Force Constants for Polar Substances: Their Prediction from Critical Properties

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Stiel and Thodos (*11*) used a dimensional analysis approach to develop relationships for the Lennard-Jones force constants ϵ/κ and σ of nonpolar substances. These relationships can be expressed as

$$\frac{\epsilon}{\kappa} = 65.3\ T_c\ z_c^{18/5} \tag{1}$$

and

$$\sigma = 0.1866\ v_c^{1/3}/z_c^{6/5} \tag{2}$$

Equations (1) and (2) were found to reproduce more accurately Lennard-Jones force constants obtained from viscosity data than previously proposed relationships (3) which did not include as a variable the critical compressibility factor.

Relationships for the Lennard-Jones force constants are valuable for use with the following theoretical expressions for the transport properties of pure substances at atmospheric pressure:

$$\mu^* = 2.6693 \times 10^{-5} \frac{\sqrt{MT}}{\sigma^2\, \Omega^{(2,2)*}\,[T_N]} \tag{3}$$

$$k^* = 19.891 \times 10^{-5} \frac{\sqrt{T/M}}{\sigma^2\, \Omega^{(2,2)*}\,[T_N]} \tag{4}$$

$$\mathfrak{D}^* = 262.80 \times 10^{-5} \frac{\sqrt{T^3/M}}{\pi\sigma^2\, \Omega^{(1,1)*}\,[T_N]} \tag{5}$$

where the collision integrals $\Omega^{(1,1)*}[T_N]$ and $\Omega^{(2,2)*}[T_N]$ are tabulated functions of the normalized temperature $T_N = T/(\epsilon/\kappa)$.

For polar molecules the Stockmayer potential can be used as a model for the molecular interactions. This function is a superposition of the Lennard-Jones potential and the energy of dipole-dipole interactions:

$$\varphi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] - \frac{\mu_A\mu_B}{r^3}\zeta \tag{6}$$

where $\zeta = 2\cos\theta_A \cos\theta_B - \sin\theta_A \sin\theta_B \cos\varphi$ and μ_A and μ_B are the dipole moments of the two interacting molecules, and the angles θ_A, θ_B, and φ describe the relative orientation of the molecules. Monchick and Mason (7) assumed that the relative orientation of the molecules is fixed during a collision and that each such orientation is equally probable. These assumptions enable the use of spherically symmetrical potentials in the form of Equation (6), with the angular dependence of the dipole-dipole interaction ζ as a constant. They obtained collision integrals for use with Equations (3), (4), and (5), which are dependent not only on the normalized temperature but also on the reduced dipole energy modulus $\delta^* = \mu^2/2\epsilon\sigma^3$. Monchick and Mason (7) concluded that their use of the Stockmayer potential for polar gases gives as good results as the previous use of the Lennard-Jones potential for nonpolar gases. Therefore in the present study a dimensional analysis approach has been used to develop relationships between the force constants for the Stockmayer potential and the critical constants of the polar substance.

DIMENSIONAL ANALYSIS

In the development of relationships for the Lennard-Jones force constants of nonpolar substances Stiel and

Table 1. Stockmayer Force Constants, Critical Constants, and Deviations for Polar Gases Not Exhibiting Hydrogen Bonding

	z_c	T_c, °K.	v_c, cc./g.-mole	μ, debyes	δ^*	ϵ/κ, °K. Literature	Present study	% dev.	σ, Å Literature	Present study	% dev.
HCl	0.266	324.6	86.83	1.08	0.34	328	291	11.28	3.36	3.48	−3.57
HBr	—	363.2	—	0.80	0.14	417	326	21.82	3.41	—	—
HI	—	423.2	—	0.42	0.029	313	380	−21.40	4.13	—	—
SO_2	0.269	430.7	122.2	1.63	0.42	347	386	−11.24	4.04	3.90	3.46
H_2S	0.283	373.6	97.6	0.92	0.21	343	335	2.33	3.49	3.62	−3.72
NOCl	—	—	—	1.83	0.4	690	—	—	3.53	—	—
$CHCl_3$	0.293	536.6	238.8	1.01	0.07	355	481	−35.49	5.31	4.87	8.29
CH_2Cl_2	0.277	510.2	193	1.57	0.2	483	458	5.18	4.52	4.54	−0.44
CH_3Cl	0.276	416.3	143.0	1.87	0.5	414	373	9.90	3.94	4.11	−4.31
CH_3Br	0.361(?)	464 (?)	165	1.80	0.4	382	416	19.63	4.25	4.31	−1.41
C_2H_5Cl	0.274	460.4	199	2.03	0.4	423	413	2.36	4.45	4.58	−2.92
$(CH_3)_2O$	0.307	400.1	190.4	1.30	0.19	432	359	16.90	4.21	4.52	−7.36
$(C_2H_5)_2O$	0.261	467.2	280.8	1.15	0.08	362	419	−15.74	5.49	5.14	6.38
$(CH_3)_2CO$	0.238	508.7	212.7	2.88	0.06	549	456	16.94	4.50	4.68	−4.00
$CH_3COOC_2H_5$	0.254	506.9	227.9	1.72	0.2	418	455	8.85	5.04	4.80	4.76
CH_3COOCH_3	0.252	523.3	286.0	1.78	0.16	499	469	6.01	5.24	5.17	1.34
								13.67			4.00

