data by minimizing Q . Table 1 shows also Q , T_B , and the Joule–Thompson temperature, T_{JT} , predicted by our model. In order to assess the goodness of the fit, the same table includes the values of Q resulting from other approaches. First, two models give an expression for $B(T)$ but do not provide information about the potential; these are the corresponding states model of Kestin and co-workers¹⁵ and the empirical correlation of Tsonopoulos based on the well-known Pitzer acentric factor.¹⁶ Second, we show Q for several models that provide an explicit pair potential but no expression for $B(T)$: the accurate pair potentials of Aziz and Slaman⁷ and of Barker, Fisher and Watts (BFW)¹⁷ and the simple LJ/12-6 and Kihara potentials.²⁶

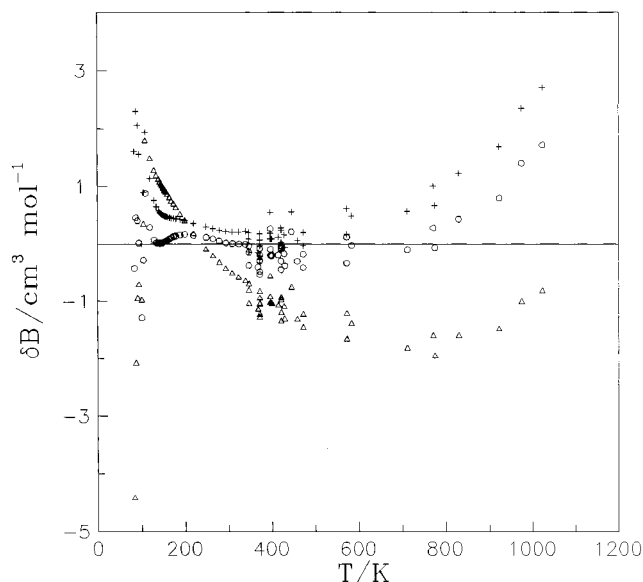


Figure 5. Plot of the deviations $\delta B = B_{\text{exp}}(T) - B_{\text{theo}}(T)$ for argon calculated for the ANC theory in this work (○), the Aziz–Slaman potential (+),⁷ and the correlation of Tsonopoulos (Δ).¹⁶

Of all the models considered for Ar, the ANC model gives clearly the best fit to $B_{\text{exp}}(T)$; the value $Q = 0.4$ cm³/mol is well within the estimated experimental errors, being equaled only by the Kihara potential, and the quality of the available experimental data leaves little room for further improvement. Indeed, introducing the higher order two- S approximation in the ANC theory, implying $S_A \neq S_R$ for the attractive and repulsive sides of the potential^{18,19} does not improve the goodness of the fit. As an illustration, Figure 5 shows a plot of the deviations $\delta B = B_{\text{exp}}(T) - B_{\text{theo}}(T)$ for argon in the temperature range from 84.74 to 1024 K. The figure shows also the deviations of $B_{\text{theo}}(T)$ calculated from the Aziz–Slaman potential⁷ and from the correlation of Tsonopoulos.¹⁶ Our model has the smallest δB , which are always within the estimated experimental errors; these are of ± 2 cm³/mol at the lowest temperatures, ± 0.5 cm³/mol for $110 \text{ K} < T < 340 \text{ K}$,²² and about ± 1 cm³/mol for $T > 340 \text{ K}$. The pattern of δB against T at high temperatures is similar for the three models, suggesting that the experimental points in this range, all from the same laboratory,²⁷ could have a systematic error. The fact that the Aziz–Slaman and BFW potentials have a slightly larger mean deviation than our model is not meaningful, since these potentials are based on sets of properties wider than just second virial coefficients; by doing this, systematic errors in the measured virial coefficients, particularly those at low temperatures, can be eliminated at the cost of degrading the fit to the pure $B(T)$ data.

From eq 1 the Boyle temperature is obtained directly from the reference virial coefficient by

$$B_0^*(T_B^*) = (S - 1)/S \quad (7)$$

so that the reduced Boyle temperature is a function of S only. From eq 7 and $B_0^*(T^*)$ as given in the appendix we obtain the Boyle temperature as a function of softness:

$$T_B^* = 0.189754 + 2.09123S - 1.404325S^2 + 3.87119S^3 - 3.225S^4 + 1.27345S^5 \quad (8)$$

For the reference $S = 1$ system $T_{B0}^* = 2.7976$. The Boyle temperatures reported for the noble gases in Table 1 compare

TABLE 2: Pair Potential Parameters for the Noble Gases^a

| substance | model | ϵ/k (K) | r_m (Å) | S |
|-----------|---------------------------------------|------------------|-----------|--------|
| He | this work | 7.264 | 2.98187 | 1.1152 |
| | Aziz et al. ⁵ | 10.80 | 2.9673 | 1.0120 |
| | LJ/12-6 ²¹ | 10.30 | 2.910 | 1.1315 |
| Ne | this work | 40.447 | 3.05437 | 1.0583 |
| | Kihara ²⁰ ($a = 0.0281$) | 38.542 | 3.071 | 1.0887 |
| | LJ/12-6 ²¹ | 35.800 | 3.090 | 1.1315 |
| | Slaman & Aziz ⁸ | 42.250 | 3.091 | 1.0184 |
| | Ahlrichs et al. ³⁰ | 41.200 | 3.080 | |
| Ar | Maitland ³¹ | 39.600 | 3.070 | |
| | this work | 145.906 | 3.68504 | 0.9993 |
| | BFW ¹⁷ | 142.095 | 3.7612 | 1.0075 |
| | Aziz & Slaman ⁷ | 143.224 | 3.7565 | 1.0058 |
| | Kihara ²⁶ ($a = 0.0973$) | 146.520 | 3.6794 | 0.9858 |
| Kr | LJ/12-6 ²⁶ | 118.13 | 3.9270 | 1.1315 |
| | this work | 202.846 | 3.98496 | 0.9993 |
| | Barker ¹⁷ | 201.900 | 4.0067 | 0.9810 |
| | Aziz & Slaman ⁷ | 201.200 | 4.0080 | 0.9947 |
| | Kihara ²⁶ ($a = 0.1137$) | 213.730 | 3.9112 | 0.9612 |
| Xe | LJ/12-6 ²⁶ | 162.740 | 4.3170 | 1.1315 |
| | this work | 280.643 | 4.33332 | 0.9993 |
| | Kihara ²⁶ ($a = 0.1335$) | 298.15 | 4.2851 | 0.9315 |
| | Barker ¹⁷ | 281.00 | 4.3623 | 0.9767 |
| Rn | LJ/12-6 ²⁶ | 222.32 | 4.6021 | 1.1315 |
| | this work | 365.0 | 5.072 | 0.9993 |

