1978

Transport Properties of Binary Mixtures of Dense Hard-Sphere Fluids.

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Louisiana State University and Agricultural & Mechanical College

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MCELHANNON, WILLIAM ANDREW, JR.
TRANSPORT PROPERTIES OF BINARY MIXTURES OF
DENSE HARD-SPHERE FLUIDS.

THE LOUISIANA STATE UNIVERSITY AND
AGRICULTURAL AND MECHANICAL COL., PH.D., 1978

University
Microfilms
International
300 N. ZEEB ROAD, ANN ARBOR, MI 48106
TRANSPORT PROPERTIES OF
BINARY MIXTURES OF DENSE
HARD-SPHERE FLUIDS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctorate of Philosophy

in

The Department of Chemical Engineering

by

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B.S., Louisiana State University, 1972
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December 1978
ACKNOWLEDGMENT

I should like to thank my major professor, Dr. D. McLaughlin for his direction which was a *sine qua non* for this dissertation. Also due for thanks are Hazel LaCoste, who untied more than one bureaucratic knot for me, and my typists, Linda Oxford and Kay Owens.

The National Science Foundation provided a fellowship which helped to support this work and I thank them.

Finally, I would like to thank my family, parents and three sisters, whose encouragement, prodding and occasional nagging are in large part responsible for my having this opportunity to get even in print.

*Ad astra per aspirin.*
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f_{ij} \quad - \text{Mayer f-bond}

f \quad - \text{distribution function after molecular collision}

G \quad - \text{Gibb's free energy}

g^{(i)} \quad - \text{radial distribution function}

\dot{G} \quad - \text{mass average velocity of two colliding molecules}

H \quad h \quad - \text{Planck's constant}

H \quad - \text{enthalpy}

\mathbf{I} \quad I \quad - \text{identity tensor}

\mathbf{J} \quad J \quad - \text{heat flux vector}

\dot{J}_{q} \quad - \text{molar flux vector of species } l \text{ relative to the molar average velocity}

\dot{j}_{m_{l}} \quad - \text{mass flux velocity of species } l \text{ relative to the mass average velocity}

K \quad k_{T} \quad - \text{thermal diffusion ratio}

k \quad - \text{Boltzmann's constant}

\mathbf{k} \quad - \text{unit vector along the apse-line}

k_{T}^{C} \quad - \text{thermal diffusion ratio as defined in Chapman-Cowling}

L \quad \mathbf{L} \quad - \text{a linear operator}

\bar{q}^{2} \quad - \text{mean square of the distance between the ends of a polymer}
M  $m_i$ - molecular mass of species $i$

$m_o = m_1 + m_2$

$M_i = m_i/m_o$

$\bar{m}_n$ - number average mass

$\bar{m}_w$ - weight average mass

$\bar{m}_v$ - viscosity average mass

M - molar mass

m - mean molecular mass

N  $N_A$ - Avogadro's number

N - number of particles in a system

$n(i)$ - configurational distribution function

n - number density ($n_i$ for species $i$)

$n$ - number of moles

P - pressure tensor

$p_o$ - hydrostatic pressure

p - uniform steady-state pressure

Q  Q - a transport property

r  $r$ - position vector

R  R  

- (a) gas constant

- (b) mass ratio of molecules 2 and 1

r - diameter ratio of molecules 2 and 1
$S$  - molecular separation distance

$S$  - entropy

$\overline{s^2}$  - mean square radius of gyration of a polymer

$T$  - temperature

$t$  - time

$u$  - mass average velocity

$U$  - internal energy

$u^*$  - number average velocity

$u_s$  - surface element velocity

$V$  - partial molar volume of species $i$

$V$  - volume of the system

$v$  - velocity vector

$v_i^*$  - volume of a molecule of species $i$

$v$  - volume of the system per molecule

$W$  - weight fraction of species $i$

$W$  - interchange energy

$X$  - (a) mole fraction

(b) Cartesian coordinate

(c) number of monomer segments

$xs$  - subscript referring to excess property
\( Y \ y \) - (a) = \( \frac{p}{nkT} - 1 \)

- (b) Cartesian coordinate

\( Z \ Z_N \) - canonical partition function

\( z \) - Cartesian coordinate

\( \alpha \ a \) - expansion factor of a polymer

\( \beta \ \beta \) - excluded volume

\( \gamma \ \gamma \) - hard diameter of Kihara potential

\( \varepsilon \ \varepsilon \) - molecular potential bowl depth

\( \eta \ \eta \) - shear viscosity

\([\eta]\) - intrinsic viscosity

\( \eta_{sp} \) - specific viscosity

\( \Theta \ \Theta \) - ideal temperature of a polymer in solution

\( \kappa \ \kappa \) - (a) bulk viscosity

- (b) constant for a polymer

\( \lambda \ \lambda \) - thermal conductivity

\( \mu \ \mu \) - chemical potential
\( \xi \) - total volume fraction taken up by molecules in the system

\( \rho \) - density

\( \rho_i \) - \( n_i m_i \)

\( \sigma \) - hard-sphere molecular contact diameter

\( \tau \) - viscous stress tensor

\( u \) \( T_s (\chi) \) - mean molecular flux of property \( \chi \) across surface element \( ds \) moving with velocity \( C_s \)

\( \phi \) - molecular potential function

\( \phi \) - total potential energy

\( \phi(i) \) - correction factor from \( f^o \) to \( f(i) \)

\( \phi_i \) - volume fraction of species \( i \)