Stockmayer force constants obtained from Monchick and Mason (7).

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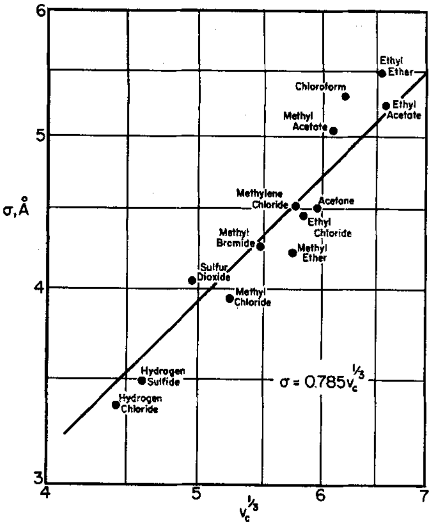

Fig. 1. Relationship between σ and $v_c^{1/3}$ for polar gases not exhibiting hydrogen bonding.

Thodos (*11*) assumed that ϵ/κ and σ are functions of only the molecular weight and critical constants of the substance. It has been shown that the critical compressibility factor is an appropriate variable representing the electrostatic properties of the polar molecules (*4, 10*). Therefore no additional variable such as the dipole moment is necessary in the treatment for the force constants ϵ/κ and σ for the Stockmayer potential, and the application of dimensional analysis to these quantities is the same as in the previous development for nonpolar substances in which the following equations resulted (*11*):

$$\frac{\epsilon}{\kappa} = \alpha \, T_c \, z_c^m \tag{8}$$

and

$$\sigma = \beta \, v_c^{1/3} \, z_c^n \tag{9}$$

TREATMENT OF DATA

The force constants for the Stockmayer potential obtained by Monchick and Mason (*7*) were used to establish the coefficients α and β and the exponents m and n of Equations (8) and (9). The data used in these calculations are presented in Tables 1 and 2. For the thirteen polar substances listed in Table 1 which do not exhibit hydrogen bonding, and for which all the critical properties were available, the collision diameter was found to be proportional to $v_c^{1/3}$ and essentially independent of z_c, as shown in Figure 1. The resulting relationship can be expressed analytically as follows:

$$\sigma = 0.785 \, v_c^{1/3} \tag{10}$$

Table 2. Stockmayer Force Constants and Critical Constants for Polar Gases Exhibiting Hydrogen Bonding

	z_c	T_c, °K.	v_c, cc./ g.-mole	μ, debyes	δ^*	ϵ/κ, °K.	σ, Å
NH_3	0.242	405.5	72.47	1.47	0.7	358	3.15
H_2O	0.231	647.4	56.31	1.85	1.0	775	2.52
CH_3OH	0.220	513.2	117.8	1.70	0.5	417	3.69
C_2H_5OH	0.248	516.2	166.9	1.69	0.3	431	4.31
n-C_3H_7OH	0.251	537.2	220.1	1.69	0.2	495	4.71
i-C_3H_7OH	0.278	508.8	219.3	1.69	0.2	518	4.64

Stockmayer force constants obtained from Monchick and Mason (*7*).

Collision diameters calculated from Equation (10) were found to have an average deviation of 4.0% from the corresponding reported values for the thirteen substances. Although slightly better agreement could be obtained by the introduction of the critical compressibility factor, the improvement was not considered to be sufficient to warrant the use of an additional variable.