^a The number of digits in the parameters of “this work” are those necessary to reproduce the values of Q quoted. The parameters for Rn are a corresponding-states estimate as explained in the text.

very well with those reported in the literature. For instance, for argon we obtain $T_B = 408$ K, identical to $T_B = 408$ K as reported by Tegeler et al.²⁸ and just smaller than $T_B = 413$ K as determined by Stewart and Jacobsen.²⁹

The Joule–Thompson inversion temperature T_{JT} is obtained as function of S from

$$T_{JT}^* \left. \frac{dB_0(T^*)}{dT^*} \right|_{T_{JT}} - B_0(T_{JT}^*) = (1 - S)/S$$

and for argon is $T_{JT} = 769$ K, whereas Tegeler et al. have determined $T_{JT} = 753$ K²⁸ and Stewart and Jacobsen report $T_{JT} = 759$ K.²⁹

In the ANC model the reduced Joule temperature T_J^* defined by

$$\left. \frac{dB_0(T^*)}{dT^*} \right|_{T_J} = 0$$

is independent of S and hence is the same for all substances: $T^* = 22.68$. Since T_J is usually too high it has been seldom measured. For argon we find $T_J = 3310$ K, whereas Tegeler et al.²⁸ and Stewart and Jacobsen²⁹ report $T_J = 3060$ K and 2520 K, respectively.

We now turn to discuss the ANC potential (eq 5) obtained. For argon, excellent pair potentials are available from independent sources and the softness S was calculated for each one. The ANC potential whose parameters appear in Table 2 agrees well with the Aziz–Slaman and BFW pair potentials.^{7,17} The desired ANC potential function is obtained directly by substituting the parameters ϵ , r_m , and S of Table 2 in eq 5. The ANC argon potential is compared explicitly in Figure 6 with the Aziz–Slaman, BFW, and LJ potentials; we notice that besides small discrepancies in ϵ and r_m , the shape of the ANC potential ($S = 0.9993$, reported in Table 2) is within 1% of those of Aziz–Slaman and BFW. Our values of ϵ and r_m differ by about 2% from those of Aziz–Slaman and BFW; these small errors are

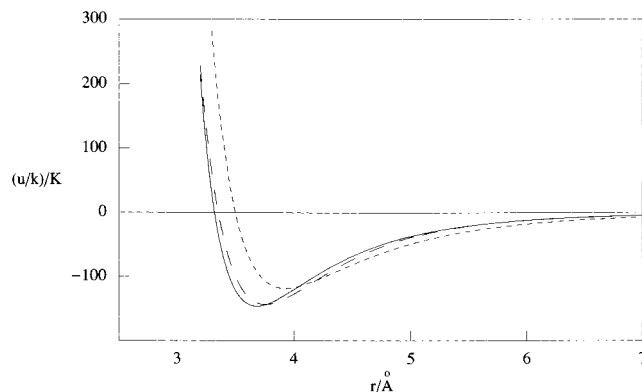


Figure 6. Comparison of the ANC potential for Ar (solid line) with the pair potentials of Aziz–Slaman (long-dashed line)⁷ and LJ/12-6 (short-dashed line).²⁶ The BFW potential¹⁷ is undistinguishable from that of Aziz–Slaman on this scale.

characteristic of the constant- S approximation as has been found by the inversion of spherical model potentials.²³ Further, our results lie in between those of Aziz–Slaman and of Smith and co-workers:^{11,12} $\epsilon(\text{Aziz}) < \epsilon(\text{this work}) < \epsilon/k = 150 \pm 5$ K (Smith and co-workers). Smith et al. do not report r_m but values of d , where $u(d) = 0$; they are $d = 3.35$ Å (Aziz) $< d = 3.322$ Å (this work) $< d = 3.320$ Å (Smith and co-workers). The fact that the approaches relying exclusively on $B(T)$ data produce slightly deeper wells has been attributed to a possible systematic error in $B_{\text{exp}}(T)$ data at the lowest temperatures.^{12,14} Nevertheless, we must notice that our set of $B_{\text{exp}}(T)$ data for argon include the very recent and accurate results of Gilgen et al.,²² thereby improving the input data for the inversion over those used by Smith and co-workers.

It is also worth noticing that the spherical Kihara potential, which best fits the $B_{\text{exp}}(T)$ data for argon,²⁶ whose parameters are also reported in Table 2, is also a good potential function for argon and is very close to the ANC potential. This is not surprising since for argon $S \cong 1$, and hence the ANC effective potential is very close to the reference u_0 , which is itself a spherical Kihara. On the other hand, the inadequacy of the constant-shape LJ/12-6 potential is apparent from both Figure 6 and Table 2. Actually, except for helium, the LJ/12-6 potential, which has a constant shape with $S = 1.1315$, always gives ϵ much too small and r_m too large.

3.2. Krypton. For krypton, we compare the ANC model with the Aziz–Slaman and Barker pair potentials.^{7,17} Initially, determining the potential parameters from the $B_{\text{exp}}(T)$ krypton data gave a very good $B(T)$ fit with $Q = 1.1$ cm³/mol only and $S = 0.9613$. This softness is just 3% smaller than that of argon ($S = 0.9993$), showing not unexpectedly that both substances have nearly conformal potentials. In order to test the extent of this conformality we assumed for krypton the same value of S as for argon and determined again the rest of the parameters. The results of the fit of $B(T)$ and the effective potential parameters are given in Figure 3 and in Tables 1 and 2, showing that the virial coefficient of Kr with the CS parameters is still very close to the experimental data, with Q increasing only slightly to 1.3 cm³/mol. Thus, not surprisingly, the assumption that the argon and krypton pair potentials are conformal is fully substantiated to this approximation. Furthermore, as can be seen by comparing the values of Q in Table 1, the ANC model for krypton agrees better with $B_{\text{exp}}(T)$ than either the Aziz–Slaman, Barker, or LJ/12-6 potentials and is also better than the Tsouopoulos correlation and Kestin’s theory. Again, due to the similarity of the Kihara potential to eq 5 with $S = 0.9993$, it is as much in agreement with experiment as the ANC model.

