The Indeterminacy of the Values of Potential Parameters as Derived from Transport and Virial Coefficients

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The present work originated in a re-examination of the application of the Lennard-Jones (12:6) potential function to the viscosity-temperature relations of gases and vapors at low pressures. In particular, attention was focused on a phenomenon mentioned by Mueller and Lewis (1957) and described in more detail by Reid and Sherwood (1966) and Reid (1968) whereby disparate sets of values of σ and ϵ/k (the Lennard-Jones potential parameters) represent experimental data equally well. Several examples of this behavior are quoted in the paper by Reid (1968), but only one example will be considered here. Flynn and Thodos (1962) obtained the values $\sigma = 0.5869$ nm and $\epsilon/k = 208$ K from experimental viscosity data on *n*-butane for the temperature range 290 to 390 K, whereas Svehla (1962) obtained $\sigma = 0.4930$ nm and $\epsilon/k = 513.4$ K *from the same data.* Despite the large differences in the values of the two sets of parameters, each reproduced the experimental viscosity values quite closely (Reid and Sherwood, 1966, Figure 92).

Reid and Sherwood point out that the respective authors used somewhat different numerical methods to evaluate the parameters. However, such differences in the methods do not in themselves explain either the enormous differences in the values obtained or the remarkably good fit which each set gives to the experimental viscosity values.

An explanation for these facts was given by Kim and Ross (1967) in a brief but important note which appears to have been overlooked by later authors. When the work reported here was begun, the author, too, was unaware of Kim and Ross's note and analyzed the problem independently. The solution obtained in the present study is virtually identical with that obtained by these authors, but since the scope of the present work is wider, some degree of restatement is necessary.

A number of physical properties of gases are affected by the mutual interaction of molecules at close distances. In relation to the properties of gases at relatively low pressures, only binary interactions are significant. Numerical values for a number of properties of gases can then be predicted from the kinetic theory of gases, provided one assumes a particular pairwise interaction potential function, expressing the energy of interaction of two molecules as a function of their distance apart and (where relevant) relative orientation. This note is concerned only with cases where orientation is not significant. In these circumstances, the theoretical expressions often take the form

$$y = A\sigma^{i}T^{j}D^{*} \tag{1}$$

where y is the predicted numerical value of the physical property (for example, viscosity, or second virial coefficient) and A is a constant (at least for a particular substance) not depending in any way on the parameters of the interaction potential function. The collision diameter σ is one of the parameters of the interaction potential function and may be defined as the distance (other than infinity) between the centers of the two molecules when the net potential energy is zero. T is the absolute temperature, i and j are absolute constants, and D^* is a dimensionless quantity dependent on the form of the particular interaction potential function.

If a particular potential function is assumed, values of D^* may be calculated from theoretical considerations, classical or quantum-mechanical; D^* can then be expressed as a function of dimensionless variables, one of which is always $T^* = kT/\epsilon$. k is here the Boltzmann constant, and ϵ, the depth of the potential well, is another parameter of the potential function. ϵ may be defined as the absolute value of the net potential energy at such a distance of separation that this energy is most negative (the energy at infinite separation being taken as zero).

If $y = \eta$ (the coefficient of gas viscosity), $A = (5/16)(mk/\pi)^{1/2}$, where m is the mass of a single molecule of the gas, $i = -2$, $j = 1/2$ and $D^* = f_\eta/\Omega^{(2,2)*}$. Here f_η, the viscosity correction factor, is a dimensionless quantity, as is also $\Omega^{(2,2)*}$. Theoretically, f_η and $\Omega^{(2,2)*}$ are dependent both on T^* and the particular potential function but in practice f_η is very close to unity over a wide range of values of T^* and for all reasonable potential functions. $\Omega^{(2,2)*}$ is a collision integral which enters into the expressions for gas viscosity and gas thermal conductivity.

If these values or expressions for y, A, i, j, and D^* are substituted in (1), we obtain the well-known Chapman-Enskog equation for gas viscosity

$$\eta = (5/16)(mkT/\pi)^{1/2} f_\eta/(\sigma^2\Omega^{(2,2)*}) \tag{2}$$

Now $m = (1.66053 \times 10^{-27}\,\text{kg})M$, where M is the relative molecular mass, and $k = 1.38062 \times 10^{-23}$ kg m^2 s^{-2} K^{-1}, so that (2) becomes

$$\eta = (2.6695 \times 10^{-26}\,\text{kg m s}^{-1}\,\text{K}^{-1/2})\,(MT)^{1/2} f_\eta/(\sigma^2\Omega^{(2,2)*}) \tag{3}$$

If T is expressed in degrees Kelvin and σ in meters, then (3) will give η in kg m^{-1} s^{-1} or N s m^{-2}.

If $y = B$ (the second virial coefficient), $A = 2\pi N/3$, where N is the Avogadro constant; $i = 3$, $j = 0$, and $D^* = B^*$. B^* is dimensionless and is a calculable function of T^*.

