Some Properties of Polar Substances: A Survey

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The current understanding of the macroscopic (bulk) properties of polar substances in terms of molecular theory, or the correlation of them in terms of corresponding-states principles is summarized.

Some electrical properties of molecules are defined, and the way in which they contribute to the intermolecular force field is indicated. Then the calculation of the bulk properties for various molecular models is summarized, and finally some of the recent proposals for corresponding-states correlations are discussed, with particular emphasis on the polar compounds.

Polar substances are those consisting of molecules which possess a permanent dipole moment. It should be noted, however, that many polar molecules are rather complex and that consequently their physical properties are dependent on a number of molecular properties: (*a*) the dipole moment, (*b*) the quadrupole and higher multipole moments, (*c*) the polarizability, (*d*) the shape, and (*e*) the tendency to form hydrogen bonds. Hence methods of prediction and correlation of physical properties of polar molecules which involve only the dipole moment must be regarded from the very outset as oversimplifications.

SOME ELECTRICAL PROPERTIES OF MOLECULES

A continuous distribution of electronic charge such as that shown in Figure 1 is considered. The charge density is given by $\rho(\mathbf{R})$. The first three multipole moments are

$$C = \int \rho \, d\mathbf{R} \tag{1}$$

= electric charge (a scalar)

$$\boldsymbol{\mu} = \int \rho\mathbf{R} \, d\mathbf{R} \tag{2}$$

= electric dipole moment (a vector with components μ_x, μ_y, μ_z).

$$\boldsymbol{\Theta} = \int \rho\mathbf{RR} \, d\mathbf{R} \tag{3*}$$

= electric quadrupole moment (a second-order tensor with nine components

$\Theta_{xx}, \Theta_{yy}, \Theta_{zz}, \Theta_{xy} = \Theta_y$, etc.)

in which the integrals are all taken over the entire charge distribution. According to Equation (1) the total charge is just the integral over the charge density. The dipole moment is the first moment of the charge distribution; the strength of the dipole of the distribution is given by the scalar value $\mu = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2}$. For the quadrupole moment a second definition is frequently used:

$$\begin{aligned} \mathbf{Q} &= \int \rho(3\mathbf{RR} - R^2\mathbf{U}) \, d\mathbf{R} \\ &= 3\boldsymbol{\Theta} - (\Theta_{xx} + \Theta_{yy} + \Theta_{zz})\mathbf{U} \end{aligned} \tag{4}$$

Hence this traceless quadrupole moment bears a simple relation to the quadrupole moment defined in Equation (3). For a linear charge distribution along the z axis or for a charge distribution symmetric about the z axis $Q_{xz} = Q_{yz} = Q_{xz} = 0$, and $Q_{xx} = Q_{yy} = -Q_{zz}/2$. The scalar quantity $Q_{zz} \equiv Q$ is then referred to as the strength of the quadrupole. Other definitions of the quadrupole moment are also used (*13*).

The multipole moments arise in the calculation of the electrostatic potential at a point r resulting from a continuous charge distribution. The contribution to the electrostatic potential dV_e , because of the interaction of a unit test charge at $\mathbf{r}$ with an infinitesimal element $\rho \, d\mathbf{R}$ of the distribution, is, according to Coulomb's law,

$$dV_e = \frac{\rho \, d\mathbf{R}}{|\mathbf{r} - \mathbf{R}|} = \frac{\rho(X, Y, Z) \, dX \, dY \, dZ}{\sqrt{(x - X)^2 + (y - Y)^2 + (z - Z)^2}} \tag{5}$$

The square-root expression can be expanded in a Maclaurin series about the origin ($\mathbf{R} = 0$) to give

$$\begin{aligned} dV_e = \rho \, d\mathbf{R}\Bigg[\frac{1}{\mathbf{r}} &- \left(\mathbf{R}\cdot\nabla \frac{1}{r}\right) \\ &+ \tfrac{1}{2}\left(\mathbf{RR}:\nabla\nabla \frac{1}{r}\right) - \cdots\Bigg] \end{aligned} \tag{6}$$

Integration over the entire charge distribution gives the potential resulting from the distribution

$$\begin{aligned} V_e = &\left(\int \rho \, d\mathbf{R}\cdot\frac{1}{r}\right) \\ &- \left(\int \rho\mathbf{R} \, d\mathbf{R}\cdot\nabla \frac{1}{r}\right) \\ &+ \tfrac{1}{2}\left(\int \rho\mathbf{RR} \, d\mathbf{R}:\nabla\nabla \frac{1}{r}\right) - \cdots \end{aligned} \tag{7}$$