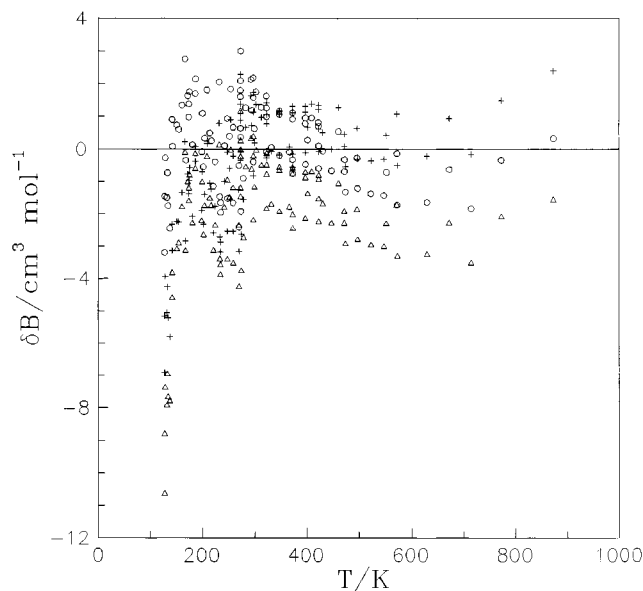


Figure 7. Plot of the deviations δB for krypton. Symbols as in Figure 5.

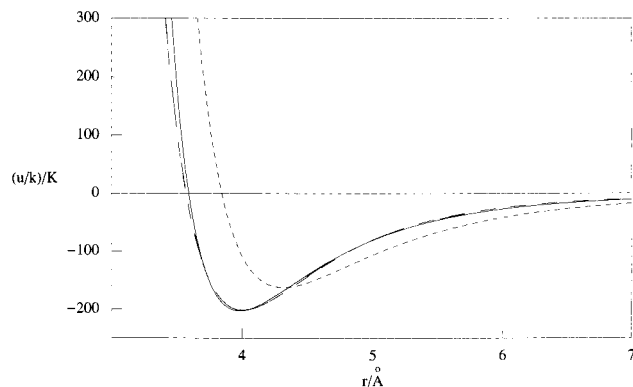


Figure 8. Comparison of the ANC potential for Kr (solid line) with the pair potentials of Aziz–Slaman (long-dashed line)⁷ and LJ/12-6 (short-dashed line).²⁶ The Barker potential for krypton¹⁷ is undistinguishable from that of Aziz–Slaman on this scale.

A comparison between $B_{\text{theo}}(T)$ and $B_{\text{exp}}(T)$ for krypton is shown in Figure 3 and the plot of the deviations δB in Figure 7. The deviations are evenly distributed throughout, including the region around T_B , which implies that our value for krypton's $T_B = 567$ K is highly reliable.

In Figure 8 we compare the resulting potential $u_{\text{ANC}}(z)$ with the pair potentials of Aziz–Slaman⁷ and of Barker.¹⁷ Here again, the ANC potential is excellent; ϵ , r_m , and S differ by less than 1% from the Aziz–Slaman potential, which in turn is almost identical to Barker's, whose parameters are also quoted in Table 2. The Kihara potential obtained from the $B_{\text{exp}}(T)$ data for krypton²⁶ turns out to be slightly too hard: S is smaller by 4% and deviations in ϵ and r_m are 5 times larger than for the ANC potential. The LJ/12-6 krypton potential is in poor agreement with the more accurate potential functions, as Figure 8 illustrates.

3.3. Xenon. The case of xenon is very similar to that of krypton. Initially, application of the ANC model to the experimental $B(T)$ data for Xe gave very good agreement, with a softness S only 4% less than S for argon, confirming the conformality between Xe, Ar, and Kr. The final mean deviation of the ANC model from $B_{\text{exp}}(T)$, given in Table 1, is equal to those of the Barker and Kihara potentials and smaller than those of Kestin et al.,¹⁵ Tsonopoulos,¹⁶ and the LJ/12-6 potential.²⁶ Figure 4 shows the agreement between $B(T)$ of the ANC model

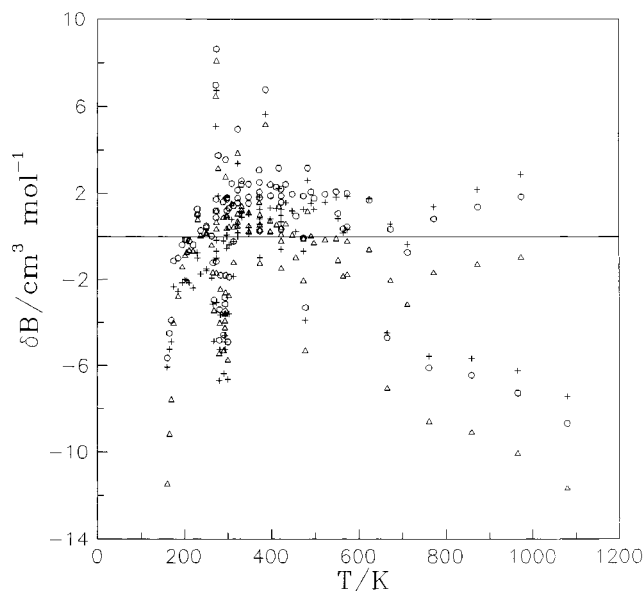


Figure 9. Plot of the deviations δB for Xe calculated for the ANC theory in this work (\circ), Barker's potential ($+$),¹⁷ and the correlation of Tsonopoulos (Δ).¹⁶

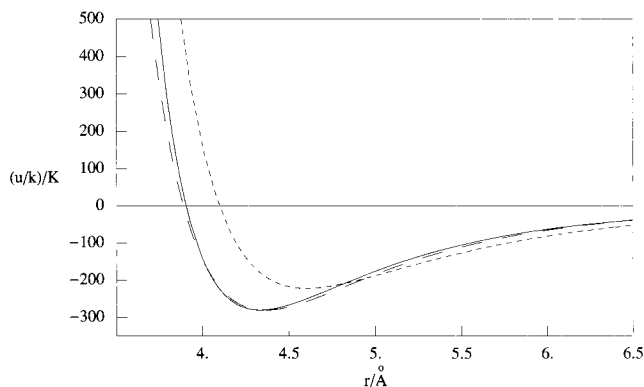


Figure 10. Comparison of the ANC potential for Xe (solid line) with the pair potentials of Barker (long-dashed line)¹⁷ and LJ/12-6 (short-dashed line).

for Xe and the experimental data, and Figure 9 shows the associated deviation plot together with the deviations of Barker's potential¹⁷ and Tsonopoulos' correlation.¹⁶

The ANC potential function for xenon, whose parameters are also shown in Table 2, has almost identical depth ϵ than the Barker potential for this gas¹⁷ and r_m is only 0.7% smaller. The shape parameter S of Barker potential is 2% smaller than the corresponding states $S = 0.9993$. Figure 10 compares the Barker, ANC, and LJ potentials for xenon; the ANC potential is very close to that of Barker, except at very short distances.

