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# EXTENDED PRINCIPLE OF CORRESPONDING STATES AND INTERMOLECULAR FORCES

*Although the classical principle of corresponding states dates back to 1880, and its statistical-mechanical basis was firmly established in the period 1939-1950, it is only in the past ten years that its remarkable scope and accuracy have begun to be fully appreciated. Improvements in experimental accuracy and in knowledge about intermolecular forces have both contributed to these recent advances. In 1972 Kestin, Ro, and Wakeham gave a remarkably accurate correlation, involving only two adjustable parameters, for nearly all the low-density thermodynamic and transport properties of the noble gases and their multicomponent mixtures. They carefully avoided models of the intermolecular forces on the grounds that the latter were inadequate to do justice to the experimental data. Subsequently, they were also able to correlate some properties of polyatomic gases, but not all. These advances were due almost entirely to improvements in the accuracy and range of experimental data. Since then, important advances have also occurred in our knowledge of intermolecular forces, and these can be used as the basis for extensions and improvements to the two-parameter correlation.*

*This paper briefly reviews the two-parameter correlation, and then summarizes the improvements in the range and accuracy of the correlation that have been achieved for the noble gases. Finally, a short summary in given of one of the most interesting crucial advances in knowledge of intermolecular forces, namely direct numerical inversion of transport coefficients.*

## CONTENTS

## INTRODUCTION

The principle of corresponding states goes back over 100 years, to J.D. van der Waals in 1880, in connection with the equation of state and the critical constants of gases. It played an important role around the turn of the century in the liquefaction of the last of the so-called permanent gases, hydrogen and helium, by Dewar and by Kamerlingh Onnes, respectively, who used it to predict boiling points and other properties. Thereafter it was widely applied to many other substances. In the period of about 1939-1950, the molecular basis of the principle was firmly established through statistical mechanics, and it was extended to include quantum effects and transport properties.

Unfortunately, the quantitative aspects of the principle were often considered a bit dubious — it was considered to furnish a useful correlation scheme, but to have only moderate accuracy. Perhaps this was at first caused by its association with the approximate van der Waals equation of state, and then by its over-enthusiastic application to so many different substances. At any rate, it was essentially abandoned by chemists and physicists as a subject of serious study, although of course it was much used by engineers.

Why do we now bother with a 100-year old theory of only modest accuracy? In the first place, it turns out that the accuracy and the range of properties covered are much better than had been thought. Secondly, there have been important advances in our knowledge of intermolecular forces in the last ten years or so. Together, these two developments have completely revitalized the subject. The purpose here is to give a brief survey of these developments.

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In 1972, Kestin, Ro, and Wakeham [1,2] assembled a large body of consistent, accurate results, especially on the low-density gas viscosity, and decided to try taking the principle of corresponding states very seriously, at least for the noble gases. To the surprise of nearly everyone, they achieved a remarkable accuracy, an improvement of nearly one order of magnitude. Moreover, they were able to correlate nearly all the low-density thermodynamic and transport properties of the noble gases and their multicomponent mixtures. They needed to assign only two parameters to each of the fifteen possible pair interactions between two noble gas atoms. For concreteness, the parameters can be thought of as an energy parameter $\epsilon$ representing the depth of the potential energy well, and a range or distance parameter $\sigma$ representing the interatomic separation for which the potential is zero. However, they carefully avoided using models of the potentials on the excellent grounds that the latter — such as the Lennard-Jones (6,12) model — were inadequate to do justice to the experimental data, and they based their results exclusively on general statistical-mechanical theory and accurate experimental measurements. The numerical values of $\epsilon$ and $\sigma$ were thus found by fitting (primarily) viscosity data. Subsequently [3-5], they were also able to correlate some properties of diatomic and polyatomic gases, but not all.

These advances were due almost entirely to improvements in the accuracy and range of experimental data. But at about the same time there were important advances occurring in our knowledge of intermolecular forces. Certainly for the noble gases it is now safe to refer to the potential itself without undue fear of degrading the accuracy of the correlations, and there is hope that the same will soon be true for some of the simpler polyatomic gases. A number of extensions and improvements to the two-parameter correlation thereby become possible, which are now largely worked out. Although the details are rather voluminous [6,7], it is possible to summarize the essential results succinctly.

This report is organized as follows. A brief review of the basis of the two-parameter correlation is first given, together with indications of where failure is likely to start. Second, the most important new developments on intermolecular forces are summarized, and it is shown how they can be used to extend the range and accuracy of the two-parameter correlation for the noble gases and their mixtures. Finally, a short summary is given of one of the most interesting recent advances in knowledge of intermolecular forces, namely the direct numerical inversion of transport coefficients. Until recently, this was thought to be impossible, both in principle and in practice. The literature connected with all these topics is understandably extensive, and only a few of the key references are given here.

## REVIEW OF TWO-PARAMETER CORRELATION

The molecular theory underlying the principle of corresponding states involves only very general results from statistical mechanics, plus relatively straightforward dimensional analysis. The pair potential V(r) can always be written in a dimensionless form as

$$V(r) = \epsilon\, f(r/\sigma, \alpha_1, \alpha_2, \dots)\,, \qquad (1)$$

where $\epsilon$ and $\sigma$ are the energy and range parameters already mentioned, and $\alpha_1$, $\alpha_2$, ... are additional dimensionless parameters characterizing the shape (rather than the scale) of the potential. The fundamental assumption used by Kestin, Ro, and Wakeham can be divided into two parts:

(1) The function $f(r/\sigma, \alpha_i)$ is the same for all noble gas pairs.

