APPLICABILITY OF MOLECULAR INTERACTION POTENTIALS IN VISCOSITY CALCULATION FOR STEAM

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Parameters have been determined for some effective spherically symmetrical potentials by reference to the viscosity data for water vapor, and conclusions are drawn on the applicability of the models.

It has long been recognized that there are major difficulties in applying kinetic theory to calculate transport parameters for polyatomic polar gases [1]. In that case, the Chapman – Enskog solution may not be appropriate, as it employs effective spherically symmetrical potentials, and so the discrepancies between the calculated and measured transport coefficients may be due not only to assumptions made in the theory, but also to imperfection in the models. Here we use data on the dynamic viscosity at zero density $\eta_0(T)$ for water vapor to examine various molecular-interaction potentials. For convenience in comparison with experiment, the model calculations have been compared with the following interpolation formula [2]:

$$\eta_0(T) = \left(\frac{T}{T_{\text{cr}}}\right)^{\frac{1}{2}} \left[\sum_{i=0}^{n} a_i \left(\frac{T_{\text{cr}}}{T}\right)^i\right]^{-1}, \tag{1}$$

which reproduces the most reliable measurements very closely.

The parameters of the molecular-interaction potentials were determined by minimizing the sum of squares of the residuals:

$$\Phi = \sum_{j=1}^{n} W_j \left[\eta_{0j}^{\text{en}} - \eta_{0j}^{\text{calc}}\left(T_j^*, \sigma, \frac{\varepsilon}{k}, \ldots\right)\right]^2 = \min. \tag{2}$$

Then the Chapman – Enskog theory gives

$$\eta_{0j}^{\text{calc}}\left(T_j^* \sigma, \frac{\varepsilon}{k}, \ldots\right) = 0.26693 \cdot 10^{-5} \frac{\sqrt{MT_j}}{\sigma^2 \Omega^{(2.2)*}(T_j^*)} f_\eta^{(k)}. \tag{3}$$

The number of measured values (n = 225), namely, $\{\eta_{0j}^{\text{en}}\}$, and the relative errors $\delta\eta_{0j}$ were taken as in the definition of the coefficients of (1) in [2].

It is useful to describe the tabulated collision integrals $\Omega^{(2.2)*}(T^*)$ for the corresponding potentials in terms of some suitable analytical function such as the polynomial

$$\Omega^{(2.2)*}(T^*) = \sum_{i=0}^{m} b_i (T^*)^{-i}. \tag{4}$$

The coefficients b_i were determined by least-squares fitting.

The Stockmayer potential [3] is the most widely used in examining the properties of polar gases, in which the angle-dependent term is replaced by a term corresponding to the interaction between two point dipoles lying on a common line:

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TABLE 1. Parameters of Molecular-Interaction Potentials

Potential	Φ	$\left(\frac{\varepsilon}{k}\right)_0$, °K	σ, Å	μ, Debye
L-J (9-6)	518	775±90	2,61±0,09	—
L-J (12-6)	2268	740±60	2,73±0,05	—
L-J (15-6)	6268	705±100	2,94±0,09	—
Keesom (9-6-6)	74	633±7	2,65±0,01	1,11±0,01
	3560	119	3,62	1,84 (fixed)
Keesom (12-6-6)	98	515±19	2,76±0,02	1,38±0,01
	6601	110±6	3,05±0,01	1,84 (fixed)
Keesom (15-6-6)	112	380±6	2,85±0,01	1,55±0,01
Stockmayer $\delta^* = 1,0$	1190	1430±12	2,12±0,01	1,94
Stockmayer $\delta^* = 1,5$	953	386±4	2,79±0,01	1,86
Stockmayer $\delta^* = 2,0$	201	1106±13	1,92±0,01	2,08
Stockmayer $\delta^* = 2,5$	189	528±30	2,27±0,04	2,06
Kihara + dipole—dipole $\delta^*_* = 2,0$; $\gamma^* = 0,6$	178	1045±42	2,00±0,03	
Potential of (10)	86	461	2,79	1,46 ($\alpha = 0$, Å³ — fixed)
	86	452	2,79	1,46 ($\alpha = 0,35$ Å³)

$$\varphi(r) = 4\left(\frac{\varepsilon}{k}\right)_0 [r^{*-12} - r^{*-6} - \delta^* r^{*-3}]. \tag{5}$$

One expects that such a model would give good results for the transport parameters at high temperatures, where the repulsive forces are decisive.