3.4. Helium and Neon. A few words on the inclusion of helium and neon in this analysis may not be out of place at this point. As shown by the values of Q in Table 1, the ANC model reproduces surprisingly accurately $B_{\text{exp}}(T)$ of He with $Q = 0.5$ cm³/mol and of Ne with $Q = 0.6$ cm³/mol. Surprisingly, because helium is a very light molecule with a de Broglie wavelength $\lambda_B = h/\sqrt{2\pi mkT}$ that is large except at high temperatures, the correct treatment of $B(T)$ has to proceed quantum mechanically. The use of a classical approach such as the ANC theory is in principle inadequate for He. For neon, being heavier than He, the classical treatment can be expected to give a good zeroth-order approximation. Taking $T = \epsilon/k$ as a characteristic temperature for each gas, λ_B/r_m falls successively from 3 for He, through 0.2 for Ne, to 0.06 for Ar. Therefore, the effective

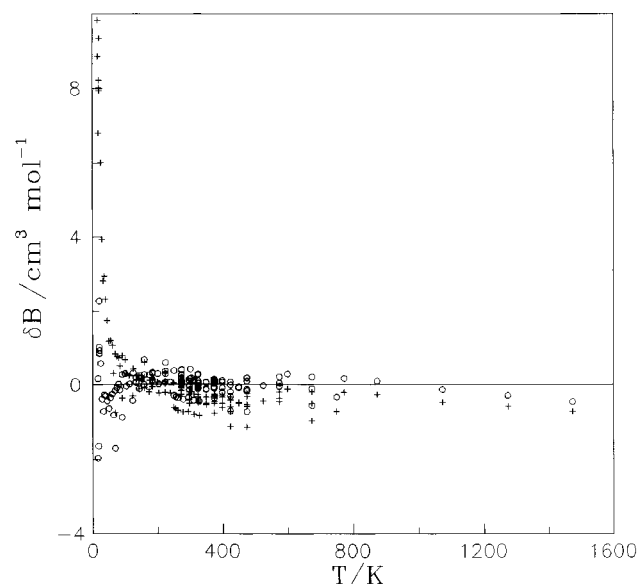


Figure 11. Plot of the deviations δB for He calculated for the ANC theory of this work (O) and Aziz et al. (+).⁵

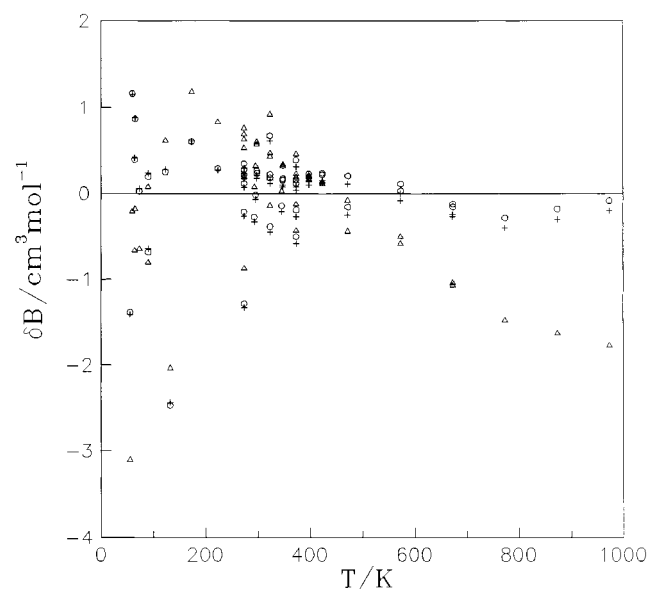


Figure 12. Plot of the deviations δB for Ne calculated for the ANC theory of this work, (O), Kihara (+),²⁰ and Tsonopoulos' correlation (Δ).¹⁶

ANC potential, irrespective of the goodness of the fit of the virial coefficient, being obtained from a classical approach, should give the pair potential for Ne only approximately and that for He much less well.

The experimental data and the theoretical curves for $B(T)$ are shown in Figure 2 for Ne, and Figures 11 and 12 show the respective deviation plots for He and Ne. Given all the above reservations, it is noteworthy that the ANC value of r_m for He, listed in Table 2, is very close to that of Aziz and coworkers⁵ and that ϵ is of the correct order of magnitude. Since in a quantum treatment the energy of the ground state of the He–He dimer is above of the energy at the minimum of $u(r)$, it is not surprising that an effective potential derived from the inversion of $B(T)$ by a classical theory should lead to a more shallow well. The softness of the Aziz potential is $S = 1.012$ and hence it is very close in shape to the effective potential of this work ($S = 0.9993$). For Ne, the depth ϵ differs only in 2% from the pair potentials of Ahlrichs et al.³⁰ and of Maitland³¹

and in 5% from the more recent Slaman–Aziz potential⁶ so that these deviations are within the estimated error of the constant- S ANC theory. The ANC diameter r_m is 3% smaller than that of the other potentials. For similar reasons as for Ar and Kr, a Kihara potential works very well^{21,20} and again the LJ/12-6 potential shows the largest mean deviation Q .¹⁸

The potential parameters of the heavier noble gases behave very regularly with atomic number. Parts a, b, and c of Figure 13 show ϵ , r_m , and S respectively in terms of the atomic number as obtained from the ANC theory assuming corresponding states (CS, i.e. $S = 0.9993$) for Ar, Kr, and Xe and show also the values obtained when S is allowed to vary from one molecule to the next. The same figures show the parameters of the more accurate potentials from the literature listed in Table 2. Of course, ϵ and r_m grow steadily with atomic number. These figures show that He and Ne do not follow the same patterns as the heavier gases, whose parameters lie in a very smooth curve. For ϵ and r_m there is good agreement between the values obtained from the CS assumption, the individual fittings, and the independent potentials from the literature. Nevertheless, Figure 13c shows that, except for Ne, which seems to be softer, the CS value of $S = 0.9993$ is close to those of the other potentials, whereas there is small disagreement in the S obtained independently for Ne, Kr, and Xe.