(2) the parameters $\alpha_i$ have the same values for all noble gas pairs.

The first part is required in order to have any corresponding states at all, and the second part allows a correlation involving only the two parameters $\epsilon$ and $\sigma$. Improved knowledge of V(r) enables us to relax this second condition and thus to make extensions of the correlation.

We can illustrate the success of the two-parameter correlation with a few samples [1,3,4]. The top part of fig. 1 shows a universal reduced collision integral for viscosity, $\Omega_{22}$, as a function of reduced temperature, $T^*$, for noble gases. These quantities are defined as

$$\frac{5}{16}(mkT/\pi)^{\frac{1}{2}}\eta^{-1} \equiv \sigma^2\,\Omega_{22} \equiv \sigma^2\,\Omega^{(2,2)*}/f_\eta, \qquad (2)$$

$$T^* \equiv kT/\epsilon\,, \qquad (3)$$

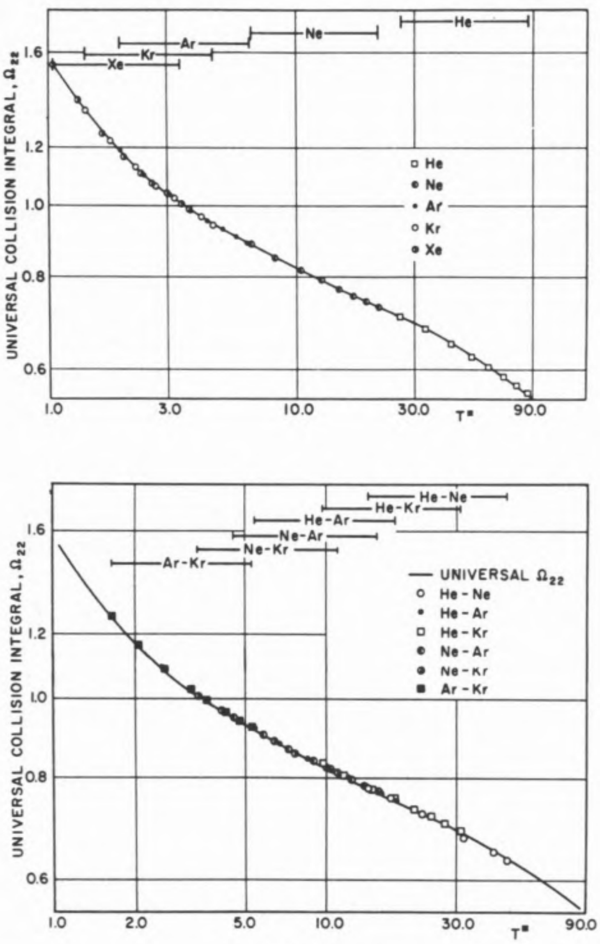

*Fig. 1*

*Two-parameter correlation for the viscosity collision integral as a function of reduced temperature, $T^* = kT/\epsilon$, for noble gases (upper) and noble gas mixtures (lower). The horizontal lines show the temperature ranges covered by the experimental data*

where m is the molecular mass, k is Boltzmann's constant, $\eta$ is the viscosity, and $f_\eta$ is a higher-order kinetic-theory correction [8] that deviates only slightly from unity. The curve shown is arranged to fit the points, which are seen to all lie on a single curve with remarkable precision (about 0.4% deviation, on the average). The bottom part of fig. 1 shows a similar plot for noble gas mixtures. Here the viscosity is not the total mixture viscosity, but only the interaction viscosity, $\eta_{12}$, which is equivalent to the viscosity of a hypothetical pure gas having the given V(r) and a mass $m = 2m_1m_2/(m_1 + m_2)$ [8]. The curve here is the *same* as the one for the single gases, with no tinkering. Fig. 2 shows a similar result for some polyatomic gases and gas mixtures. Again the curve is the same as in fig. 1, with no adjustment.