The integrals which arise are then just the multipole moments, so that Equation (7) can be written in one of two forms:

$$\begin{aligned} V_e = C\cdot\frac{1}{r} &- \left(\boldsymbol{\mu}\cdot\nabla \frac{1}{r}\right) \\ &+ \tfrac{1}{2}\left(\boldsymbol{\Theta}:\nabla\nabla \frac{1}{r}\right) - \cdots \end{aligned} \tag{8}$$

$$\begin{aligned} V_e = \frac{C}{r} &+ \frac{(\boldsymbol{\mu}\cdot\mathbf{r})}{r^3} \\ &+ \tfrac{1}{2}\frac{(\mathbf{Q}:\mathbf{rr})}{r^5} + \cdots \end{aligned} \tag{9}$$

The general expressions for the electric potential at points within and without charge distributions (both continuous and discrete) and the general expressions for the interaction energy between two arbitrary charge distributions (both overlapping and nonoverlapping) are given elsewhere (*13*). The electric field associated with V_e is then given by $\mathbf{E} = -\nabla V_e$.

The physical significance of Equation (9) is that the potential due to a charge distribution is given by a superposition of (a) potential due to a point charge + (b) the potential due to a point dipole + (c) the potential due to a point quadrupole + etc., each of these point multipoles being located at the origin. For a neutral molecule, then, the dipole moment gives the first approximation to the electrostatic field surrounding the molecule. Until recently little has been done in connection with the examination of the role of the quadrupole in intermolecular force fields and bulk properties.

The polarizability of a molecule is a second-order tensor describing the extent to which the electron cloud becomes distorted in an electric field. If the molecule is placed in an electric field of strength $\mathbf{E}$, then an induced dipole moment is produced:

$$\boldsymbol{\mu}^{(ind)} = (\boldsymbol{\alpha}\cdot\mathbf{E}) \tag{10}$$

In many calculations it is assumed that the molecule is isotropic, so that the polarizability may be regarded as a scalar. In such instances the scalar value of the polarizability is usually defined as the arithmetic average of the three principal components of the polarizability: $\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$.

Extensive tables of dipole moments (*19, 30*) and polarizabilities (*19*) are available. Very little information is available about molecular quadrupole moments; what little is known has been obtained from molecular orbital calculations (*8*), broadening of microwave spectra (*10, 11*), and second virial-coefficient calculations (*27*). It is possible that pressure-induced absorption measurements may be another source of information (*29*).

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*For example

$$\Theta_{xy} = \iiint\limits_{\substack{\textit{volume of} \\ \textit{charge dist.}}} \rho(X, Y, Z)XY \cdot dX \, dY \, dZ \tag{4}$$

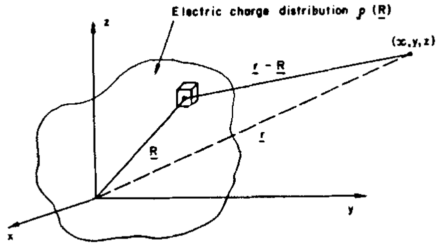

Fig. 1. Calculation of electrostatic potential V_e at position r. It is assumed in the text that $|r| > |R|_{max}$.

FORCES BETWEEN POLAR MOLECULES

Extensive discussions of intermolecular forces are given elsewhere (*13a*). Here the important contributions to the interaction energy between two neutral polar molecules which are chemically alike are briefly summarized. It is assumed that the electronic distribution is symmetrical about the z axis, so that the quadrupole can be described by the single scalar Q, and that the molecules are isotropic, so that the polarizability is given by the single scalar α.

It is convenient (but also artificial) to subdivide the contributions to the intermolecular potential energy into the following types:

Short-Range Forces

When molecules are very close, they generally repel one another quite strongly. The detailed dependence of this energy on intermolecular distance and orientation is complex, and the details have been calculated for only very simple systems. Generally the interaction energy is approximated by a simple exponention or inverse power function just because further details are lacking:

$$\phi^{(s.r.)} \approx b \exp(-ar) \text{ or } \approx d/r^n \quad (11)$$

with n usually between 9 and 15.