Calculations have been performed [4] on the collision integrals for the Kihara model with a contribution from dipole—dipole interaction, i.e.,

$$\varphi(r) = 4\left(\frac{\varepsilon}{k}\right)_0 \left[\left(\frac{1-\gamma^*}{r^*-\gamma^*}\right)^{12} - \left(\frac{1-\gamma^*}{r^*-\gamma^*}\right)^6 - \delta^* r^{*-3}\right]. \tag{6}$$

It is assumed that a model with a spherical core reproduces approximately the effects of the internal energy on the collisions; collision integrals were derived [4] for specified orientations and then averaged over the orientations.

Recently, numerous calculations have been performed with the Keesom average potential [5, 6]:

$$\varphi(r) = 4\left(\frac{\varepsilon}{k}\right)_0 \left[r^{*-12} - r^{*-6} - \frac{y}{T_0^*} r^{*-6}\right]. \tag{7}$$

This function is a superposition of the Lennard-Jones (12-6) potential and the averaged dipole—dipole attraction (the first term in the expansion of [7]). A similar procedure can be used for any Lennard-Jones n — 6 potential, i.e.,

$$\varphi(r) = \left(\frac{n}{6}\right)^{\frac{6}{n-6}} \left(\frac{n}{n-6}\right)\left(\frac{\varepsilon}{k}\right)_0 \left[r^{*-n} - r^{*-6} - \frac{y}{T_0^*} r^{*-6}\right]. \tag{8}$$

It is then readily shown that the potential of (8) amounts to a Lennard-Jones n — 6 model with the molecular-interaction potential dependent on temperature:

$$\sigma = \sigma_0\left(1 + \frac{y}{T_0^*}\right)^{-\frac{1}{n-6}}; \quad \left(\frac{\varepsilon}{k}\right) = \left(\frac{\varepsilon}{k}\right)_0 \left(1 + \frac{y}{T_0^*}\right)^{\frac{n}{n-6}};$$
$$y = \frac{2}{3}\left(\frac{n-6}{n}\right)\left(\frac{6}{n}\right)^{\frac{6}{n-6}} \frac{\mu^4}{k^2\sigma_0^6\left(\frac{\varepsilon}{k}\right)_0^2}. \tag{9}$$

Calculations have been performed [7] on the second and third nonadditive virial coefficients for certain polar gases in terms of the potential

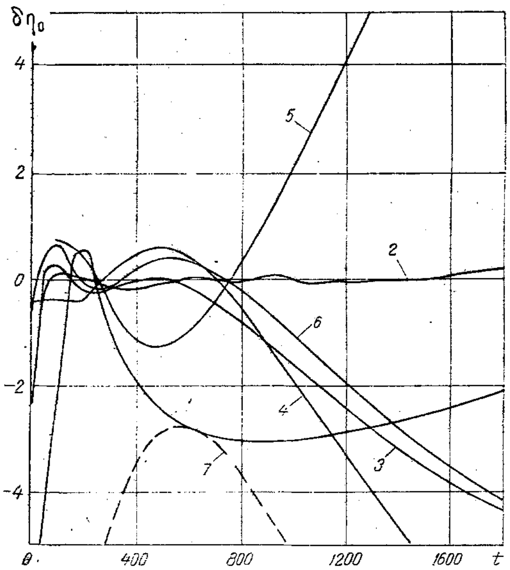

Fig. 1. Comparison of $\eta_0(T)$ given by [2] with results for various potentials: 1) L-J (9-6); 2) Keesom (9-6-6); 3) Keesom (15-6-6); 4) Keesom (15-6-6); 5) Stockmayer, $\delta^* = 2.5$; 6) potential of (10), $\alpha = 0.35$ Å^3; 7) Keesom (12-6-6) with the parameters of [6]; $\delta\eta_0$, %, t, °C.

$$\varphi(r) = 4\left(\frac{\varepsilon}{k}\right)_0 \left\{\left(1 + 0.56\,\frac{y^2}{T_0^{*3}}\right) r^{*-12} \left[1 + \frac{y}{T_0^*} + \frac{1}{2}\,\alpha^* (6\,y)^{\frac{1}{2}}\right] r^{*-6}\right\}. \tag{10}$$

The model of (10) incorporates not only the dipole — dipole attraction, but also dipole — dipole repulsion (second term in the expansion of [7]), as well as the interaction between a dipole and an induced dipole.

Some of the above potentials have never been used to calculate $\eta_0(T)$ for water vapor.