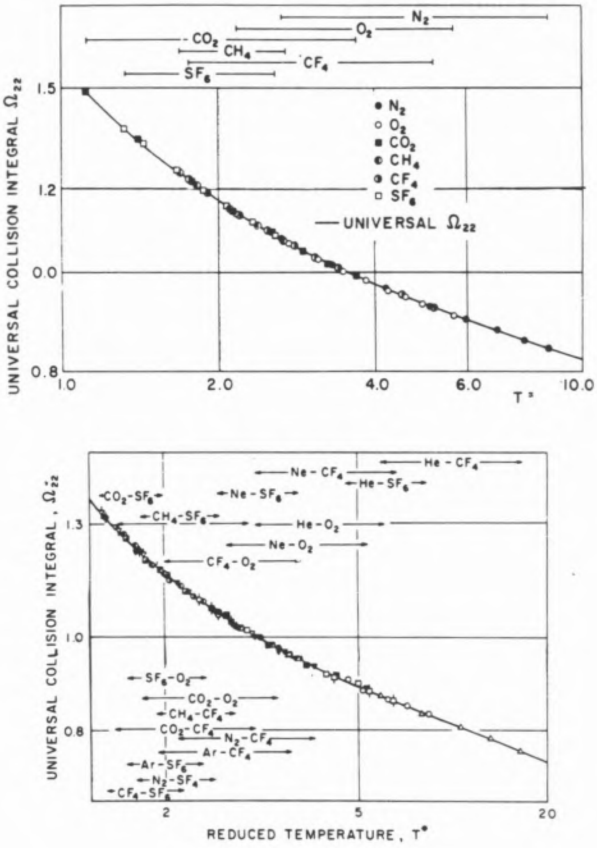

*Fig. 2*

*Same as fig. 1, for polyatomic gases and gas mixtures*

Fig. 3 shows the reduced second virial coefficient,

$$B^* \equiv B(T)/(\frac{2}{3}\pi N_0\sigma^3)\,, \qquad (4)$$

where $N_0$ is Avogadro's number, as a function of $T^*$ for noble gases. The correlation is quite good.

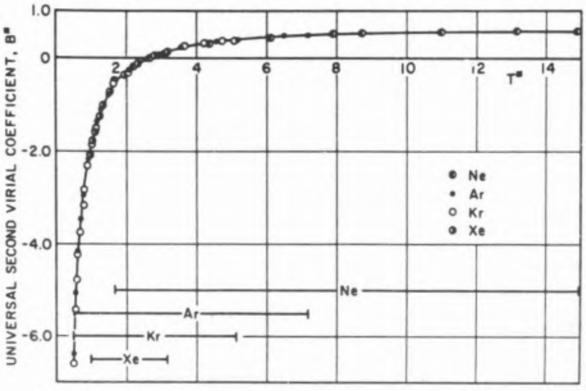

*Fig. 3*

*Two-parameter correlation for the reduced second virial coefficient as a function of $T^*$ for noble gases. A similar correlation for polyatomic gases fails*

No comparison is shown for noble gas mixtures because of the scarcity of accurate measurements. The lack of a comparison for single plyatomic gases is more significant — here the correlation fails. This was no surprise at the time, because it was known that the second virial coefficient is much more sensitive to the non-spherical parts of the potential than is the viscosity [9]. What was somewhat surprising was the fact that the viscosities of polyatomic gases were so well correlated with only two parameters. We shall see the reason for this is the next section. If accurate data were available at lower and higher temperatures, we might expect to see some deviations from the excellent correlations illustrated in figs. 1-3, but as far as direct experimental results can tell us, a two-parameter correlation is adequate. To do better we must know something about V(r), either from theory or from some entirely different type of measurement whose only link to thermodynamic and transport properties is indirectly through V(r).

A qualification must be added at this point. Deviations *are* seen for some noble gas pairs at lower temperatures [1], but these are quantum deviations, not deviations from a two-parameter correspondence of V(r). That is, even if the potentials scaled strictly according to the assumptions of Kestin, Ro, and Wakeham, there would be deviations at low temperatures because the collisions do not follow classical mechanics. A third parameter is then needed, but it is so obviously available that it is not even regarded as a parameter — it is the atomic mass. It usually is introduced through the so-called de Boer parameter, $\Lambda^*$, which is a reduced de Broglie wavelength [10],

$$\Lambda^* \equiv h/\sigma(m\epsilon)^{\frac{1}{2}}, \qquad (5)$$

where h is Planck's constant. These quantum deviations are virually impossible to isolate by the methods of Kestin, Ro, and Wakeham, and reference to V(r) is necessary.

## EXTENSIONS BASED ON INTERMOLECULAR FORCES

### A — *ADVANCES IN DETERMINATION OF V(r)*

Fifteen years ago, a review [11] of intermolecular forces closed with the following remark: "We seem to be on the verge of accurate determinations of 'true' potential energy curves for simple atoms". This prospect seems now to have been realized, at least for many of the noble-gas interactions. The specific advances in our knowledge of V(r) that have been crucial for extending and improving the principle of corresponding states are as follows:

(1) Development, by Smith, Maitland, and coworkers [12], of numerical methods for direct inversion of measured transport coefficients to find the potential, without any explicit assumption about the functional form of the potential.

(2) Collection of a body of experimental data, largely by Y.T. Lee and his coworkers [13], on the scattering of beams of noble gases by noble gases in the thermal energy range.

(3) Accurate values of the coefficients of the long-range dispersion energy are now available through a combination of quantum theory plus dielectric and optical data [14].

(4) Accurate information on the repulsive wall of the potential is now available from a synthesis [15] of theoretical calculations [16,17] and high-energy beam scattering [18].

In addition, two other advances have been helpful but not crucial:

(5) Determination of vibrational levels in noble-gas dimers from their vacuum ultraviolet absorption spectrum [19]. The data can be inverted by the Rydberg-Klein-Rees method [11] to find the width of the potential well as a function of its depth.

(6) Direct inversion of second virial coefficients [20], similar to the inversion of transport coefficients in (1) above.

As a result of these advances, we can now see directly that V(r) does not scale perfectly with only two parameters, even for the noble gases. This is illustrated in fig. 4, which shows $V/\epsilon$ *vs.* $r/r_m$, where $r_m$ is the position of the potential minimum, for several noble gas systems for which the potentials have been rather accurately determined [21-24]. Although the correspondence is rather close around the bottom of the potential well, deviations are apparent at both smaller and larger r. This result suggests two questions:

(1) How do the deviations shown in fig. 4 affect the gas properties?