Long-Range Forces

The electrostatic contributions to the energy of interaction are the interactions of the various permanent multipoles (See Figure 2 for the definition of angles):

$$\phi^{(\mu,\mu)} = -(\mu^2/r^3)(2c_1c_2 - s_1s_2c) \quad (12)$$

$$\phi^{(\mu,Q)} = -(3/4)(\mu Q/r^4) \cdot (c_1 - c_2)(2s_1s_2c - 3c_1c_2 - 1) \quad (13)$$

$$\phi^{(Q,Q)} = +(3/16)(Q^2/r^5) \cdot [1 - 5c_1^2 - 5c_2^2 - 15c_1^2c_2^2 + 2(s_1s_2c - 4c_1c_2)^2] \quad (14)$$

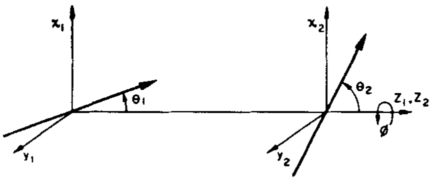

Fig. 2. Angles used to described mutual orientation of two dipoles or two symmetry axes. In the text the following abbreviations are used: $c_1 = \cos\theta_1$, $s_1 = \sin\theta_1$, $c = \cos(\phi_2 - \phi_1)$.

Equation (12) represents the interaction energy of two ideal dipoles; deviations because of the finite size of a dipole are discussed elsewhere (13). Equation (13) represents the electrostatic interaction between two charge distributions each having a permanent dipole and a permanent quadrupole.

The induction contributions arise because the permanent multipoles in one molecule induce multipole moments in the other molecule, and then these interact with one another:

$$\phi^{(\mu,ind\mu)} = -(1/2)(\mu^2\alpha/r^6)(3c_1^2 + 3c_2^2 + 2) \quad (15)$$

$$\phi^{(\mu Q,ind\mu)} = -6(\mu Q\alpha/r^7)(c_1^3 + c_2^3) \quad (16)$$

$$\phi^{(Q,ind\mu)} = -(9/32)(Q^2\alpha/r^8) \cdot (s_1^4 + s_2^4 + 4c_1^4 + 4c_2^4) \quad (17)$$

Equation (15) represents the interaction energy of two molecules with permanent rigid dipole moments which produce an instantaneous induced dipole moment with which they interact; if the distortion of the permanent dipoles is accounted for, then an additional term proportional to $\mu^2\alpha^2/r^9$ must be introduced (*3*, *9*). Equations (16) and (17) are contributions to the intermolecular potential energy when permanent quadrupoles participate in the induction effects.

The dispersion contributions, which may be explained quantum mechanically, are attractive forces arising because of instantaneous mutually induced moments. These contributions have the following form for simple molecules:

$$\phi^{(ind\mu,ind\mu)} = -c'/r^6 \quad (18)$$

$$\phi^{(ind\mu,indQ)} = -c''/r^8 \quad (19)$$

$$\phi^{(indQ,indQ)} = -c'''/r^{10} \quad (20)$$

These forces occur between molecules which have no permanent multipole moments. The forms given here are for spherical molecules [for nonspherical molecules see (*13*)].

On the basis of the various contributions summarized above a number of molecular models, listed in Table 1. have been proposed. These models can be divided into two general classifications: rigid molecules to which multipoles are added and Lennard-Jones (6–12) molecules to which multipole interactions are added.

MOLECULAR CALCULATIONS OF PHYSICAL PROPERTIES

The theory of the equation of state of moderately dense gases has been worked out in detail for molecules with angular dependent potential functions (*13b*). Hence formulas are available for the calculation of the virial coefficients, but these involve manifold integrals which require considerable effort to evaluate. The second virial coefficient has been evaluated for all the models listed in Table 1, the details being given in the publications referred to there. The third virial coefficient has been calculated only for the Stockmayer potential (*26*). The second virial coefficients for all the rigid models listed in Table 1 may be written in the form

$$B = \tfrac{2}{3}\pi N\sigma_0^3 \cdot \sum_{h=0}^{\infty}\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}\sum_{k=0}^{\infty} B_{hijk} \cdot \left(\frac{\mu^2}{\sigma_0^3kT}\right)^h \left(\frac{Q^2}{\sigma_0^5kT}\right)^i \left(\frac{\alpha}{\sigma_0^3}\right)^j (x)^k \quad (21)$$