If these values or expressions are substituted in (1), the following expression is obtained for the second virial coefficient:

$$B = (2\pi N/3)\sigma^3 B^* \tag{4}$$

and since

$$N = 6.0222 \times 10^{23}\,\text{mol}^{-1}$$

$$B = (1.2613 \times 10^{24}\,\text{mol}^{-1})\sigma^3 B^* \tag{5}$$

If σ is expressed in meters, (5) will give B in m^3 mol^{-1}. The theoretical equations for the coefficients of thermal conductivity and self-diffusion fit into this pattern in an analogous manner. So, too, do the third and higher virial coefficients, provided that appropriate approximations can be made relating the multibody interaction energy to the pairwise interaction potential function.

Since y is an explicit function of σ and of D^* [Equation (1)] and the latter is an explicit (even if not necessarily an analytical) function of T^* (that is, of kT/ϵ), it should be possible, in principle, to obtain separate and physically meaningful numerical values for σ and ϵ/k by fitting Equation (1) [or rather an appropriate derived form, for example (3) or (5)] to experimental values of y as a function of T. Consideration shows that this is so unless the numerical values of D^* are such that, over a range of values of T^*, the quantity $\log|D^*|$ is approximately a linear function of $\log T^*$, that is,

$$D^* \simeq E(T^*)^L \tag{6}$$

where E and L are constants with respect to variation of T^*. If (6) does hold over a range of T^* values, then (1) becomes

$$y = AE[\sigma^i(k/\epsilon)^L]T^{j+L} \tag{7}$$

in which σ and ϵ/k have collapsed into a single parameter $[\sigma^i(k/\epsilon)^L]$. Equation (7) may be written

$$y = cT^s \tag{8}$$

where c and s are constants over a range of temperature corresponding to the range of T^* values for which (6) holds. We may note that c will be different for different substances [even where A in Equation (1) is not] but $s(= j + L)$ should be the same for all substances, with a given potential function.

Whenever (6) holds, therefore, the parameters σ and ϵ/k will not be separately determinable. If, over a range of T^* values, (6) were to hold very closely, comparatively small differences (in either the experimental data or the numerical methods) will lead to large differences in the numerical values obtained for σ and ϵ/k. It will be seen, however, that the actual occurrence of the phenomenon is independent either of the particular experimental data or numerical methods but dependent solely on the numerical behavior of the table of D^* values being used. For this purpose, it is immaterial whether the molecular model underlying this table is realistic or otherwise or whether the treatment is classical or quantum-mechanical.

Conversely, if over a range of temperature, experimental values of y happen to conform to a relationship of the form of (8), then either (1) the values of D^* calculated from the potential function will accurately reflect the experimental values of y, in which case, indeterminacy of the parameters must occur or (2) calculated values of D^* will not accurately reflect the experimental values of y, in which case any values obtained for σ and ϵ/k will be of little use since they cannot be used to reproduce accurately the experimental values of y. In either case, therefore, little or no physical significance should be attached to any numerical values obtained for σ and ϵ/k if most or all of the datum points come within a range over which a plot of $\log|y|$ against $\log T$ is linear. This does not, of course, affect the validity or significance of the underlying definitions of σ and ϵ/k in this temperature range.

To examine the detailed applicability of these conclusions, we need to choose particular potential functions.

VISCOSITY

For the present purpose, f_η may be taken as unity, without significant error. Kim and Ross (1967) have shown that with the Lennard-Jones (12:6) potential function, $\Omega^{(2,2)*}$ is equal to 1.604 $(T^*)^{-0.5}$ to within ± 0.7% over the range $T^* = 0.4$ to 1.4. Table 1, which uses the same set of values of $\Omega^{(2,2)*}$ (Monchick and Mason, 1961) shows values of $\Omega^{(2,2)*} \cdot (T^*)^{0.5}$

The data of this table indicate, in fact, a slightly wider range (from $T^* = 0.39$ to 1.55) within the above percentage error (that is, ± 0.7%). Thus, with $L = +0.5$, (6) is satisfied over this range (to within the error usually associated with the experimental determination of η) by the Lennard-Jones (12:6) classically calculated values of $\Omega^{(2,2)*}$.

TABLE 1. RANGE OF APPLICABILITY OF KIM AND ROSS'S EQUATION

T^*	$\Omega^{(2,2)*} \cdot (T^*)^{0.5}$	T^*	$\Omega^{(2,2)*} \cdot (T^*)^{0.5}$
0.1	1.297	0.8	1.601
0.2	1.459	0.9	1.596
0.3	1.555	1.0	1.593
0.4	1.601	1.2	1.594
0.5	1.615	1.4	1.603
0.6	1.614	1.6	1.619
0.7	1.608	1.8	1.639

Collision integrals derived from other potential functions also satisfy (6). The present author has shown this for the modified Buckingham (or exp:6) potential (Mason, 1954) for which a plot of log $\Omega^{(2,2)*}$ against log T^* gave (over a range of T^*) straight lines with slopes close to − 0.5 and for which $\Omega^{(2,2)*} . (T^*)^{0.5}$ was nearly constant over a range of T^* values—so, too, with the 9:6 potential (Smith et al., 1965) where, however, the best value of L lay between + 0.55 and + 0.60, and the 28:7 potential (Smith et al., 1965) where the best value lay between 0.32 and 0.38. It appears probable that any reasonable potential function will obey Equation (6) over at least one substantial range of T^* values.