(2) What new parameters are needed to characterize these deviations?

Before answers to these questions are attempted, it is interesting to make a short digression to

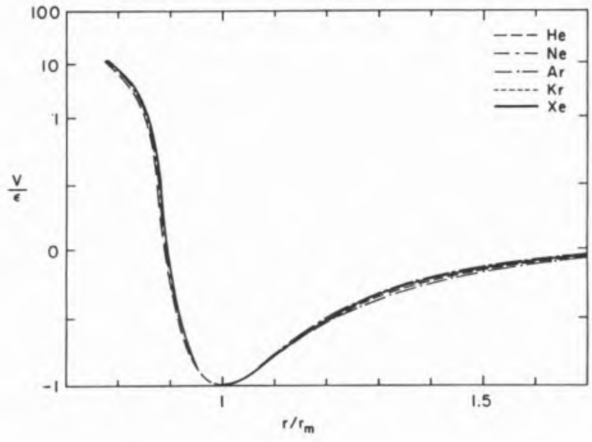

*Fig. 4*
*Reduced plot of noble-gas potentials, showing deviations from correspondence at large and small separations*

illustrate some of the insight that can be obtained through consideration of V(r). It was mentioned previously that it was a bit puzzling why the two-parameter correlation worked so well for viscosities of polyatomic gases. A direct inversion [25] of the viscosity correlation curve of figs. 1 and 2 showed that only the repulsive wall of V(r) was involved (i.e., $r < r_m$) in the temperature range covered by the correlation. It is not surprising that this rather featureless section of V(r) can be fitted with only two parameters, but reference to fig. 4 shows that an adjustment that makes the repulsive walls agree will spoil the agreement of the wells. The correlation based on viscosities will therefore fail for other properties — such as second virial coefficients — that depend on the well region of the potential.

## B — *NEW PARAMETERS NEEDED*

The long-range part of V(r) has the form

$$V(r) = -C_6/r^6 - C_8/r^8 - C_{10}/r^{10} - \ldots, \qquad (6)$$

and the coefficients $C_6$, $C_8$, ... have been determined from quantum theory plus dielectric and optical data [14]. This part of the potential is dominant in determining the transport coefficients at low temperatures, but not the second virial coefficients. If a two-parameter principle of corresponding states held to very low temperatures, we would find that the reduced parameters $C_6^* \equiv C_6/\epsilon\sigma^6$, $C_8^* \equiv C_8\epsilon\sigma^8$, ... were the same for all the noble gas pairs. Table 1

*Table 1*
*The low-temperature scaling parameter, $C_6^* = C_6/\epsilon\sigma^6$*

| | He | Ne | Ar | Kr | Xe |
|---|---|---|---|---|---|
| He | 3.09 | 2.940 | 2.681 | 2.498 | 2.346 |
| Ne | | 2.594 | 2.429 | 2.424 | 2.204 |
| Ar | | | 2.210 | 2.426 | 2.053 |
| Kr | | | | 2.164 | 2.051 |
| Xe | | | | | 2.162 |

shows that the $C_6^*$ have systematic variations. A low-temperature correlation of transport coefficients thus requires the introduction of $C_6^*$ as a new parameter, in addition to ε and σ. KESTIN, RO, and WAKEHAM [1] were of course well aware of all this, but the accuracy of the $C_6$ coefficients available to them was still too low to justify anything beyond the assumption of a universal value for $C_6^*$. The values of $C_8^*$ (not shown) also vary, but their effect on the transport properties is small enough that the variations can be neglected for most purposes.

The second virial coefficients at low temperatures are determined by the region of the potential around the minimum (dimer formation) [9], and fig. 4 shows that the two-parameter correlation holds in this region. Hence there is no need to introduce another new parameter representing, for instance, the reduced curvature of the potential at the minimum.

Both the transport and equilibrium properties at high temperatures depend on the short-range repulsive portion of V(r), which can be conveniently represented by an exponential function,

$$V(r) = V_0 \exp(-r/\varrho), \qquad (7)$$

where $V_0$ and ϱ are energy and range parameters. Since there are only two parameters, it is obvious that a two-parameter correlation must hold at high temperatures. Unfortunately, this turns out to be a different correlation than that given by the parameters ε and σ, as shown by the fact that $V_0^* \equiv V_0/\epsilon$ and $\varrho^* \equiv \varrho/\sigma$ are not the same for all noble gas pairs, as recorded in Table 2. The values of $V_0$ and ϱ in Table 2 were obtained from various theoretical calculations and scattering results [15,16]. The high-temperature correlation of transport and equilibrium properties therefore requires the introduction of $V_0^*$ and $\varrho^*$ as additional parameters. To summarize, the present extension of the principle of corresponding states requires five para-

*Table 2*

*The high-temperature scaling parameters,* $V_o^* = V_o/\epsilon$ *and* $\varrho^* = \varrho/\sigma$

$V_o^* \times 10^{-5}$

| | He | Ne | Ar | Kr | Xe |
|---|---|---|---|---|---|
| He | 8.50 | 10.60 | 9.740 | 10.89 | 13.37 |
| Ne | | 11.09 | 9.235 | 9.929 | 11.20 |
| Ar | | | 5.117 | 4.849 | 4.878 |
| Kr | | | | 4.491 | 4.337 |
| Xe | | | | | 3.898 |