\( \chi \) - molecular property

\( \psi \) - polymer constant

\( \frac{\partial}{\partial r} \) or \( \nabla \) - gradient

\( \Sigma \) - summation

\( \Pi \) - multiplication

\( x \)
\[ < > \quad \text{average over velocity space} \]

\[ \frac{\partial f}{\partial t} \quad \text{change in total distribution function with respect to time} \]

\[ \quad \text{due to molecular collisions} \]
ABSTRACT

The Enskog-Thorne solution to the Boltzmann equation provides expressions for the transport properties of binary dense fluid mixtures of hard spheres. This work uses the Percus-Yevick approximation for the virial equation of state to evaluate the Thorne expressions and obtain "mixing laws" for thermal conductivity and viscosity. These expressions are compared with experimental results to help correlate the excess transport properties. The expression for viscosity is applied to a dilute suspension of macromolecules and certain simplifications result. This final result, a power series in volume fraction, is analogous to the Einstein fluid viscosity equation. Unlike the Einstein result, however, it predicts a dependence of specific viscosity on macromolecular size, which is shown to have some experimental corroboration in reported data.

Finally, this work shows that recent modifications to the Enskog theory produce results for thermal diffusivity identical to those obtained by McLaughlin when he chose the chemical potential gradient instead of the concentration gradient as the diffusive driving force.
CHAPTER I. INTRODUCTION

A. Background

The transport properties of mixtures are of both theoretical and practical importance. For example, many industrial process designs depend on the ability to accurately predict the behavior of mixtures. Various experimentally determined empirical correlations do exist, and within the range of their applicability, many of these are excellent. However, extensions of correlations can reliably be made only with a theoretical underpinning.

The study of transport phenomena began as a study of bulk properties. Viscosity, thermal conductivity, and diffusivity are defined by the laws of Newton, Fourier, and Fick respectively for cases in which the bulk properties of the substance are assumed to be smooth and differentiable functions. Such macroscopic premises are useful as the foundations for classical thermodynamics and fluid mechanics. They further form a large part of the basis for heat and mass transfer theory.

A macroscopic vantage is not, however, the only viewpoint available. Statistical mechanics deals with many of the same problems from the microscopic view. Statistical mechanics is a bridge between the subjects of thermodynamics and transport phenomena.

The results of statistical mechanics most relevant to this work had their inceptions in the rigorous kinetic theory of gases begun by Boltzmann\(^1\) and Maxwell\(^2\) in the late 1800's. The crux of
the usefulness of statistical mechanics is that bulk properties are the effects of averages of molecular attributes which vary from molecule to molecule with a certain probability distribution. The Boltzmann equation is an integro-differential equation which relates the change in this probability distribution function with time. By using a sequence of successive approximations, Chapman and Enskog independently arrived at a method of solution for the probability distribution function from the Boltzmann equation. This solution is related in detail in The Mathematical Theory of Non-Uniform Gases by Chapman and Cowling. These equations could be evaluated for simple forms of the molecular potential to yield expressions for the transport coefficients of dilute gases. The appearance of computers allowed the evaluation of the solution for more realistic potentials. This was a contribution of Hirschfelder and his colleagues in the 1950's.

For pure systems of hard spheres, the dilute gas solution of Chapman and Enskog was extended by Enskog to dense fluids. H. H. Thorne further extended the theory to dense fluid mixtures. Until recently, the application of the Thorne-Enskog equations lay dormant. The Thorne equations contain terms involving the contact pair distribution function, and even now there exist no exact solutions for it. However, the approximations obtained by Percus and Yevick give the contact pair distribution function in very good agreement with Monte Carlo computer calculations for hard spheres. Thus, the Thorne equations have been solved yielding expressions for the mixing laws of the various transport properties. As most practical situations of interest involve mixtures, the prediction of transport properties is incomplete without such a functionality of concentration.
References


B. Mixing Laws

Various empirical and semi-empirical formulae have been postulated in the past for the mixing laws of transport properties. An obvious relation to propose for a binary mixture is the quadratic:

\[ Q_{\text{mix}} = A_1 x_1^2 + 2x_1 x_2 Q_{12} + x_2^2 Q_2 \]  

where \( Q \) is the property and \( x \) the mole fraction. The single subscripts refer to the individual species and \( Q_{12} \) is a cross-coefficient term to be determined. Figure 1.1 shows that many binary mixtures have composition dependences that suggest the quadratic form for thermal conductivity, and the use of equation (1) is further suggested by analogy with the quadratic mixing law for the second virial coefficient. This formula has a firm basis in theory.

The solution of Thorne's equations for transport properties provides a theoretical basis for the evaluation of equations such as equation (1). If formulae for the transport phenomena are known, excess properties for an \( n \)-component mixture are defined by:

\[ Q_{xs} = Q_{\text{mix}} - \sum_{i=1}^{n} x_i Q_i \]  

For a binary mixtures (as shown in Figure I.2) the excess property represents the difference between the actual transport property and the straight line representing ideal behavior drawn between the two pure component values.
Figure I.1
Composition Dependence of Thermal Conductivity
Figure I.2
Illustration of an Excess Property

\[ Q_{\text{ideal}} \]

\[ Q_{\text{mix}} \]

\[ Q_{xs} \]
In the past, Thorne's equations have been examined by McLaughlin et al. He has exhaustively studied the problem of diffusivity and solved it in detail. For this reason diffusivity is not further examined in this work. Thermal conductivity, viscosity, and thermal diffusivity are the properties considered in this thesis. The bases for consideration are the following: compositional dependence of the mixing laws with consequent functionality of size and mass ratios, methods of characterizing excess properties, viscous behavior of dilute suspensions of macromolecules, and an examination of diffusive driving forces.