TABLE 1. MOLECULAR MODELS FOR POLAR-POLAR INTERACTIONS

Electrical characteristics	Rigid molecules	Lennard-Jones (6–12) molecules
Embedded point dipoles (nonpolarizable)	Keesom I (*15*) Rigid spheres of diameter σ_0 with $\phi = \phi^{(\mu,\mu)}$ for $r > \sigma_0$	Stockmayer (*28*) $\phi = \phi^{(L.J.)} + \phi^{(\mu,\mu)}$
Embedded point dipoles (polarizable)	Falkenhagen (*9*) Rigid spheres of diameter σ_0 with $\phi = \phi^{(\mu,\mu)} + \phi^{(\mu,ind\mu)} + (\mu^2\alpha^2/r^9)(-8c_1c_2 + s_1s_2c)$	Buckingham and Pople I (*3*) $\phi = \phi^{(L.J.)} + \phi^{(\mu,\mu)} + \phi^{(\mu,ind\mu)} + (\mu^2\alpha^2/r^9)(-8c_1c_2 + s_1s_2c)$
Embedded point linear quadrupoles (nonpolarizable)	Keesom and Van Leeuwen (*16*, *17*) Rigid spheres of diameter σ_0 with $\phi = \phi^{(Q,Q)}$ for $r > \sigma_0$	
Embedded point linear quadrupoles (polarizable)	Keesom II (*18*) Rigid spheres of diameter σ_0 with $\phi = \phi^{(Q,Q)} + \phi^{(Q,ind\mu)}$ for $r > \sigma_0$	
Embedded point dipoles and quadrupoles (nonpolarizable)		Rowlinson (*27*) $\phi = \phi^{(L.J.)} + \phi^{(\mu,\mu)} + \phi^{(\mu,Q)}$ Buckingham and Pople II (*3*) $\phi = \phi^{(L.J.)} + \phi^{(\mu,\mu)} + \phi^{(\mu,Q)} + \phi^{(Q,Q)}$
Embedded point dipoles in nonspherical molecules (nonpolarizable)	Muckenfuss, Curtiss, and Bird (*22*) Rigid ellipsoids of revolution with symmetry axis σ_0, and other axes σ_1; eccentricity $x = [1 - (\sigma_1/\sigma_0)^2]^{\frac{1}{2}}$ Interact according to $\phi = \phi^{(\mu,\mu)}$.	Buckingham and Pople III (*3*) $\phi = \phi^{(L.J.)} + \phi^{(\mu,\mu)} + 4D\epsilon(\sigma/r)^{12}(3c_1^2 + 3c_2^2 - 2)$ in which D is a dimensionless parameter

TABLE 2. TABULATION OF EXPANSION COEFFICIENTS B_{hijk} FOR CALCULATION OF THE VIRIAL COEFFICIENTS FOR VARIOUS RIGID MODELS

B_{h0j0}—Coefficients for Keesom I and Falkenhagen models

h \ j	0	1	2	3	4
0	1	0	0	0	0
1	0	−4	0	0	0
2	−1/3	0	−3.27	0	0
3	0	−0.533	0	−4.93	0
4	−1/75	0	−0.920	0	−9.47

B_{h00k}—Coefficients for Keesom I and Muckenfuss-Curtiss-Bird models

h \ k	0	2	4
0	1	−1	1/15
2	−1/3	−4/15	−26/105
4	−1/75	−17/525	−151/3675

B_{0ij0}—Coefficients for Keesom-Van Leeuwen and Keesom II models

i \ j	0	1
0	1	0
1	0	−9/20
2	−3/80	0
3	+9/7840	−27/1600
4	−639/1066240	. . .

the values of the coefficients B_{hijk} being given in Table 2. This table can be used for estimating the order of magnitude of the various effects considered. The extensive tables needed for calculating B for the modified Lennard-Jones models can be found in the original references; the same dimensionless groups appear as in Equation (21). Although quite a bit of work has been done on second virial coefficients, no calculations at all have been made for the equation of state of polar liquids.

A usable theory of transport porperties of dilute and dense gases has been worked out only for molecules with spherically symmetrical potential functions. Hence it is not at present possible to make any rigorous calculations of the transport properties. The only calculations which have been made are for the Krieger potential (*13c*), which is $\phi = \phi^{(L.J.)} - 2(\mu^2/r^3)$; this is a spherically symmetric potential function, in which the angle-dependent dipole-dipole interaction is approximated by the maximum value of the function, that is the value corresponding to perfect alignment of the dipoles. This potential is however so unrealistic that the integral for the second virial coefficient does not converge; hence there is no possibility of interrelating transport coefficients and equation of state in terms of the parameters of the Krieger potential. The only moderately successful molecular calculation method involving polar gases is one for the calculation of the coefficient of binary diffusion for a polar-nonpolar binary mixture (*13d*). Nothing seems to have been done along the line of developing even a rough theory for the transport coefficients of polar liquids.