$\varrho^*$

| | He | Ne | Ar | Kr | Xe |
|---|---|---|---|---|---|
| He | 0.0797 | 0.0788 | 0.0791 | 0.0772 | 0.0764 |
| Ne | | 0.0784 | 0.0795 | 0.0786 | 0.0785 |
| Ar | | | 0.0836 | 0.0833 | 0.0835 |
| Kr | | | | 0.0831 | 0.0837 |
| Xe | | | | | 0.0854 |

meters arising from the potential — $\epsilon$, $\sigma$, $C_6^*$, $V_o^*$, and $\varrho^*$ — plus the quantum parameter $\Lambda^*$. As an example of how such an extension appears, fig. 5 shows the correlation curves for the viscosity

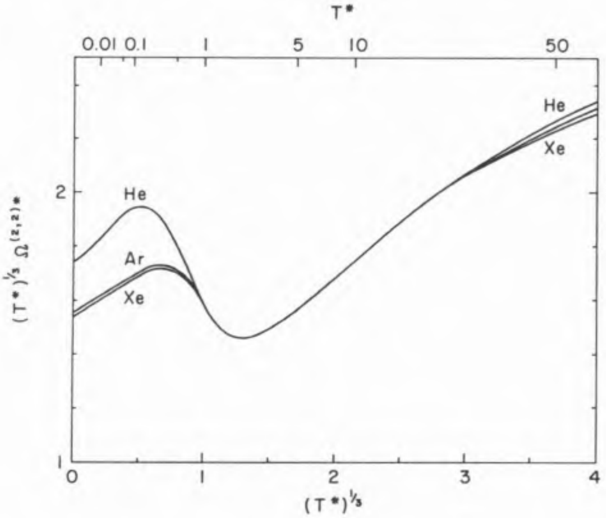

*Fig. 5*

*Correlation curves for* $\Omega^{(2,2)*}$*, the reduced collision integral for viscosity. The single curve at intermediate* $T^*$ *is the region of the two parameter (*$\epsilon$*,* $\sigma$*) correlation. At low temperatures the additional parameter* $C_6^*$ *is needed, and at high temperatures the repulsion parameters (*$V_o$*,* $\varrho^*$*) are needed*

reduced collision integral, $\Omega^{(2,2)*}$, defined in Eq. (2). The region where only one curve appears is the same as represented by the original two-parameter correlation curves in figs. 1 and 2, but the result is plotted in a different way to take advantage of the theoretically known asymptotic behavior of $\Omega^{(2,2)*}$ at low $T^*$. The splitting of the single curve into families appears at both low and high temperatures. This splitting is indexed by $C_6^*$ at low temperatures and by ($V_o^*$, $\varrho^*$) at high temperatures.

## C — *EXTENSION OF CORRESPONDING STATES PRINCIPLE*

Here we set out explicitly what advantages can be obtained in a corresponding-states correlation by knowledge of V(r), but can give only a brief selection of actual results.

(1) The range of validity of the two-parameter ($\epsilon$, $\sigma$) correlation can be specified more precisely. Outside of this range, deviations gradually set in and more than two parameters are needed. As an example, notice that the correlation for $\Omega_{22}$ in fig. 1 appears to be universal up to $T^* = 90$, whereas in fig. 5 it does not extend beyond $T^* = 30$. A closer look at fig. 1 shows that the high-temperature end of the correlation is based entirely on He, and is thus not demonstrated to be universal.

(2) Values of one property that is known accurately can be used to refine or predict other properties that are known less accurately from experiment. As an example, viscosity is usually measured with substantially greater accuracy than are diffusion coefficients and thermal diffision factors. By proceeding through V(r) we can use the accuracy of viscosity to improve that of diffusion coefficients.

(3) Joint analysis of two properties through the potential can improve the accuracy and range of validity of both, because different properties give information on different regions of the potential. For example, the second virial coefficient at very low temperatures is determined by the region near the potential minimum, whereas the viscosity at very low temperatures is determined by the long-range tail of the potential. Thus, viscosity data at only moderately low temperatures could be used to specify the second virial coefficient at very low temperatures, or *vice versa*.

(4) Data not directly related to the thermodynamic and transport properties of the gases can be used to extend the temperature range of the correlations to both lower and higher temperatures, as well as to improve accuracy in the original temperature range. Such data include scattering measurements, theoretical calculations, dielectric and optical data, and spectroscopic measurements that locate the

bound states in the potential well. This has allowed the temperature range of the correlation to be extended from virtually 0 K to the onset of first ionization.

(5) Statistical-mechanical theory can be used with knowledge of V(r) to find useful asymptotic forms for the temperature dependence of gas properties, and to include new properties. An example of the first is shown in fig. 5. An example of the second are the quantum corrections for the second virial coefficient, which can be isolated through V(r) but which are virtually impossible to extract accurately from experimental data alone.

Space permits only a few selected examples of the correlations obtained. A deviation plot for the viscosity of krypton is shown in fig. 6, including the experimental data considered best [26-29] and the results calculated from an accurate potential [24]. A similar deviation plot for the second virial coefficient of krypton is shown in fig. 7, together with experimental data [30-34]. The agreement shown in these two figures is typical. It should be remembered that the parameters $\epsilon$ and $\sigma$ have been adjusted to optimize the fit, but the parameters $C_6^*$, $V_o^*$, and $\varrho^*$ are specified independently.