Table 1 gives the molecular-interaction potentials derived for models (5)-(8) and (10); the errors in the parameters are given on the assumption that there are no systematic errors. Note that the molecular-interaction potentials are strongly correlated (correlation coefficient about 1). Figure 1 shows the deviations of the calculated viscosity from the values given by (1) for the various molecular-interaction functions. The residuals of Φ (Table 1) indicate the performance in the description of measurements.

Figure 1 shows that the best results are obtained for the potential of (8) ($n = 9$) and (10) (with $\alpha = 0.35$ Å^3); in the case of the 9-6-6 potential, there is almost complete agreement between the theoretical values for $\eta_0(T)$ and (1) within the relevant region, and also on extrapolation to high temperatures (up to 1800°C). Figure 1 also shows that below 100°C there are systematic deviations for all the model potentials (although some of these deviations are small). However, these may be due not only to approximations used in the models, but also to errors in extrapolating from (1).

The following conclusions can thus be drawn:

1. The molecular-interaction potentials derived by modifying the Lennard-Jones model all share the disadvantage of having a potential well excessively narrow by comparison with the realistic potential [8], so they cannot reproduce with sufficient precision the behavior of $\eta_0(T)$ throughout the temperature range, which is seen in the unduly large energies at the equilibrium internuclear distances $(\varepsilon/k)_0$ (Table 1), namely, values large by comparison with those found from the virial coefficients [6], while the results for the dipole moment μ are less than the measured values.

2. Some molecular-interaction potentials, however, describe the measured $\eta_0(T)$ almost as well as the best interpolation formulas.

3. It is clear that measurements of various types must be employed in choosing the parameters of any particular potential, since the individual potentials are not equally dependent on the various kinetic or equilibrium parameters. However, it has been pointed out [1] that the results are of little significance in relation to

interpretations of molecular forces if the field for a polar gas is replaced by an effective symmetrical field. On the one hand, this is confirmed by our calculations for $\eta_0(T)$ for water vapor, including those with the molecular potentials of [6], which were derived from the p — V — T data (curve 7 of Fig. 1). The deviations from (1) are up to 3-5%, and they increase toward high and low temperatures. On the other hand, these deviations are comparatively small, so one can say that one gets reasonably satisfactory results within the framework of the Chapman — Enskog theory by using various types of experimental data with a reasonably realistic potential.

NOTATION

T, temperature; $\eta_0(T)$, zero-density dynamic viscosity; $T_{cr} = 647.27°K$; a_i, interpolation parameters for viscosity; $T^* = kT/\varepsilon$, reduced temperature; $W_j = 1/(\Delta\eta_{0j})^2$, statistical weight; $\Delta\eta_{0j} = \delta_{\eta_{0j}}\eta_{0j}$, absolute error; $\delta_{\eta_{0j}}$, relative error; σ, ε/k, μ, δ, α, parameters of potentials; $\Omega^{(2.2)*}(T^*)$, reduced collision integral; b_i, parameters of interpolation formula for collision integrals $\Omega^{(2.2)*}(T^*)$; $r^* = r/\sigma$, reduced internuclear distance; $\delta^* = \mu^2/[2(\varepsilon/k)_0\sigma_0]$, reduced dipole moment; $\gamma^* = 2a/\sigma_0$; $2a$, diameter of spherical core; $\delta^{**} = \delta^* G(\theta_1, \theta_2, \Phi)$; $G(\theta_1, \theta_2, \Phi) = 2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\Phi$, function incorporating the effects of dipole orientation; $T_0^* = T/(\varepsilon/k)_0$, reduced temperature; $\alpha^* = \alpha/\sigma_0^3$, reduced molecular polarizability.

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ACCURACY OF A ONE-DIMENSIONAL APPROXIMATION FOR DOUBLE RODS

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Limits of applicability of one-dimensional models in computing temperatures in two-layered rods are established on the basis of comparing the one-dimensional approximation with the exact two-dimensional solution.

To solve heat-conduction problems in cylindrical armature elements of constant and variable cross section, a one-dimensional approximation method is used. The one-dimensional approximation yields satisfactory results for homogeneous rods with low values of the Biot criterion [1]. The limits of a possible application of this method were established in [2] in an example of a solid homogeneous cylinder. Meanwhile, strict criteria for double rods consisting of heterogeneous materials are completely absent.

In order to establish admissible quantitative limits for the applicability of the one-dimensional approximation method for double rods, let us consider a cylinder consisting of heterogeneous materials with the coefficients of thermal conductivity λ_1 and λ_2. The cylinder is heated at the base and exchanges heat with the surrounding medium of temperature T_m via the side surface because of convection and radiation with a total constant coefficient of heat emission α. The end-face surface is considered heat-insulated, which is the

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