3.5. Potential Parameters and Critical Properties. Since Ar, Kr, and Xe have been corroborated to be conformal, and since they also follow corresponding states to very good accuracy in their liquid–vapor properties, it is not surprising at all that for these three substances the ratio of kT_c/ϵ is almost constant; in fact, using the values of T_c from a recent compilation³² and ϵ from Table 2 we find that $kT_c/\epsilon = 1.033 \pm 0.001$. Of course, since Ne, and He are not conformal with the heavier noble gases, we find that for Ne, $kT_c/\epsilon = 1.098$, which is close to the CS value and that for He, $kT_c/\epsilon = 0.714$.

Except for He, the critical volumes of these substances also scale very regularly with the ANC diameter r_m . To illustrate this, Figure 14a shows a graph of V_c against r_m^3 , which is remarkably close to a straight line $V_c = 1.4502r_m^3$. The fact that Ne also follows this rule implies that V_c seems to depend on the scale factor r_m only but not on the shape parameter S .

3.6. Radon. The regularities in the heavier noble gas parameters with atomic number and critical properties allow us to estimate the potential parameters of radon. Assuming that Rn is conformal with Ar, Kr, and Xe its shape factor is the same, i.e., $S = 0.9993$; the values of ϵ and r_m are shown in Table 2. ϵ was obtained from the corresponding states value of $kT_c/\epsilon = 1.033$, giving $\epsilon/k = 365.0$ K; Figure 13a shows that this value of ϵ for Rn lies on a smooth continuation of the Ar–Kr–Xe tendency with atomic number. According to this tendency, the value of ϵ should be larger by about 7% a discrepancy perhaps due to error in the reported value of T_c for Rn.³² The diameter was calculated as $r_m = 5.072$ Å by extrapolating the smooth Ar–Kr–Xe line with atomic number in Figure 13b and it allows us to estimate V_c from the linear fit to the Ne, Ar, Kr, and Xe data of Figure 14a, obtaining $V_c = 189.2$ cm³/mol. Figure 14b shows that this estimate of V_c also lies on a smooth line with the Ar, Kr, and Xe data against atomic number.

Figure 15 compares $B(T)$ for Rn obtained from the ANC potential via eq 1 with that obtained using the Tsonopoulos correlation based on the critical properties and the acentric factor of radon. This figure shows that the ANC prediction is very similar to the Tsonopoulos correlation at high temperatures. At low temperatures, however, Tsonopoulos results take on in-

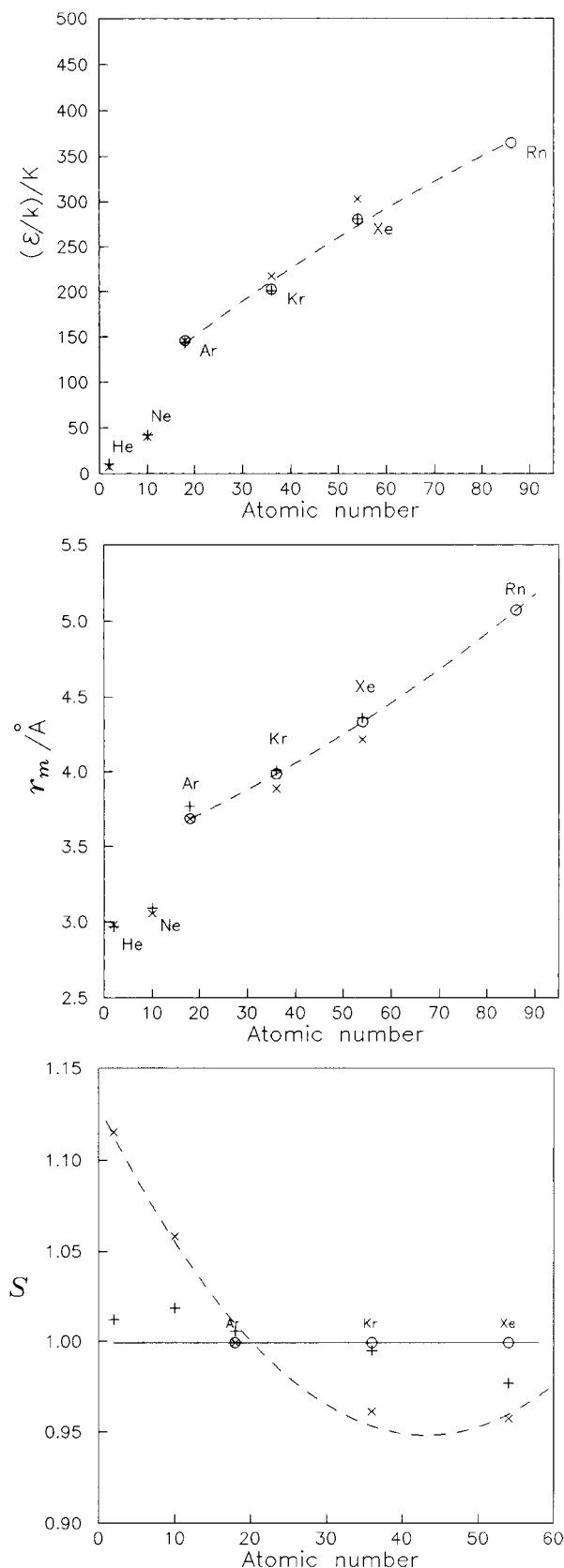


Figure 13. ANC potential parameters of the pure noble gases as function of atomic number: (a) energy depth ϵ , (b) diameter r_m , (c) softness S . Corresponding state values of this work (O), individual values for each gas (x), parameters from the pair potentials of other authors (+): He, Aziz et al.,⁵ Ne, Slaman–Aziz;⁸ Ar and Kr, Aziz–Slaman;⁷ Xe, Barker.¹⁷ The dashed lines in a and b are quadratic fits through the ANC points for Ar, Kr, and Xe. The dashed line in c is drawn to help the eye.