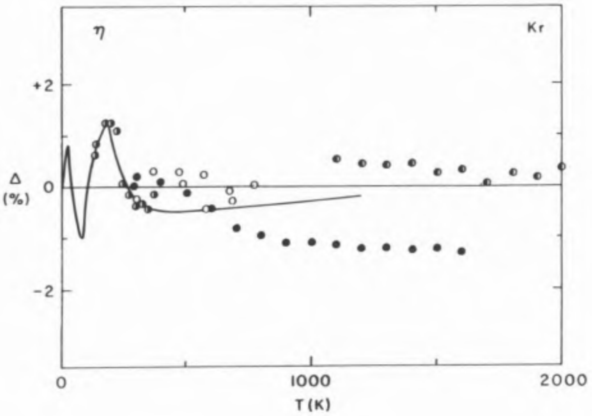

*Fig. 6*
*Deviation plot for the viscosity η of Kr as a function of temperature. △(%) ≡ 100(expt − calc)/calc.*
○ *Ref. [26];* ● *Ref. [27];* ◐ *Ref. [28];*
◑ *Ref. [29];* ——— *Ref. [24]*

The deviation plot for the self-diffusion coefficients of the noble gases, shown in fig. 8, supplies an independent test of the correlations, since these data were not used in any parameter adjustment.

Comparable results are obtained for other properties, and for mixtures of any number of components.

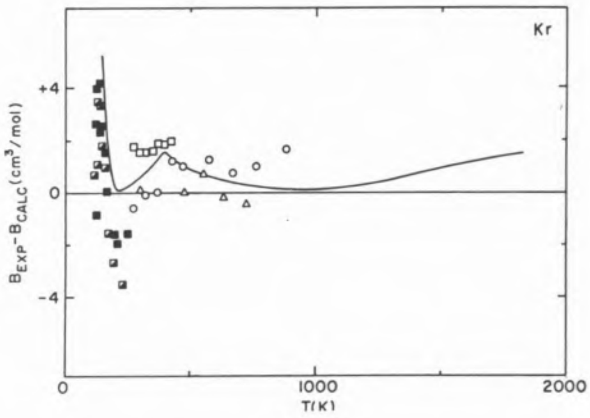

*Fig. 7*
*Deviation plot for the second virial coefficient B of Kr as a function of temperature*
○ *Ref. [30];* □ *Ref. [31];* ◪ *Ref. [32];* ■ *Ref. [33];*
△ *Ref. [34];* ——— *Ref. [24]*

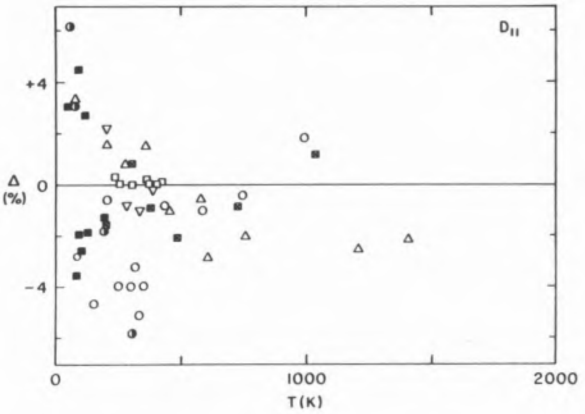

*Fig. 8*
*Deviation plot for the self-diffusion coefficients, $D_{11}$, of the noble gases as a function of temperature. △(%) ≡ 100(expt − calc)/calc.*
○ , ◑ *He;* △ *Ne;* □ , ■ *Ar;* ⊠ *Kr;* ∇ *Xe*

## AN EXAMPLE: DIRECT INVERSION OF GAS VISCOSITY

Historically, the earliest estimates of intermolecular potentials were based on macroscopic properties, such as second virial coefficients or low-density transport coefficients, and proceeded through parameterized models. Until fairly recently, computing limitations restricted the number of adjustable parameters to two or three, so that the models used were always a bit too crude. The direct inversion problem, proceeding from data to potential without explicit assumption of a mathematical model, was considered hopeless both in principle and in practice, since there were direct demonstrations that such inversions cannot be unique [3]. Thus one of the surprising results of the past decade has been the development of direct inversion methods for both transport and second virial coefficients. The unexpected success of these methods is, in fact, still somewhat puzzling, although some progress has been made in understanding their success [12]. Here we give a brief account of direct inversion, using viscosity as an example.

From Eq. (2) we see that V(r) is entirely contained in the quantity $\sigma^2\Omega_{22}$, or in $\sigma^2\Omega^{(2,2)*}$, which is a thermally averaged cross section [8],

$$\pi\sigma^2\Omega^{(2,2)*} = \\ = [6(kT)^4]^{-1} \int_0^\infty Q^{(2)}(E)\exp(-E/kT)E^3 dE\,, \qquad (8)$$

where E is the relative energy of collision. Two further layers of integration still shield V(r):

$$Q^{(2)}(E) = 3\pi \int_0^\infty [1-\cos^2\theta(E,b)]b\,db\,, \qquad (9)$$

$$\theta(E,b) = \pi - 2b \int_{r_0}^\infty \left[1 - \frac{b^2}{r^2} - \frac{V(r)}{E}\right]^{-\frac{1}{2}} r^{-2} dr\,, \qquad (10)$$

where $\theta$ is the angle of deflection in a collision of energy E with impact parameter b.