Of particular interest is the viscosity of dilute suspensions of macromolecules. In fluid mechanics, as a later chapter will show, there is a relationship derived for just such a physical system—the Einstein viscosity equation. When McLaughlin examined the diffusivity of a dilute macromolecular suspension, he found a relationship analogous for diffusivity to that of Einstein for viscosity. This work derives the viscosity analogue and analyzes it.
References

C. Property Definitions

To begin a discussion of transport properties requires an understanding of the term flux (which will be dealt with in greater detail later in this work). For now, a flux will be considered to be the amount of a property transported in a unit time across a unit of surface area.

One of the properties that can be transported is momentum. The transport can occur in two essentially different ways: parallel or perpendicular to the direction of momentum. The viscous stress tensor element $\tau_{yx}$ is used to represent the flux in the $y$-direction of momentum in the $x$-direction. For this simplest case, Newton's law defines the coefficient of shear viscosity $\eta$ by the equation

$$\tau_{yx} = -\eta \left( \frac{du}{dy} \right)$$  \hspace{1cm} (1)

In a more general context, transfer of momentum parallel to the direction of momentum must also take into account overcoming the hydrostatic pressure $p_0$. The pressure tensor $P$ is given by

$$P = p_0 I - \tau$$  \hspace{1cm} (2)

where $I$ is the identity tensor and $\tau$ is the viscous stress tensor. A generalization of Newton's law gives an empirical form for the pressure tensor:

$$P = [p + \left( \frac{2}{3} \eta - \kappa \right) \frac{\partial}{\partial r} \cdot \vec{u}] I - 2\eta \text{sym} \left( \frac{\partial}{\partial r} \vec{u} \right)$$  \hspace{1cm} (3)
where $p$ is the uniform steady-state (or thermodynamic) pressure, $\kappa$ is the bulk viscosity, $\frac{\partial}{\partial r}$ is the gradient and $\vec{u}$ is the mass average velocity. $\text{sym} \left( \frac{\partial}{\partial r} \vec{u} \right)$ is the symmetric part of the tensor $\left( \frac{\partial}{\partial r} \vec{u} \right)$.

$$[\text{sym} \left( \frac{\partial}{\partial r} \vec{u} \right)]_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial z_j} + \frac{\partial u_j}{\partial z_i} \right)$$  \hspace{1cm} (4)

where $\vec{u} = (u_1, u_2, u_3)$ and $\vec{r} = (z_1, z_2, z_3)$. It can be seen that given expressions for $P$ and $p_0$, the viscosity $\eta$ can be obtained.

Just as the viscosity is defined in terms of a velocity gradient, the thermal conductivity $\lambda$ is defined by Fourier's law for a temperature gradient.

$$\vec{J}_q = -\lambda \frac{\partial T}{\partial r}$$  \hspace{1cm} (5)

$\vec{J}_q$ is the heat flux and $T$ is the temperature. The expression for the heat flux gives the thermal conductivity directly.

In the case of diffusion, the situation is not quite so simple. Fick's first law of diffusion can be written

$$\vec{J}_{m_1} = -c D_{12} \frac{\partial}{\partial r} x_1$$  \hspace{1cm} (6)

where $\vec{J}_{m_1}$ is the molar flux of species 1 relative to the molar average velocity. $x_1$ is the molar fraction of species 1, $c$ the total molar concentration, and $D_{12}$ is the mass diffusivity of species 1 into species 2 where $D_{12}$ is defined by equation (6). For the same $D_{12}$, the mass flux of species 1, $\vec{J}_{m_1}$, relative to the mass average velocity is given
where $\rho$ is the density, $m_i$ is the molecular mass, and $N_A$ is Avogadro's number.

In the above situation, there are no temperature gradients, pressure gradients, nor external forces, each of which contributes to the diffusion flux. Inclusion of all these terms gives the total diffusion flux. If the driving force is the chemical potential, $\mu$, a different mass diffusivity $D_{12}$ is defined.

\[
\dot{j}_{m_1} = - \left( \frac{C^2}{\rho RT} \right) N_A^2 m_1 m_2 D_{12} \frac{\partial}{\partial r} x_1 (7)
\]

\[
\dot{j}_{m_1} = - \left( \frac{C^2}{\rho RT} \right) N_A^2 m_1 m_2 D_{12} x_1 \left[ \left( \frac{\partial}{\partial x_1} \frac{\mu_1}{N_A m_1} \right)_T + \rho \frac{\partial}{\partial r} x_1 \right]
\]

\[
- \frac{\rho}{\rho} (F_1 - F_2) + \left( \frac{\dot{V}_1}{N_A m_1} - \frac{1}{\rho} \frac{\partial}{\partial r} \rho \right) D_{12} \frac{\partial}{\partial r} \ln T \quad (8)
\]

where $F$ is an acceleration due to an outside force, $R$ is the universal gas constant, $\dot{V}_1$ is the partial molar volume of species $1$, and $D_1^T$ is the thermal diffusivity, also defined in this equation.