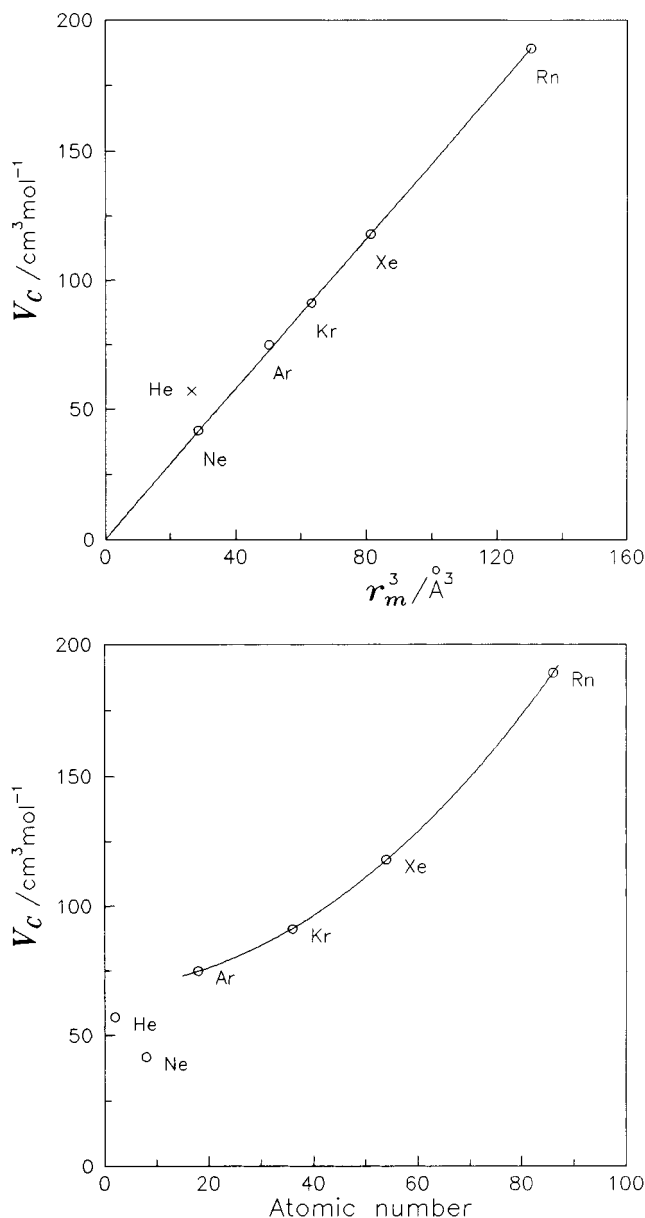


Figure 14. (a) Critical volumes V_c against r_m^3 from this work for the noble gases. The solid line is a straight-line fit through the points from Ne to Xe. The values of V_c are taken from the work of Ambrose.³² (b) Critical volumes V_c in terms of the atomic number. The solid line is the quadratic fit of the points from Ar to Rn.

creasingly less negative values than ours until at very low temperatures they display an unphysical minimum.

4. Mixtures

Logic compels us to use the ANC theory for the cross interactions $u_{12}(r)$ and virial coefficients $B_{12}(T)$ in binary mixtures of the noble gases. Then to treat the mixtures and to obtain $B_{12}(T)$ from eq 1 we need only find suitable combination rules for the cross diameter r_{12} , well depth ϵ_{12} , and softness S_{12} . The suitability of these combination rules must be tested against experimental data $B_{12}^{\text{exp}}(T)$ for a selected case. In our case the Ne + Ar mixture is particularly useful because the two pure components have potentials differing in the softness S , and hence we can test the combination rule for this parameter. For the diameters we employ the common Lorentz additive rule

$$r_{12} = \frac{r_{m1} + r_{m2}}{2} \quad (9)$$

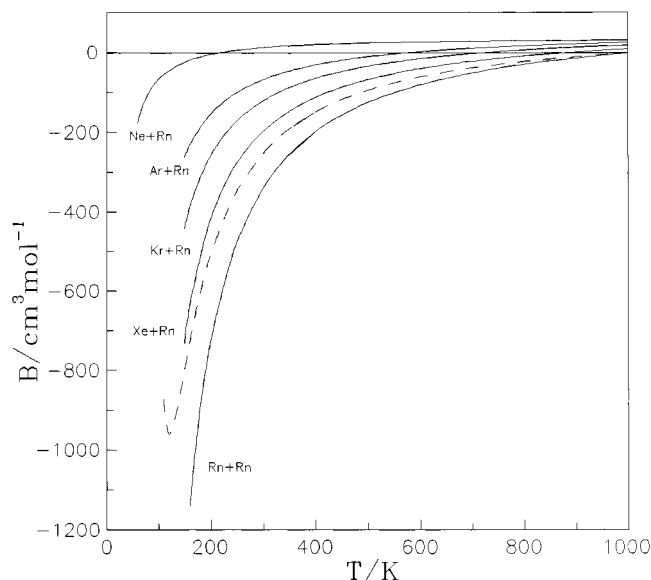


Figure 15. Predicted virial coefficients of Ne + Rn, Ar + Rn, Kr + Rn, Xe + Rn, and Rn + Rn systems: solid lines, $B_{\text{theo}}(T)$ from ANC theory; dashed line, Tsionopoulos' correlation for Rn + Rn.¹⁶

In order to find combination rules for ϵ_{12} and S_{12} we first consider the Boyle temperature T_{B12} for the cross interaction. The experimental data on $B_{12}(T)$ for the Ne + Ar mixture^{9,33} allow us to locate by interpolation $T_{B12} \approx (190 \pm 3)$ K. As can be seen in Figure 2, T_{B12} is much closer to T_B of the lighter component, in this case Ne. The values of T_B for pure Ne and Ar are given in Table 1; trying the usual geometric mean rule $T_{B12} = \sqrt{T_{B1}T_{B2}}$, we obtain $T_{B12} = 224.83$ K, which is too large. Now, instead of proposing an ad hoc deviation from the geometric mean, we propose a harmonic-mean rule which shifts the mean toward the (smaller) value of the lighter pure component, i.e.,

$$\frac{2}{T_{B12}} = \frac{1}{T_{B1}} + \frac{1}{T_{B2}} \quad (10)$$

A similar combination rule for the cross energies ϵ_{12} is known, as the Fender–Halsey rule,^{6,34} as recently discussed by Elias et al.³⁵ With this combination rule we find that $T_{B12} = 190.1$ K, in excellent agreement with the experimental value.