In addition to the above-mentioned properties there are also molecular theories for some electrical and optical properties, and ultimately these theories coupled with experimental measurements should lead to information about intermolecular forces. Of interest are recent publications on the second dielectrical virial coefficient (*2*), the second refractivity virial coefficient (*5*), and a virial development of the pressure-induced absorption in homopolar diatomic gases (*29*).

CORRESPONDING-STATES CORRELATIONS

From the previous section it is clear that only for the second virial coefficient have practical results been obtained. And at the present the amount of accurate equation-of-state data for polar molecules is so small that it is not possible to make meaningful deductions in terms of the various molecular models proposed.

Hence one is led to explore the possibility of correlating physical properties by means of dimensional analysis or corresponding-states methods. First the equation of state of a substance which is made up of molecules which interact according to a potential function which contains a length parameter σ, an energy parameter ϵ, the electrical properties α, μ, and Q, and some shape factor will be considered. Then the pressure will depend on two state variables, all the molecular parameters, the molecular mass, and also on Planck's constant:

$$p = p(V, RT, \sigma, \epsilon, \mu, Q, \alpha, x, m, h) \qquad (22)$$

According to the Buckingham Pi-Theorem of dimensional analysis a possible functional relationship between these various quantities is the dimensionless relationship

$$pV/RT = Z(V/\sigma^3, RT/\epsilon, \mu^2/\epsilon\sigma^3, Q^2/\epsilon\sigma^5, \alpha/\sigma^3, h/\sigma\sqrt{m\epsilon}, x) \qquad (23)$$

It is not at present possible to use this relation as a basis for correlation of experimental data for polar molecules because of lack of information about the molecular parameters and the electrical properties. For simple molecules (with negligible effect of μ, Q, α, and x) this relation reduces to the quantum mechanical principle of corresponding states which enabled de Boer and his collaborators to predict many of the physical properties of He³; the group containing h is important only for correlating quantum deviations at very low temperatures (*7*) and is not further discussed here.

Because of the lack of information about molecular force parameters, another possibility is to use the macroscopic quantities V_c and RT_c as units of volume and energy (instead of σ^3 and ϵ). In that case a similar dimensional analysis leads to

$$pV/RT = Z(V/V_c, T/T_c, \mu^2/V_cRT_c, Q^2/V_c^{5/3}RT_c, \alpha/V_c, x) \qquad (24)$$

A correlation more or less of this form was used by Hall and Ibele (*12*), who presented a graph including the effect of the reduced dipole moment (but neglecting the explicit dependence on Q, α, and x, which are, however, included implicitly in the critical constants). These forms of the principle of corresponding states have been fully discussed by Nelson and Obert (*23*).

Corresponding-states correlations based on Equation (24) have not been pushed very var because very little is known about the quadrupole and higher moments and extensive accurate experimental data are needed to sort out the dependence on the various groups. Hence in recent years there has been a flurry of activity in connection with modified principles of corresponding states in which a single characterizing parameter is used in addition to the reduced-state variables; that is, for the equation of state the two most widely proposed principles are

$$pV/RT = Z(p/p_c, T/T_c, Z_c)$$

in which (25)

$$Z_c = p_cV_c/RT_c$$

$$pV/RT = Z(p/p_c, T/T_c, Y_c)$$

in which (26)

$$Y_c = \left(\frac{d \ln p_{vap}}{d \ln T}\right)_{T=T}$$

The first of these was suggested by Meissner and Seferian (*21*) and was used to prepare extensive tables by Lydersen, Greenkorn, and Hougen (*20*). The second has been used extensively by Riedel (*25*) and is very similar to correlating procedures suggested by Pitzer and colleagues (*6*, *24*). Because the parameters Z_c and Y_c do not seem to be simply related (*20a*) a method employing both of these parameters has recently been developed by Hirschfelder, Buehler, McGee, and Sutton (*14*). Equation (25) states that one needs a separate compressibility-factor chart with Z as a function of p/p_c and T/T_c for each value of Z_c (the latter quantity varies from about 0.21 to 0.30 for various substances). When the available equation-of-state data are presented in this way, the resulting charts enable one to predict compressibility data for a wide variety of polar and nonpolar substances to within about 5%. Equation (26) leads to similar satisfying results.