If just ordinary diffusion is considered in equation (8) and compared with equation (7), the two diffusion coefficients are related:

\[
D_{12} = \frac{x_1}{RT} \frac{\partial \mu_1}{\partial x_1} D_{12} \quad (9)
\]

If $(d\mu_1) = RT(d \ln a_1)_T$, $p$ and $k_T$ is defined as $D_1^T / D_{12}$, the thermal diffusion ratio, equation (8) can alternatively be written
In order to use the equations in this section to predict property fluxes, expressions for the transport properties must be known. It is the purpose of this work to indicate the derivation of expressions for the transport properties from intermolecular principles. The intermolecular forces will determine the macroscopic transport properties.
A. Intermolecular Forces

The initial basis for the study of macroscopic properties from microscopic principles begins with the intermolecular potentials used to model molecular behavior. Several assumptions are commonly made with regard to these potentials. One is that the potential is a function only of the separation between particles. This is clearly justified for spherical molecules—the spatial orientations are equivalent. This has also been found to be adequate for dilute gases in which the distance of separation between molecules tends to lessen the configurational effect of the molecules. Another important assumption is that the total potential energy can be expressed as the sum of potential functions for two, three, four, etc. bodies.

The particular form of the intermolecular pair potential must itself be assumed. From quantum mechanics, the attractive potential can be shown to decrease with the inverse sixth power of distance and the repulsive potential to increase exponentially with distance. One of the most widely used expressions to model this behavior has been the Lennard-Jones n-m potential:

$$\varphi(s) = \frac{c}{n-m} \{ m\left(\frac{\sigma}{s}\right)^n - n\left(\frac{\sigma}{s}\right)^m \} \quad n > m > 3$$  \hspace{1cm} (1)

(shown in Figure II.1) where \(\varphi\) is the intermolecular potential and \(s\) the separation distance. The most popular choices for \(m\) and \(n\) are 6 and 12 since 12 is adequate to approximate exponential decay.
Figure II.1
The Lennard-Jones Potential
Another potential, proposed by Kihara,\(^5\) is of the form:

\[
a(s) = A\left(\frac{m}{n}\right) \in \left\{ \left(\frac{1-\gamma}{s/p-\gamma}\right)^n - \left(\frac{1-\gamma}{s/p-\gamma}\right)^m \right\}
\]

where

\[
A(x) = \frac{x^x}{(1-x)(1-x)^{-1}}
\]

Although slightly more complicated, the Kihara potential is more realistic as a model of molecular behavior.

Despite the better performance of the previous two potentials, this work deals with the hard sphere potential (shown in Figure II.2).

\[
\frac{a(s)}{kT} = \begin{cases} \infty & s > \sigma \\ 0 & s \geq \sigma \end{cases}
\]

The hard sphere potential is simpler to deal with because only the repulsive force is taken into account. Collisions between molecules are much easier to describe because no interaction takes place at a distance, and therefore, near misses produce no collisional effect. Furthermore, the time of contact is zero in contrast to the Lennard-Jones and Kihara potentials. Therefore, restriction to two-body collisions is relatively more likely for hard spheres than, say, Lennard-Jones particles. This mitigates to a certain extent (for hard-sphere as opposed to Lennard-Jones potentials) the assumption that only two-body collisions take place, and consequently, that the total potential energy \(\phi\) of a group of \(N\) particles with vector positions \(\vec{r}_1, \ldots, \vec{r}_N\) is the sum of the two-body potentials.
Figure II.2
The Hard Sphere Potential

\[ \frac{\varphi(s)}{kT} \]

vs.

\[ \frac{s}{\sigma} \]
\begin{equation}
\Phi (\mathbf{r}_1, \ldots, \mathbf{r}_N) = \sum_{i \neq j} \varphi (\mathbf{r}_{ij})
\end{equation}

where \(\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i\).

Once \(\Phi\) is calculable, the canonical partition function \(Z_N\) is given by the equation:

\begin{equation}
Z_N = \frac{(2\pi m k T)^{3N}}{N!} \int \cdots \int \exp \left[-\frac{\Phi}{kT}\right] d\mathbf{r}_1 \cdots d\mathbf{r}_N
\end{equation}

Thermodynamic properties are then related to the intermolecular potential through the Helmholtz free energy \(A\) which is given by

\begin{equation}
A = - kT \ln Z_N
\end{equation}

The other thermodynamic properties are then obtainable from their basic definitions and combinations of \(A\) and its partial derivatives with respect to volume and temperature.

\begin{equation}
A = U - TS
\end{equation}

where \(U\) is internal energy and \(S\) is entropy. The first and second laws of thermodynamics can be combined and written

\begin{equation}
dU = TdS - pdV
\end{equation}
for the volume \( V \). Solving for the differential \( dA \) gives

\[
dA = -SdT - pdV
\]  

(10)

which implies that for \( S \) and \( p \)

\[
S = - \left( \frac{\partial A}{\partial T} \right)_V \quad ; \quad p = - \left( \frac{\partial A}{\partial V} \right)_T
\]  

(11)

Therefore, since \( G = A + pV \) for \( G \), the Gibb's free energy,

\[
G = A - \left( \frac{\partial A}{\partial V} \right)_T V
\]  

(12)

Likewise, for enthalpy and internal energy

\[
H = A - \left( \frac{\partial A}{\partial V} \right)_T V - \left( \frac{\partial A}{\partial T} \right)_V T
\]  

(13)

\[
U = A - \left( \frac{\partial A}{\partial T} \right)_V T
\]  

(14)

This gives all the first order thermodynamic functions in terms of \( A \).