Since ϵ/κ is very sensitive to small errors in σ and thus cannot be determined exactly, no attempt was made to relate this force constant directly to the critical temperature. Instead the product $\epsilon\sigma^3/\kappa$ was related to $T_c v_c$ as shown in Figure 2. The best straight-line relationship can be expressed analytically as follows:

$$\frac{\epsilon}{\kappa} \sigma^3 = 0.434 \, T_c v_c \tag{11}$$

This equation is very similar to those obtained previously for the Lennard-Jones force constants of nonpolar substances (*2, 11*). Equations (10) and (11) can be combined to produce the following relationship for ϵ/κ:

$$\frac{\epsilon}{\kappa} = 0.897 \, T_c \tag{12}$$

For the thirteen substances Equation (12) reproduced the reported temperature-force constants with an average deviation of 13.7%. It is surprising that for polar substances not exhibiting hydrogen bonding the force constants are virtually independent of z_c, as indicated by Equations (10) and (12). However this may be attributed to the fact that for these substances the collision integrals are dependent on an additional variable δ^* which accounts for the polarity of the molecules. Therefore the critical compressibility factor is not required to represent the electrostatic forces, while for nonpolar molecules the use of z_c is necessary to account for the varying sizes and shapes of the molecules. No correlation was found to exist between δ^* and z_c. Therefore a value of the dipole moment must be available before Equations (10) and (12) can be used with the collision integrals presented by Monchick and Mason (*7*) for the calculation of the transport properties of the substance. Equation (11) indicates that the following relationship can be used for the calculation of δ^*:

$$\delta^* = \frac{\mu^2}{0.868 \, \kappa \, T_c \, v_c} = 8{,}530 \frac{\mu^2}{T_c v_c} \tag{13}$$

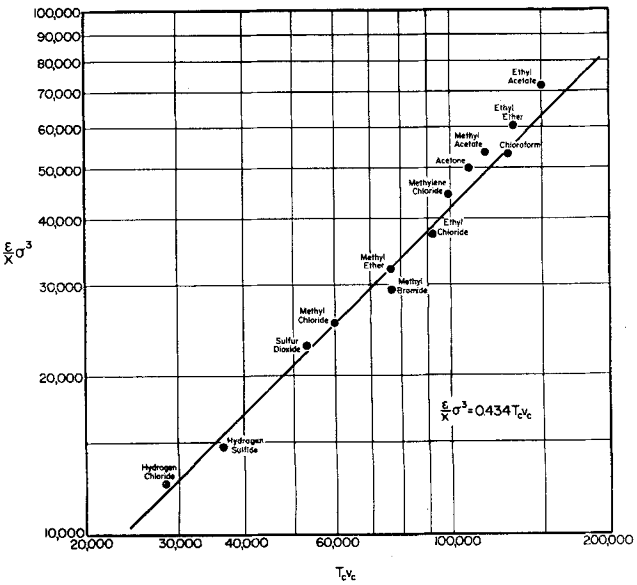

Fig. 2. Relationship between $\epsilon\sigma^3/\kappa$ and $T_c v_c$ for polar gases not exhibiting hydrogen bonding.

The assumption inherent in the Stockmayer potential that the molecules have point dipoles is too unrealistic for polar molecules exhibiting hydrogen bonding. Therefore for the calculation of the viscosity of these substances the following equation which was developed previously (*10*) should be used:

$$(\mu^*\xi)^{1.25} z_c = [7.55\, T_R - 0.55] \times 10^{-7} \tag{14}$$

where $\xi = T_c^{1/6}/M^{1/2}\, P_c^{2/3}$. For the calculation of other properties for which no alternate methods are available the following approximate relationships derived from the force constants reported by Monchick and Mason (*7*) for the six hydrogen bonded substances presented in Table 2 may be used:

$$\sigma = 36.9\, v_c^{1/3}\, z_c^{2.75} \tag{15}$$

and

$$\frac{\epsilon}{\kappa} = 0.003313\, T_c/z_c^4 \tag{16}$$

Thus it can be seen that for polar substances which exhibit hydrogen bonding the force constants are highly dependent on the critical compressibility factor.