The key idea is that $\eta$ at a given T is determined by the interaction of two atoms over only a small range of separations. This is surely not obvious from Eqs. (8)-(10), but we return to the point later. This range is centered around some distance $\bar{r}$, such that $V(\bar{r})$ is of the order of kT, and $\sigma^2\Omega^{(2,2)*}$ is about equal to $\bar{r}^2$. This result is known to be roughly true, and we can make it exact by defining a suitable function G such that

$$G\,kT = V(\bar{r})\,, \qquad (11)$$

$$\bar{r}^2 = \sigma^2\Omega^{(2,2)*}\,. \qquad (12)$$

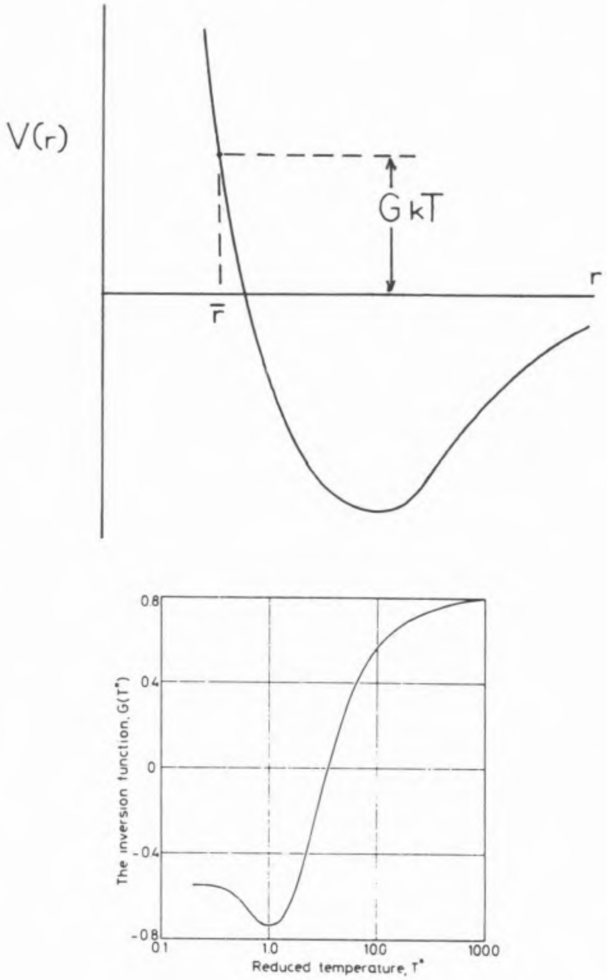

*Fig. 9*

*Upper; Significance of G and $\bar{r}$. Lower: Typical inversion function G(T*)*

These quantities are illustrated in the upper part of fig. 9. In general, G depends in a complicated way on V(r) and T, but a remarkable feature emerges for potentials with the simple shape shown in fig. 9-G depends almost entirely on the single variable $T^*$, and is relatively insensitive to details of the shape of V(r). A typical function $G(T^*)$ is shown in the lower part of fig. 9. This almost miraculous behavior of G makes a direct inversion possible.

First a rough model of V(r) is used to calculate a first approximation to $G(T^*)$. The values of $\bar{r}$ are known from the measured $\eta(T)$ according to Eqs. (2) and (12). The corresponding values of $V(\bar{r})$ are then found from Eq. (11), using the first approximation to $G(T^*)$. This step requires the assumption of a provisional value of $\epsilon$. From the series of measured points constituting $\eta(T)$, a corresponding series of points $V(\bar{r})$ is thus obtained. (Actually $\bar{r}(V)$ is obtained). This $V(\bar{r})$ is then used to calculate an improved approximation to $G(T^*)$, and the process is repeated until $V(\bar{r})$ becomes stable. Then this $V(\bar{r})$ is used to calculate $\eta(T)$ for comparison with experiment. The value of $\epsilon$ is found by numerical search to be the one that produces the best fit of the data. The results are remarkably good when V(r) has a reasonably simple shape (e.g., as in fig. 9). How is this possible?

The first question to consider is how V(r) manages to survive three layers of integration. We can see how this happens from a closer examination of Eqs. (8)-(10). From Eq. (10) we find that the dominant contribution to $\theta$ for given b and E comes from the region of r near $r_o$, the distance of closest approach — the integrand is infinite at $r_o$. From Eq. (9) we notice two things: the factor $(1-\cos^2\theta)$ suppresses small-angle scattering, and the factor b db emphasizes collisions at large impact parameters. The appearance of b db is a result of the three-dimensional nature of the problem. The result is that $Q^{(2)}$ at a given E is dominated by a very small range of b (or, equivalently, of $r_o$) in which both $\theta$ and b are simultaneously large. Thus V(r) survives the second integration. The third integration of Eq. (8) has a peaked weighting factor of $E^3$ exp $(-E/kT)$, which only smears the results a bit without washing them out entirely.