Thermodynamic properties are not the only results from knowledge of the potential \( \phi \). Probability densities (distributions) can be calculated.\(^4\) There are three distribution functions of interest to us; the configurational distribution function \( n^{(i)} \), the total distribution function \( f^{(i)} \) and the radial distribution function \( g^{(i)} \).
The configurational distribution function \( n^{(i)} \) gives the probability of finding \( i \) particles at time \( t \) in the small volume elements \( dr_1 \ldots dr_i \) around the coordinates \( r_1 \ldots r_i \) as \( n^{(i)}(r_1 \ldots r_i, t)dr_1 \ldots dr_i \). For the case where \( i = 1 \) in an isotopic fluid, the configuration distribution function is the number density.

\[
\begin{align*}
n^{(1)}(t) &= n(t) = (N/V)(t) \quad (15) \\
\end{align*}
\]

for the \( i^{\text{th}} \) particle distribution

\[
\begin{align*}
n^{(i)}(t) &= \frac{[N!/(N-i)!]}{V^i} (N-i)! \quad (16)
\end{align*}
\]

The configurational distribution function is dependent only on the positions of the molecules. For hard spheres, the molecules are described by the position and momentum (or velocity) coordinates. Therefore, the total distribution function, \( f^{(i)} \), gives, at time \( t \), the probability of \( i \) molecules being within the neighborhood \( dr_1 \ldots dr_i dv_1 \ldots dv_i \) of the space-velocity coordinates \( r_1 \ldots r_i, v_1 \ldots v_i \) as \( f^{(i)}(r_1 \ldots r_i, v_1 \ldots v_i, t) \)

\[
\begin{align*}
&dr_1 \ldots dr_i dv_1 \ldots dv_i . \quad \text{The normalization of } f^{(i)} \text{ over velocity space yields } n^{(i)} .
\end{align*}
\]

\[
\int f^{(i)} dv_1 \ldots dv_i = n^{(i)} \quad (17)
\]
The radial distribution, $g^{(i)}$, unlike the previous two functions, $f^{(i)}$ and $n^{(i)}$, is normalized to unity. At equilibrium, the relationship among the pair distribution functions and the potential $\phi$ can be expressed:

$$n^{(2)}(r_1, r_2) = n^{(1)}(r_1) n^{(1)}(r_2) g^{(2)}(r_1, r_2 - r_1)$$

$$n^{(2)}(r_1, r_2) = \frac{3N}{(2\pi m k T)^{3/2}} \int \cdots \int \exp \left[ -\phi/kT \right] dr_3 \cdots dr_N$$

If the fluid is uniform, $g^{(2)}$ is a function only of $(r_2 - r_1)$ and if, as well, the particles are spherical, $g^{(2)}$ is a function only of $s$ the separation distance, i.e.

$$n^{(2)}(s) = (N/V)^2 g(s)$$

where $g$ henceforth will be used to represent $g^{(2)}$. Its behavior is given in Figure II.3.

For hard spheres, the radial distribution function behaves as in Figure II.4. One can see that the differences between the actual radial distribution and one evaluated for hard spheres by computer modeling are not quantitatively large. The major qualitative difference comes in the region $s < \sigma$ where the hard sphere distribution is zero until rising discontinuously to its contact value, whereas the actual radial distribution rises continuously from zero.
Figure II.3
Radial Distribution Function
Figure II.4
Radial Distribution Function for Hard Spheres

$g(s)$

$s/\sigma$
With the previous concepts, it is now possible to derive an equation of state. One of the ways to proceed is with the pressure equation, so-called because it is derived from the relation for pressure, equation (11). Combining equations (6), (7), (11), and (18) yields

$$\frac{p}{nkT} = 1 - \frac{2\pi n}{3kT} \int_0^\infty s^3 \varphi'(s) g(s) \, ds,$$  \hspace{1cm} (20)

the pressure equation. The use of a hard-sphere potential implies $\varphi'(s)$ corresponds to the negative Dirac delta function, and hence

$$\frac{p}{nkT} = 1 + \frac{2\pi n}{3} \sigma^3 g(\sigma)$$  \hspace{1cm} (21)

A similar procedure using the grand canonical ensemble will yield the compressibility equation:\footnote{7}

$$kT \left( \frac{\partial n}{\partial p} \right)_T = 1 + 4\pi n \int_0^\infty s^2 [g(s) - 1] \, ds$$  \hspace{1cm} (22)

The pressure and compressibility equations are themselves exact thermodynamic relationships and provide a measure of the precision of any approximations used to solve for $g$ by comparing its effects on the two equations. Because there can be divergences in the use of the different equations, this work will, for the sake of internal consistency, always use the pressure equation unless otherwise specified.

The particular approximation with which this work is concerned is the Percus-Yevick approximation,\footnote{8,9} obtained analytically by Thiele,\footnote{10}
Wertheim,11,12 and Baxter.13 The approximation of Percus and Yevick will not be derived here. However, an indication of one method of derivation will be provided.