When indeterminacy occurs, the disparate sets of values for σ and ϵ/k should yield the same value of $\sigma^i(k/\epsilon)^L$. The sets reported for n-butane by Flynn and Thodos (1962) and by Svehla (1962) satisfy this condition with $L = + 0.48$. This is in good agreement with $L = + 0.5$ obtained above. (Since both sets were themselves obtained using the 12:6 function, caution must be exercised before attempting to draw the conclusion that this agreement favors the 12:6 function over, say, the 28:7 function.)

SECOND VIRIAL COEFFICIENTS

Values of B^* tabulated (Hirschfelder et al., 1954) for the Lennard-Jones (12:6) function fit the relationship $B^* = - 2.531\ (T^*)^{-1.75}$ to within 0.3% over the range $T^* = 0.59$ to 1.22. (It is possibly something of an accident that this range happens to fall entirely within the range given above for $\Omega^{(2,2)*}$).

That indeterminacy could actually occur in practice was confirmed by numerical calculations on an artificially constructed example published by Martin (1970) which, by chance, provided datum points which could be fitted within the required range.

Other potential functions have not been investigated.

OTHER PHYSICAL PROPERTIES

For the present purpose, the correction factors for other transport coefficients may in each case be taken as unity without significant error. The fitting of experimental values of thermal conductivity coefficients to an equation of the type of (1) to obtain values of σ and ϵ/k will not normally be done, since the appropriate equation analogous to (1) must allow for internal energy and this allowance is certain only with monatomic gases. If it were done, similar considerations would apply as with viscosity since the same collision integral $\Omega^{(2,2)*}$ covers both.

Values of $\Omega^{(1,1)*}$ (which determines the coefficients of diffusion) for the Lennard-Jones (12:6) function (Monchick and Mason, 1961) fit the relationship $\Omega^{(1,1)*} = 1.452\ (T^*)^{-0.5}$ to within 1% over the range $T^* = 0.27$ to $T^* = 1.39$. Other functions have not been investigated.

A more detailed analysis (for which there is insufficient space here), with certain reasonable assumptions, shows that where indeterminacy occurs bounds exist on the values of σ and ϵ/k which might be obtained by fitting experimental values to theoretical equations. The bounds on the values of ϵ/k are determined by (and indeed are inversely proportional to) the bounds on T^* within which (6) holds. Thus any lower bound on T^* will determine an upper bound on ϵ/k and vice versa. The bounds on σ will be determined by the constancy of $\sigma^i(k/\epsilon)^L$. (Since both for viscosity and second virial coefficient, i and L are of opposite sign, for these two properties, a lower bound on T^* will determine a lower bound on σ and vice versa). In respect of viscosity (and probably the other properties, too), a region exists (at high temperature) for which there is only a lower bound on T^* (Liley, 1972).

Similarly, if the ratio of the highest absolute temperature covered by the experimental data to the lowest is insufficiently removed from unity, indeterminacy may still occur in practice even though the T^* values lie outside a range in which (6) holds closely. This is because the curvature in a plot of $\log|D^*|$ versus $\log T^*$ may be insufficient to overcome the effect of the narrowness of the experimental temperature range. (The numerical example of Martin mentioned above is an illustration of this point.)

This indeterminacy of the potential parameters for a given potential function should not be confused with the somewhat analogous phenomenon (occurring over a different though nearby temperature range) whereby various different potential functions can, by appropriate adjustments of their respective potential parameters, be made to predict indistinguishable y-T plots (Klein and Hanley, 1968; Smith et al., 1965).

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Manuscript received and accepted March 8, 1973.

A Turbulent Flow Model for Mass Transfer in Wetted Wall Columns and Packing

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Emmert and Pigford (1954) studied gas absorption in falling liquid films. This study showed that a mass transfer model based upon a parabolic velocity distribution in the film compared favorably with absorption and desorption data in which the surface rippling was suppressed by wetting agents. Data for films with rippling show mass transfer rates that are several times greater than with rippling suppressed. Portalski (1963) presented and analyzed data for film thickness on a smooth, vertical plate with the conclusion that the data appeared to be best represented by a universal velocity profile treatment. This note presents a turbulent film model for comparison with mass transfer data with rippling present.

THEORY

A turbulent falling film can be assumed to be represented by a flat velocity profile with mass transfer to the film from the wall or from the gas corresponding to the penetration theory. This is expressed by the equation

$$k_L = 2\sqrt{\frac{D}{\pi\theta}} = 2\sqrt{\frac{Du}{\pi z}} \qquad (1)$$

where the time of contact θ is obtained from the average film velocity and the distance between transverse mixings. Substitution of $\Gamma/\rho y$ for the average film velocity and rearrangement to obtain the dimensionless mass transfer coefficient in terms of the Schmidt and Reynolds numbers yields

$$k_L{}^+ = \frac{(N_{Sc})^{-1/2}}{u^*}\left(\frac{4\Gamma}{\mu}\right)^{1/2}\frac{\nu}{\sqrt{\pi z y}} \qquad (2)$$