The second question to consider is how the inversion manages to work, despite demonstrations that it cannot be unique for the general case. Here our best hope is to make a connection with other inversion problems in physics that have already been worked out, of which there are quite a number [35]. Suppose we consider the surface of $|\theta|$ as a function of E and b, as shown in fig. 10. If we slice the surface at fixed b (or at fixed angular momentum), the resultant projection of $\theta_b(E)$ can be inverted. So can the projection $\theta_E(b)$ resulting from a slice at fixed E. If we examine in more detail the calculation of $Q^{(2)}(E)$, we find that the crucial small range of b or $r_o$ that determines $Q^{(2)}$ always corresponds to a nearly constant value of the deflection angle, approximately $|\theta| = 1/\pi$. Thus the information contained in $\eta(T)$ is roughly equivalent to knowing b as a function of E at constant $|\theta| \approx 1/\pi$, which is the third orthogonal slice of the $(|\theta|, b, E)$ surface (lower half of fig. 10). It is at least plausible that an inversion is possible for $b_\theta(E)$ if it is possible for $\theta_b(E)$ and $\theta_E(b)$, and more detailed considerations show that this is so [12].

The problem of uniqueness still remains. It is clear that some extra information has to be included for uniqueness, and that this occurs through implicit assumptions about the "shape" of V(r). This has been somewhat clarified by the use of simulated experimental data generated from a known V(r), into which various pathological feactures are introduced one by one. But many fascinating questions, both fundamental and practical, remain to be answered.

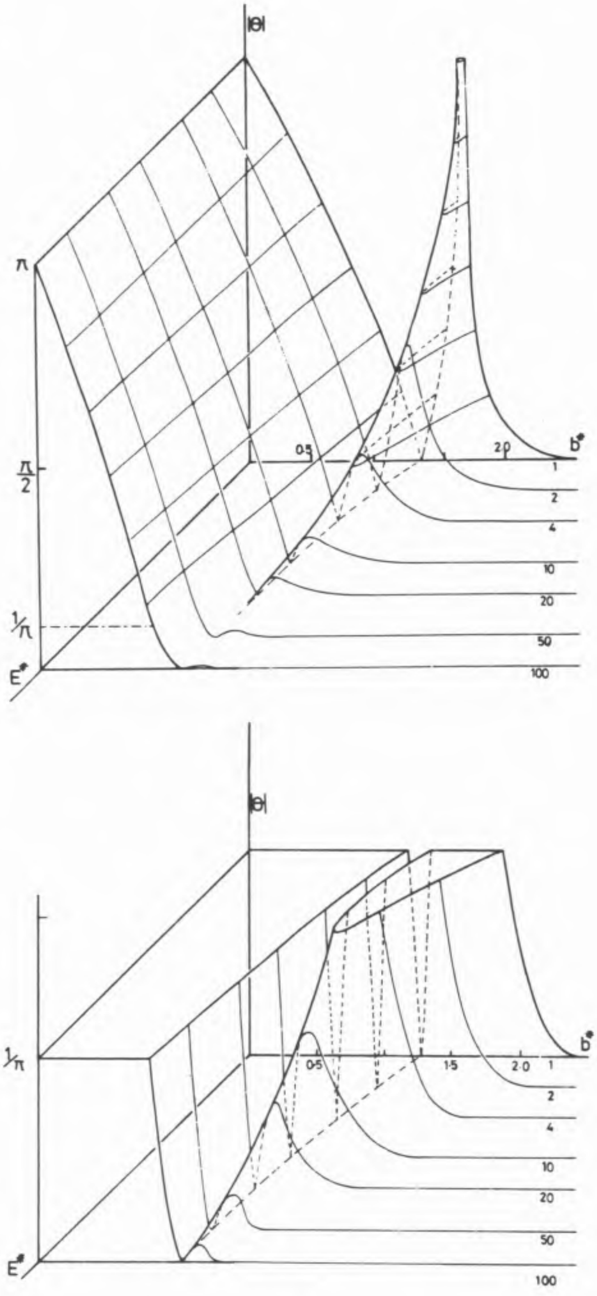

*Fig. 10*

*Upper: Three-dimensional* $(|\theta|, b, E)$ *surface. Lower: A slice through this surface at constant* $|\theta| = 1/\pi$

## CONCLUDING REMARKS

I hope that this short review has given some insight into one small aspect of recent work on transport properties. Even with a subject as old as the principle of corresponding states, there is much to be learned. Indeed, like all good scientific problems, recent work has raised at least as many questions as it has answered. Here are two. First, why is the extended principle of corresponding states so remarkably accurate for noble gas pairs? There must be an amazing similarity among the potentials involved, which persists to a very subtle degree on the energy scale at which quantum chemists currently make their calculations. It seems too much to believe that all this is merely fortuitous, but there is so far no inkling of a fundamental explanation. Second, why is the direct inversion of transport coefficients so successful? All the known mathematical theorems seem to argue against it, and it is easy enough to produce pathological cases that fail, but the method goes right on being practical. One is reminded of the old parable of the bee and the aeronautical engineers.

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## NOTE ADDED IN PROOF

Many details have now been published by B. Najafi, E.A. Mason, J. Kestin, *Physica* **119A**, 387 (1983) and by J. Kestin, K. Knierim, E.A. Mason, B. Najafi, S.T. Ro, M. Waldman, *J. Phys. Chem. Ref. Data* **13** (1984).