CONCLUSIONS

Equations (10) and (12) can be used to calculate the viscosity and self-diffusivity at moderate pressures for polar substances not exhibiting hydrogen bonding from Equations (3) and (5). For polyatomic substances a correction factor has to be applied to Equation (4) for thermal conductivity to account for the internal degrees of freedom of the molecules. These correction factors are usually not applicable to polar substances whose thermal conductivities are anomalously low (*5*).

Binary-diffusion coefficients can be calculated from Equation (5) with $1/M = 1/M_A + 1/M_B$. For mixtures of nonpolar substances Equations (1) and (2) for the Lennard-Jones force constants may be used along with the combining rules

$$\left(\frac{\epsilon}{\kappa}\right)_{AB} = \left[\left(\frac{\epsilon}{\kappa}\right)_A \left(\frac{\epsilon}{\kappa}\right)_B\right]^{1/2} \tag{17}$$

and

$$\sigma = \frac{1}{2}\,[\sigma_A + \sigma_B] \tag{18}$$

The force constant resulting from Equation (17) is then used to determine values of the collision integral $\Omega^{(1,1)*}[T_N]$ for the Lennard-Jones potential.

For mixtures containing both a nonpolar and polar constituent the approach is identical (*6*) except that the force constants for the polar member should be estimated from Equations (10) and (12) or Equations (15) and (16). For binary mixtures of polar substances the force constants for the Stockmayer potential should be determined for each substance from Equations (10) and (12) or Equations (15) and (16). The force constants for the mixture resulting from Equations (17) and (18) and the reduced dipole energy modulus of the mixture (*6*)

$$\delta^*_{AB} = [\delta_A^*\ \delta_B^*]^{1/2} \left[\frac{(\sigma_A\, \sigma_B)^{1/2}}{\sigma_{AB}}\right]^3 \tag{19}$$

are then used to determine values of the collision integrals for the Stockmayer potential $\Omega^{(1,1)*}[T_N, \delta^*_{AB}]$, presented by Monchick and Mason (*7*). The use of Equations (7) and (18) for mixtures of this type neglects the contribution of the induction energy due to dipole-induced dipole interaction, which is usually small (*6*). These methods for the calculation of binary-diffusion coefficients should be preferable to the use of the relationships presented by Chen and Othmer (*1*) for binary diffusion coefficients, since they utilized dimensionally inconsistent relationships for force constants for the Lennard-Jones potential for both nonpolar and polar substances.

Stockmayer force constants have also been determined from experimental second-virial coefficient data for several polar gases (*9*). In these calculations the reduced dipole energy modulus was taken as $\delta^*/\sqrt{2}$, and the force constants presented in Tables 1 and 2 do not agree with those resulting from the second-virial coefficient data. However Monchick and Mason (*7*) have shown that fair agreement exists between experimental second virial coefficients and values calculated with Stockmayer force constants obtained from viscosity data.

The use of the relationships developed in this study for the calculation of the transport properties of polar substances is illustrated in the following example:

Calculate the viscosity of methyl propionate at atmospheric pressure and 100°C. For methyl propionate $T_c = 519.7$°K., $v_c = 298$ cc./g. mole, $M = 88.10$, and $\mu = 1.73$ debyes.

From Equation (10) σ is calculated to be 5.24Å for methyl propionate. Similarly from Equation (12) ϵ/κ is determined to be 413.5°K. for this substance. These values produce a value of the reduced dipole energy modulus of $\delta^* = \mu^2/2\epsilon\sigma^3 \doteq 0.165$. Also at 100°C. $T/(\epsilon/\kappa) = 393.2/413.5 = 0.800$. At these conditions, the reduced collision integral for the Stockmayer potential is determined to be 1.79 from the tabulation of Monchick and Mason (*7*). The viscosity is then calculated from Equation (3):

$$\mu^* = 2.6693 \times 10^{-5} \frac{\sqrt{MT}}{\sigma^2\, \Omega^{(2,2)*}[T_N, \delta^*]} =$$

$$2.6693 \times 10^{-5} \frac{\sqrt{(88.10)\,(373.2)}}{(5.24)^2\,(1.79)} = 983 \text{ g./cm. sec.}$$

For this temperature Pochettino (*8*) reported a value of 945 g./cm. sec. for methyl propionate.