In equation (6) an expression for the partition function is given. This is not an easy expression to evaluate, and in order to do it Mayer14 defined an f-bond function $f_{ij}$:

$$f_{ij} = \exp \left[ -\varphi(r_{ij})/kT \right] - 1$$

Therefore, the integrand of equation (6) can be expressed

$$\exp \left[ -\varphi/kT \right] = \prod_{i \neq j} \left( 1 + f_{ij} \right)$$

This would not have been an improvement except that the terms in equation (24) can be shown to be topologically equivalent to a representation in a plane graph. Consider the case for $N = 3$.

$$\prod_{i \neq j} \left( 1 + f_{ij} \right) = 1 + f_{12} + f_{23} + f_{31} + f_{12}f_{23} + \ldots f_{12}f_{23}f_{31}$$

$$= + + + + + + \ldots +$$

(26)

where the lines between dots are the f-bonds between molecules. The exact procedures and terminology of graph theory are not within the realm of this dissertation. Suffice it to say that by ignoring certain types of the diagrams in an N-particle system similar to those in
Equation (26) the cluster integrals remaining can be evaluated and an expression for $g$ obtained. In just such a manner the Percus-Yevick approximation for $g$ can be obtained.\(^6\)

Cluster integrals are the integrals of the functions represented by the cluster diagrams of which those shown in equation (26) are but examples.

Thiele's result for the Percus-Yevick approximation can be written.

$$g(a) = \frac{1 + \xi}{2} \frac{(1 - \xi)\xi}{(1 - \xi)^2}$$

where $\xi = \pi n \sigma^3 / 6$ is the volume fraction taken up by the molecules in the system. Combining equations (21) and (27) produces a workable equation of state for a hard sphere single component fluid.

$$\frac{p}{nkT} = \frac{1 + \xi + 3\xi^2}{(1 - \xi)^2} = \frac{1 + \xi + \xi^2 - 3\xi^3}{(1 - \xi)^3}$$

The above procedure has been generalized to a binary mixture.\(^{15}\)

$$\frac{pV}{kT} = \frac{\xi (1 + \xi + \xi^2)}{(1 - \xi)^3 (x_1 + x_2 r^3)}$$

$$- \frac{3x_1 x_2 (1 - r^3) \xi^2 [(1 + r) + r \xi ((x_1 + x_2 r^2) (x_1 + x_2 r^3))]}{(x_1 + x_2 r^3)^3 (1 - \xi)^3}$$

$$- \frac{3\xi^4}{(1 - \xi)^3} \frac{x_1 + x_2 r^2}{x_1 + x_2 r^3}$$

(29)
where the $x_i$'s are the mole fractions, $r$ the molecular size ratio $(= \sigma_{22}/\sigma_{11})$, $v_i^* = \frac{1}{6} \pi \sigma_{ii}^3$ is the volume of species $i$ in the system, and the total volume fraction of the molecules $\xi$ is given by

$$\xi = n \left( x_1 v_1^* + x_2 v_2^* \right) = \frac{(x_1 v_1^* + x_2 v_2^*)}{v}$$

Equations (28) and (29) are derived from the pressure equation and differ slightly from the results of the compressibility equation which can be obtained by dropping the last term of equation (29).

Monte Carlo calculations are used as experimental results for hard spheres since no true experiments are possible. Equilibrium properties are obtained by modeling a system of hard spheres colliding with a random distribution of velocities and positions on a computer. A physically deterministic model of individual collisions is used, and averaged molecular properties give the macroscopic properties. This method allows the calculation of transport properties as well as equilibrium properties by superimposing a gradient of some collisional invariant on the original distribution. e.g. A temperature gradient would be reflected by different average velocities for molecules in different regions of space.

A graphic comparison of pressure results from Monte Carlo calculations with the two different approaches (compressibility and pressure equations) is given in Figure II.5.
Figure II.5
Percus-Yevick Results vs. Monte Carlo Calculations
References

B. Property Fluxes

Individual forces between molecules are of interest in this work only to the extent that they allow the calculation of macroscopic properties. Since the transport properties are defined by fluxes, a relationship must be found for property fluxes in terms of intermolecular forces.

Let the molecular behavior of a system be described by a one-particle total probability distribution function $f(r, v, t)$. From the previous chapter,

$$\int f(r, v, t) \, dv = n(r, t) \quad (1)$$

Equation (1) would also be true for an individual species $i$ in a multicomponent system with $f, r, v,$ and $n$ all subscripted by $i$. The mass density $\rho$ is then defined in terms of $m_j$, the molecular mass of the individual $i^{th}$ species particles for a total of $j$ species:

$$\rho = \sum_{i=1}^{j} \rho_i = \sum_{i=1}^{j} m_i n_i \quad (2)$$

The mean mass velocity $\vec{u}$ is defined

$$\rho \vec{u} = \int f_i (\vec{r}_i, \vec{v}_i, t) \, m_i \vec{v}_i \, dv_i \quad (3)$$

Similarly, the number average velocity, $\vec{u}^*$, is given by
The peculiar or thermal mass velocity $\mathbf{C}$ is defined

$$\mathbf{C} = \mathbf{v} - \mathbf{u}$$

and the peculiar number velocity

$$\mathbf{C}^* = \mathbf{v} - \mathbf{u}^*$$

To study a flux, an oriented surface element $\mathbf{dS}$ moving through the fluid with some velocity $\mathbf{u}_{S}$ must be defined. Another relative velocity arises naturally.

$$\mathbf{C}_{S} = \mathbf{v} - \mathbf{u}_{S}$$

If $\chi(\mathbf{v})$ is a molecular property passing through the surface element $\mathbf{dS}$, the total flux of $\chi$ through the element is given by

$$\int \chi(\mathbf{v})\mathbf{C}_{S} \cdot \mathbf{dS} f(r,\mathbf{v},t) \, dv$$

$$= n(r,t) \langle \chi \mathbf{C}_{S} \rangle \cdot \mathbf{dS}$$

The use of the brackets $\langle \rangle$ is defined here and will be used to indicate the averaging of the quantity in the brackets over the velocity space (but not time) with respect to $f$. 