Now, given the agreement obtained by the harmonic mean rule for T_B and following recent suggestions,³⁵ we also propose

$$\frac{2}{\epsilon_{12}} = \frac{1}{\epsilon_1} + \frac{1}{\epsilon_2} \quad (11)$$

Of course, in the ANC theory we also need a combination rule for the softness S_{12} . Since eq 7 shows that the reduced Boyle temperature T_B^* is only a function of S , once T_{B12}^* is found from T_{B12} and ϵ_{12} given by eqs 10 and 11, we determine S_{12} by inverting eq 8.

Table 3 shows the Ne + Ar potential parameters obtained from the combination rules above and the pure component ANC parameters in Tables 1 and 2; the values of T_B in Table 1 are given with enough significant figures to use them confidently in the combination rule eq 10. Table 3 also shows the experimental temperature range, the number of experimental points, and the rms deviation of the prediction and the predicted Boyle temperature. The experimental results $B_{12}^{\text{exp}}(T)$ were taken from Dymond and Smith's compilation,⁹ except for the addition of recent data by Shamma and Rigby³³ on the Ne + Ar mixture.

TABLE 3: Pair Potential Parameters for the Cross Interactions in Binary Mixtures of Noble Gases

| mixture | model | ϵ/k (K) | r_m (Å) | d (Å) | S |
|---------|-----------------------------|------------------|-----------|---------|--------|
| Ne + Ar | this theory | 63.336 | 3.36970 | 3.0204 | 1.0454 |
| | Kestin et al. ¹⁵ | 64.17 | | 3.119 | |
| | Aziz ³⁴ | 62.00 | | 3.110 | |
| Ne + Kr | this theory | 67.446 | 3.51966 | 3.1536 | 1.0484 |
| | Kestin et al. ¹⁵ | 67.32 | | 3.264 | |
| Ne + Xe | this theory | 70.704 | 3.69384 | 3.3086 | 1.0509 |
| | Kestin et al. ¹⁵ | 67.25 | | 3.488 | |
| Ar + Kr | this theory | 169.728 | 3.83500 | 3.4570 | 0.9993 |
| | Kestin et al. ¹⁵ | 165.8 | | 3.464 | |
| Ar + Xe | this theory | 191.994 | 4.00918 | 3.6140 | 0.9993 |
| | Kestin et al. ¹⁵ | 182.6 | | 3.660 | |
| Kr + Xe | this theory | 235.485 | 4.15914 | 3.7491 | 0.9993 |
| | Kestin et al. ¹⁵ | 225.4 | | 3.753 | |

TABLE 4: Predicted Results for the Cross Virial Coefficient in Noble Gas Mixtures

| mixture (no. points) | model | Q (cm ³ /mol) | T_B (K) T_{JT} (K) | ΔT (K) |
|-------------------------|-----------------------------|----------------------------|---------------------------|----------------|
| Ne + Ar (22) | this theory | 1.7 | 190.1 | 84–323 |
| | Kestin et al. ¹⁵ | 1.6 | 358 | |
| Ne + Kr (29) | this theory | 3.4 | 203.5 | 100–475 |
| | Kestin et al. ¹⁵ | 4.1 | 383 | |
| Ne + Xe (12) | this theory | 2.2 | 214.1 | 213–475 |
| | Kestin et al. ¹⁵ | 4.4 | 403 | |
| Ar + Kr (44) | this theory | 2.3 | 474.3 | 108–695 |
| | Kestin et al. ¹⁵ | 4.5 | 894 | |
| Ar + Xe (21) | this theory | 4.4 | 536.6 | 203–695 |
| | Kestin et al. ¹⁵ | 3.3 | 1012 | |
| Kr + Xe (29) | this theory | 4.3 | 658.1 | 160–700 |
| | Kestin et al. ¹⁵ | 2.3 | 1241 | |

The cross virial coefficient $B_{12}^{\text{theo}}(T)$ predicted by the ANC theory and the parameters in Table 3 has an absolute rms deviation from the experimental data of $Q = 1.7$ cm³/mol only, which is to be compared with experimental errors between 1.2 and 5 cm³/mol. This excellent agreement can also be seen in Figure 2 comparing $B_{12}^{\text{exp}}(T)$ with $B_{12}^{\text{theo}}(T)$. Actually, the simple ANC model in eq 1 reproduces the experimental data for $B_{12}^{\text{exp}}(T)$ as well as the much more complicated fit by Kestin et al.,¹⁵ which is indistinguishable from our prediction in Figure 2.

The same Table 3 shows the potential parameters for the cross Ne + Ar interaction as obtained by Kestin et al.¹⁵ and by Aziz (as quoted in ref 34). The ANC value for ϵ/k is in between the two others and differs from them by 2%. The ANC diameter is slightly smaller than those of Kestin and Aziz; the value of d where $u(d) = 0$ reported by them is 2.5% larger than ours.

The ANC theory, together with the combining rules 9, 10, and 11 selected for the Ne + Ar case, was used to predict the cross virial coefficients of all the binary mixtures of the noble gases not involving He. Comparison of these predictions with the experimental results available are shown also in Figure 3 for Ne + Kr and Ar + Kr and in Figure 4 for Ne + Xe, Ar + Xe, and Kr + Xe. These figures show a systematic tendency when the lighter component, which appears to dominate the B_{12} behavior, is changed. Table 3 shows the corresponding cross parameters ϵ_{12} , r_{12} , and S_{12} , and Table 4 shows for each case the experimental temperature range, the number of experimental points, the rms deviation Q , and the predicted Boyle temperature. From Figures 2 and 3 and from Table 4 it follows that the ANC theory gives an excellent prediction of $B_{12}(T)$ with rms deviations on the order of the estimated errors in these measurements which are between 3 and 5 cm³/mol. As in the case of the Ne + Ar mixture already discussed, for these five mixtures the ANC prediction is almost indistinguishable from the fit by Kestin et

al.¹⁵ and both sets of cross potential parameters, reported also in Table 3, are also in good agreement.