NOTATION

k^* = thermal conductivity at atmospheric pressure, cal./sec. cm. °K.
m, n = exponents in Equations (8) and (9)
M = molecular weight
P_c = critical pressure, atm.
r = intermolecular separation, Å
R = gas constant, 82.055 cc. atm./g.-mole °K.
T = temperature, °K.
T_c = critical temperature, °K.
T_N = normalized temperature, $T/\dfrac{\epsilon}{\kappa}$
T_R = reduced temperature, T/T_c
v_c = critical volume, cc./g.-mole
z_c = critical compressibility factor, $P_c v_c/RT_c$

Greek Letters

α = coefficient in Equation (8)
β = coefficient in Equation (9)
δ^* = reduced dipole energy modulus, $\mu^2/2\epsilon\sigma^3$
$\mathcal{D}^*$ = self-diffusivity, sq. cm./sec.
ϵ = maximum energy of attraction, erg.
ζ = angle dependent term of dipole-dipole interaction
θ = angles of inclination of the axes of the two dipoles to the line joining the centers of the molecules
κ = Boltzmann constant, 1.3805×10^{-6} erg./°K.
μ = dipole moment of molecule, debyes
μ^* = viscosity of gases at moderate pressures, g./cm. sec.

ξ = viscosity parameter, $T_c^{1/6}/M^{1/2}\,P_c^{2/3}$
π = pressure, atm.
σ = collision diameter, Å
φ = azimuthal angle between the axes of the two dipoles
$\varphi(r)$ = Stockmayer potential, Equation (6)
$\Omega^{(1,1)*}[T_N]$ = reduced collision integral for the Lennard-Jones potential
$\Omega^{(2,2)*}[T_N]$ = reduced collision integral for the Lennard-Jones potential
$\Omega^{(1,1)*}[T_N, \delta^*]$ = reduced collision integral for the Stockmayer potential
$\Omega^{(2,2)*}[T_N, \delta^*]$ = reduced collision integral for the Stockmayer potential

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A Numerical Method for the Solution of the Energy Equation for Steady Turbulent Heat Transfer

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A method is presented for solving the basic energy expression for the temperature distribution for turbulent heat transfer in a circular conduit with a digital computer. The method assumes a knowledge of the velocity distribution, the eddy conductivity term as a function of the radial position, and a constant wall temperature. For illustrative purposes only a dimensionless expression is derived from Reichardt's relationship which gives the eddy conductivity term as a function of radial position with Reynolds and Prandtl numbers as parameters.

Incorporated in the computer program is Richardson's three-point extrapolation formula which permits the determination of a more accurate eigenvalue from three previously computed values which were obtained by using three different values of the reduced radial increment. Agreement with the Crank-Nicholson method is quite good, although the method with eigenvalues is considered to be superior. Eigenvalues determined from the analytical solution of the energy expression for the laminar flow case and those computed by the numerical method are in excellent agreement. This is indicative of the accuracy and reliability of the proposed numerical method.

In heat transfer studies involving the transfer of heat to or from fluids flowing in circular conduits it has always been of interest to be able to solve the appropriate energy expression for the temperature distribution or profile in both laminar and turbulent flow regions. The energy equation in cylindrical coordinates can be written for the turbulent flow condition as

$$\rho\, C_p\, u \frac{\partial T}{\partial y} = \frac{1}{r}\frac{\partial}{\partial r}\left[r(k + k_E)\frac{\partial T}{\partial r}\right] \tag{1}$$

or as

$$u \frac{\partial T}{\partial y} = \frac{1}{r}\frac{\partial}{\partial r}\left[r\,(\alpha + \alpha_E)\frac{\partial T}{\partial r}\right] \tag{1a}$$

where

$$\alpha = \frac{k}{\rho\, C_p}$$

$$\alpha_E = \frac{k_E}{\rho\, C_p}$$

Equation (1*a*) can be expressed in dimensionless form as

$$U\frac{\partial \theta}{\partial Z} = \frac{2}{X}\frac{\partial}{\partial X}\left[X\,\epsilon\,\frac{\partial \theta}{\partial X}\right] \tag{2}$$

where the following dimensionless groups have been used:

$$\theta = \frac{T_w - T}{T_w - T_o};\quad U = \frac{u}{\bar{u}};\quad Z = \frac{L\alpha}{\bar{u}\,R^2} = \frac{2L}{N_{Re}\,N_{Pr}\,D}$$

$$X = \frac{r}{R};\quad \epsilon = \frac{\alpha + \alpha_E}{\alpha} = 1 + \frac{\alpha_E}{\alpha}$$

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