$$u^* = \frac{1}{n} \sum_{i=1}^{j} \int_{i} v_{i} f_{i} (v_{i},r_{i},t) dv_{i} = \frac{1}{n} \sum_{i=1}^{j} u_{i}^*$$  (4)
Therefore, the mean molecular flux across the element $dS$ of the property $x$, designated $T_{C_s}(x)$ is given by

$$T_{C_s}(x) = \langle x C_s \rangle$$  \hspace{1cm} (9)$$

Those properties of interest to us are the collisional invariants: those properties (mass, momentum, and energy) which are conserved in elastic collisions. It is the fluxes of these properties that yield the transport properties examined in this work.

In a uniform fluid, the flux of mass relative to a stationary surface element is simply the average momentum.

$$T_0(m) = \langle mv \rangle = mu$$  \hspace{1cm} (10)$$

For momentum, $x = mv$, the flux $T(mv)$ is given by

$$T_0(mv) = m \langle CC \rangle + muu$$  \hspace{1cm} (11)$$

since $v = C + u$. The flux, then, of momentum is composed of two parts which (for a dilute gas) correspond to the pressure tensor $\mathbf{P}$ (the negative of the stress tensor) and the momentum flux of the local mean velocity.

$$\mathbf{P} = n m \langle CC \rangle$$  \hspace{1cm} (12)$$

Similarly for energy, the flux can be broken into two components:
one relative to the mean velocity, one due to it. The heat flux $\dot{J}_q$ is given

$$\dot{J}_q = \frac{1}{2} \, m \, \langle \mathbf{C}^2 \rangle$$

(13)

by that part of the energy flux relative to the mean velocity.

The discussion of flux, so far limited to one-component fluids, can be modified slightly to reflect the fact that the molecular property $x$ may be different for each species. For species $i$

$$n_i \, T_{C_{S_i}} (x_i) = \int f_i \, C_{S_i} \, x_i \, dv$$

(14)

and

$$n \, T_{C_{S_i}} (x) = \sum_{i=1}^{j} \int f_i \, C_{S_i} \, x_i \, dv$$

(15)

The multicomponent nature also gives rise to the diffusion flux:

$$n_i \, m_i \, \mathbf{u}_{i_S} = m_i \, \int f_i \, C_{S_i} \, dv$$

(16)

For the previous examples of mass, momentum, and energy fluxes, a knowledge of the distribution function $f$ is all that is required to explicitly solve for particular fluxes and thereby obtain the diffusivity, viscosity, and thermal conductivity from their respective definitions in Fick's, Newton's, and Fourier's laws. To obtain an expression of $f$, one must solve the Boltzmann equation.
C. The Boltzmann Equation

Consider a system of molecules undergoing an acceleration \( F \) by each molecule. At time \( t \) there will be a certain number of molecules in the \( dv \, dr \) neighborhood around velocity \( \mathbf{v} \) and position \( \mathbf{r} \). This number will correspond to \( f(\mathbf{v}, \mathbf{r}, t) \, dv \, dr \). Were no molecular collisions to occur in the period of time \( dt \), the number of molecules \( f(\mathbf{v} + F dt, \mathbf{r} + v dt, t + dt) \, dv \, dr \) would be identical. The difference in the two numbers is brought about by collisions occurring during the time \( dt \), and is given the denotation \( (\partial f/\partial t) \, dv \, dr \, dt \). Setting them equal and dividing by \( dv \, dr \):

\[
\{f(\mathbf{v} + F dt, \mathbf{r} + v dt, t + dt) - f(\mathbf{v}, \mathbf{r}, t)\} = \frac{\partial f}{\partial t} \, dt
\]

Dividing by \( dt \) and taking \( dt \to 0 \) yields the Boltzmann equation:

\[
\frac{\partial f}{\partial t} + \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{r}} + F \cdot \frac{\partial f}{\partial \mathbf{v}} = \frac{\partial e f}{\partial t}
\]

Placing a subscript \( i \) for each \( f, \mathbf{v}, \) and \( F \) in the equation is valid for the \( i^{th} \) component in a multicomponent fluid.

In the particular case of a one-component gas at equilibrium with no outside forces,

\[
\frac{\partial e f}{\partial t} = \frac{\partial f}{\partial \mathbf{r}} = \frac{\partial f}{\partial t} = 0
\]

It can then be argued\(^1\) that substitution of this condition into the
Boltzmann equation produces the result that $\ln f(v)$ must be a collisional invariant. This is equivalent to the Maxwellian distribution:

$$f = n \left( \frac{m}{2\pi kT} \right)^{3/2} \exp \left( -\frac{mC^2}{2kt} \right)$$

(4)

where $m$ is the molecular mass, $k$ the Boltzmann constant, and $T$ the temperature.

The cases of our interest (and the mathematical complications) arise for situations other than those at equilibrium. For these situations, equation (2) must be solved in greater generality.

In order to solve the Boltzmann equation for $f$, Chapman and Enskog represented $f$ by an infinite series:

$$f = \sum_{i=0}^{\infty} f(i)$$

(5)

such that $f(i) \gg f(i+1)$. Additional restrictions were imposed to force $f(0)$ to give the proper moments for the collisional invariants and to prevent the higher approximations from disturbing this.