The cross coefficients $B_{12}(T)$ in mixtures of Rn with the rest of the noble gases but helium can be readily predicted from eq 1, the parameters in Table 2, and the combining rules above. As shown in Figure 15, the temperature behavior of $B_{12}(T)$ follows a regular change with the second component.

As a last point we must mention that the mixtures of He with the other noble gases are not well accounted for by the ANC theory. This failure may be due to a combination of the following factors: First, these mixtures require a quantum mechanical treatment. Second, the unphysical character of the He–He effective potential obtained with a classical theory, which even if accounting for $B_{\text{exp}}(T)$ is significantly different from more accurate potentials. Third, the mixing rules which prove excellent for the heavier gases are inadequate due also to quantum effects.

5. Conclusions

The first conclusion regards the pair potentials derived from the ANC theory. For the heavier noble gases, Ne, Ar, Kr, and Xe, the ANC theory gives very accurate pair potentials, of the general form eq 5, which differ only slightly from the best and more complicated potentials available from the literature. Hence we can expect that the theory gives reliable effective potentials for more complex molecules whose pair potentials are still not well determined. We should also stress the fact that the ANC potential has only three free parameters, whereas the pair functions of Aziz and co-workers and Barker and co-workers have at least 9 and as many as 16 parameters. Further, use of these more complicated potentials does not allow us to express the second virial coefficient explicitly in terms of the potential parameters. It has been shown also that, allowing for experimental errors in $B(T)$, Ar, Kr, and Xe have conformal potentials characterized by the same value of the softness, $S = 0.9993$. This conformality is stressed by the fact that ϵ and r_m^3 scale regularly with the critical properties T_c and V_c . Further, the three potential parameters ϵ , r_m , and S change smoothly with atomic number, so we can make a confident prediction of the pair potential of Rn. Nevertheless, the potential obtained for He has a significant difference in ϵ and S from potential functions calculated independently using a quantum mechanical approach.

A second conclusion refers to the ability to reproduce the second virial coefficient of the pure noble gases. For all of these, including He, the ANC theory represents very accurately $B(T)$ in terms of the same three parameters determining the potential function. This agreement is always within or close to the estimated experimental errors, so the ANC model competes advantageously with the corresponding states correlation of Kestin et al.¹⁵ or the acentric factor correlation of Tsonopoulos.¹⁶

Lastly, the ANC theory predicts the cross interaction potentials in mixtures of the noble gases, excluding He, with very good agreement between the predicted $B_{12}(T)$ and the experimental results. This was done with the help of combination rules including a harmonic mean rule for the cross energy ϵ_{12} .

6. Acknowledgment

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7. Appendix

The reference virial coefficient $B_0^*(T^*)$ in the basic equation 1 is given in terms of the collision diameters $\sigma_0(T^*)$ and $R_0(T^*)$ by

$$B_0^*(T^*) = b_0^*(T^*)e^{\beta\epsilon} - \Lambda_0^*(T^*) (e^{\beta\epsilon} - 1)$$

where $b^* = (\sigma/r_m)^3$ and $\Lambda^* = (R/r_m)^3$ are well-defined in terms of the collision frequency and can be calculated numerically for a given $u_0(r)$. For the applications considered in this and following papers we need $B_0^*(T^*)$ in $0.05 < T^* < 250$, which is a range much wider than that used previously.¹⁸ The results are represented by the following expressions in T^* which depend on the range. For $0.05 < T^* < 0.4$:

$$b_0^*(T^*) = \sum_{m=0}^5 c_m (T^*)^m$$

$$\Lambda_0^*(T^*) = b_0^* \sum_{m=0}^5 l_m (T^*)^m$$

For $0.4 < T^* < 250$:

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

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

the values of the coefficients c_m and l_m depend on the range and are shown in Table 5.

TABLE 5: Parameters in the Fit of the Reference Effective Volumes^a

| ΔT^* | m | c_m | l_m |
|--------------|-----|----------------------------------|----------------------------------|
| 0.05–0.4 | 0 | 0.971 554 05 | 1.060 434 24 |
| | 1 | 1.210 771 47 | 3.231 027 04 |
| | 2 | 6.596 150 30 | 11.468 358 9 |
| | 3 | 22.516 945 9 | 60.710 796 1 |
| | 4 | 38.584 281 8 | 134.302 193 |
| 0.4–10 | 5 | 25.576 908 4 | 101.561 158 |
| | 0 | $7.663\,230\,5 \times 10^{-1}$ | 2.679 786 56 |
| | 1 | $-7.247\,001\,68 \times 10^{-2}$ | $6.843\,877\,82 \times 10^{-1}$ |
| | 2 | $-5.656\,659\,11 \times 10^{-3}$ | $-7.144\,487\,40 \times 10^{-2}$ |
| | 3 | $6.161\,108\,54 \times 10^{-4}$ | $7.788\,581\,73 \times 10^{-3}$ |
| | 4 | $7.577\,863\,85 \times 10^{-5}$ | $1.644\,211\,69 \times 10^{-2}$ |
| | 5 | | $-8.736\,312\,67 \times 10^{-3}$ |
| | 6 | | $1.682\,855\,86 \times 10^{-3}$ |
| | 7 | | $5.884\,159\,73 \times 10^{-4}$ |
| | 8 | | $-4.264\,387\,53 \times 10^{-4}$ |
| 10–250 | 9 | | $8.633\,160\,56 \times 10^{-5}$ |
| | 10 | | $-4.761\,344\,07 \times 10^{-6}$ |
| | 0 | $7.642\,068\,52 \times 10^{-1}$ | 2.707 365 30 |
| | 1 | $6.871\,202\,71 \times 10^{-2}$ | $6.474\,522\,25 \times 10^{-1}$ |
| | 2 | $8.404\,608\,75 \times 10^{-3}$ | $6.453\,929\,41 \times 10^{-2}$ |
| | 3 | $1.616\,319\,74 \times 10^{-3}$ | $2.571\,863\,52 \times 10^{-2}$ |
| | 4 | $7.415\,659\,95 \times 10^{-5}$ | $1.931\,008\,54 \times 10^{-3}$ |
| | 5 | | $9.050\,994\,39 \times 10^{-5}$ |

^a The first column gives the appropriate reduced temperature range.

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