Clearly these types of corresponding-states correlations may be applied to various other physical properties. The authors (*1*) have shown that the surface-tension data for a large number of polar and nonpolar substances are summarized by the equations

$$\frac{\gamma}{p_c^{\frac{2}{3}}T_c^{\frac{1}{3}}} = \left(-0.951 + \frac{0.432}{Z_c}\right) \cdot\left(1 - \frac{T}{T_c}\right)^{11/9} \qquad (27)$$

$$\frac{\gamma}{p_c^{\frac{2}{3}}T_c^{\frac{1}{3}}} = (-0.281 + 0.133\,Y_c) \cdot\left(1 - \frac{T}{T_c}\right)^{11/9} \qquad (28)$$

For eighty-four chemical compounds studied, the average error of Equation (27) is about 6% and that of Equation (28) about 3%. Similar expressions (with different choices of the reduced variables) have been proposed by Riedel (*25*) and by Curl and Pitzer (*6*).

For thermal conductivity of liquids at atmospheric pressure (where presumably the dependence on p/p_c is negligible) Riedel (*25*) has arrived at

$$\frac{\lambda}{p_c^{\frac{1}{2}}/V_0^{\frac{1}{6}}M^{\frac{1}{2}}} = (-0.128 + 0.028\,Y_c) \cdot\left[1 + 6.7\left(1 - \frac{T}{T_c}\right)^{\frac{2}{3}}\right] \qquad (29)$$

which shows the use of the correlating parameter. No similar relations seem to have been proposed for viscosity or diffusion.

These various correlation schemes with Z_c and Y_c used apply rather well to substances which are not extremely polar and which do not exhibit hydrogen bonding. Furthermore they enable one, by summarizing the experimental data in dimensionless form, to indicate to the experimentalist in what ranges of reduced variables further measurements are most urgently needed. The usefulness of these correlations in engineering design cannot be denied, but it should be noted that they give no new information regarding the physical or chemical processes involved. Certainly increased attention to the molecular theories of polar substances should be encouraged.

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NOTATION

B = second virial coefficient
B_{hijk} = expansion coefficients in Equation (21)
C = total charge
c, c_1, c_2 = cosines of angles in Figure 2
$\mathbf{E}$ = electric field strength
h = Planck's constant
k = Boltzmann's constant
m = molecular mass
M = molecular weight
N = Avogadro's number
p, p_c = pressure, critical pressure
Q = quadrupole moment
R = gas constant
$\mathbf{R}$ = position vector for element of charge
s_1, s_2 = sines of angles in Figure 2
T, T_c = temperature, critical temperature
V, V_c = volume, critical volume, per mole
V_e = electrostatic potential
V_0 = molar volume at absolute zero
x = eccentricity of ellipsoid
Y_c = Riedel's parameter
Z = compressibility factor
Z_c = critical compressibility factor

Greek Letters

α = polarizability
γ = surface tension
ϵ, σ = parameters in potential function
$\boldsymbol{\Theta}$ = quadrupole tensor
λ = thermal conductivity
μ = permanent dipole moment
$\mu^{(ind)}$ = induced dipole moment
ρ = electric charge distribution
σ_0 = diameter of rigid sphere
ϕ = potential function
$\phi^{(L.J.)}$ = $4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ = Lennard-Jones (6–12) potential

Vector and Tensor Notation

$\mathbf{r}$ = position vector with components x, y, z and length $r = \sqrt{x^2 + y^2 + z^2}$
$\mathbf{R}$ = position vector with components X, Y, Z, and length $R = \sqrt{X^2 + Y^2 + Z^2}$
$(\boldsymbol{\mu}\cdot\mathbf{r})$ = $\mu_x x + \mu_y y + \mu_z z$
$(\mathbf{Q} : \mathbf{rr})$ = $Q_{xx}x^2 + Q_{yy}y^2 + Q_{zz}z^2 + 2Q_{xy}xy + 2Q_{xz}xz + 2Q_{yz}yz$ (for symmetrical $\mathbf{Q}$)
$(\boldsymbol{\alpha}\cdot\mathbf{E})_x$ = $\alpha_{xx}E_x + \alpha_{xy}E_y + \alpha_{xz}E_z$
$\mathbf{U}$ = unit tensor ($U_{xx} = U_{yy} = U_{zz} = 1$, all other components are zero)

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