The first approximation to $f$, $f(0)$, results from a system with molecules of no size. In this case, the ideal gas law is the prediction, and $f(0)$ is the Maxwellian distribution.

Equation (2) can be rewritten:

$$L(f) = 0$$

(6)

where $L$ is some operator on $f$. To solve for $f$ it is further assumed
that \( L \) can be expressed

\[
L(f) = L^{(0)}(f^{(0)}) + L^{(1)}(f^{(0)}, f^{(1)}) + \ldots
\]  

(7)

The \( i^{th} \) correction term to \( f \), \( f^{(i)} \), is expressed

\[
f^{(i)} = f^{(0)} \phi^{(i)}
\]  

(8)

and equation (7) can be broken up into the set of equations

\[
L^{(0)}(f^{(0)}) = 0; L^{(1)}(f^{(0)}, \phi^{(1)}) = 0, \text{ etc.}
\]  

(9)

The operator \( L \) can be factored in this way because of its form, which involves the expression used to model \( \partial_{e} f/\partial t \) which is obtained from consideration of the physics of intermolecular collisions for a given potential function \( \phi(s) \).

For a binary dilute gas, the expression for \( \partial_{e} f_{1}/\partial t \) can be written

\[
\partial_{e} f_{1}/\partial t = \int \int (f'f_{1}' - ff_{1}) k_{11} \, dk dv_{1} \\
+ \int \int (f'f_{2}' - f_{1}f_{2}) k_{12} \, dk dv_{2}
\]  

(10)

where \( k \) is a unit vector along the apse-line, the line through the molecules at point of contact. The prime is used to indicate the condition after collision. \( k_{11} \) and \( k_{12} \), corresponding respectively to like and unlike particles colliding, are functions of \( \hat{k} \) and \( \hat{G} \),
Figure II.6

Molecular Collision
the mass average velocity of the two particles. The exact functional form of $k_{ii}$ is dependent on the potential function chosen. The integration is therefore over all possible angles and velocities at which the intersecting molecules could meet and rebound.

The use of the terminology in equations (6-9) allows the approximation of the average of some property $x$:

$$< x > \approx < x^0 > + < x^1 > = \int x f(o) \, dv + \int x f(o) \phi(1) \, dv$$

The Boltzmann equation, solved by this method, yields expressions for the transport properties. For a dilute hard-sphere gas of only one component, the thermal conductivity $\lambda_0$ can be written

$$\lambda_0 = \frac{75}{64\sigma^2} \left( \frac{kT}{m} \right)^{1/2}$$

This comes from the equation for the heat vector $\mathbf{j}_q$

$$\mathbf{j}_q = \frac{m}{2} \int C^2 C f \, dv$$

and $\lambda$ is defined, for any system, from Fourier's Law

$$\mathbf{j}_q = -\lambda \frac{\partial T}{\partial r}$$

Similarly, to obtain an expression for the viscosity of a dilute hard-sphere gas, $\eta_{10}$, the pressure tensor $\mathbf{P}$ is expressed:
\[ \frac{\hat{p}}{p} = \text{nm} \int \frac{u}{f} \, dv \]  

(15)

Alternatively, since \( \hat{p} \) is given by equations (I.C.2) and (I.C.3), the following can be formulated for \( n_0 \).

\[ n_0 = \frac{5}{16\sigma^2} \left( \frac{k T}{\pi} \right)^{1/2} \]  

(16)

For a dilute binary gas mixture, the expressions for thermal conductivity and viscosity in the first approximation are the following

\[ \lambda = \frac{x_1}{x_2} \frac{R_1 \lambda_{10} x_2}{R_1 x_2 + R_2 \lambda_{20} x_1 + R_{12}} + \frac{x_2}{R_2 x_1 + R_2 \lambda_{20} x_1 + R_{12}} \]  

(17)

\[ \eta = \frac{x_1}{x_2} \left( \frac{2}{3} + \frac{m_2 A}{m_1} \right) + \frac{x_2}{x_1} \left( \frac{2}{3} + \frac{m_1 A}{m_2} \right) + \frac{E}{2n_{10}} + \frac{E}{2n_{20}} + 2 \left( \frac{2}{3} - A \right) \]  

\[ \frac{x_1}{x_2} \left( \frac{2}{3} + \frac{m_2 A}{m_1} \right) / n_{10} + \frac{x_2}{x_1} \left( \frac{2}{3} + \frac{m_1 A}{m_2} \right) / n_{20} + \frac{E}{2n_{10} n_{20}} + \frac{4A}{3E M_1 M_2} \]  

(18)

where

\[ R_{12} = 3(M_1 - M_2)^2(5-4B) + 4M_1 M_2 A(11-4B) + 2F^2 / \lambda_{10} \lambda_{20} \]  

(19)

\[ R'_{12} = 2F(F / \lambda_{10} + F / \lambda_{20} + (11-4B-8A) M_1 M_2) \]  

(20)

\[ R_i = F(6M_i^2 + 5M_i^2 - 4M_i^2 B + 8M_i M_j A) / \lambda_{10} \]  

(21)

\[ M_i = m_i / m_0; \quad m_0 = m_1 + m_2. \]  

(22)
For a hard sphere,

\[ A = \frac{2}{5}; B = \frac{3}{5}; C = \frac{6}{5} \quad (23) \]

\[ E = \left( \frac{2kTm_o}{\pi M_1 M_2} \right)^{1/2} / 8 \sigma_{12}^2 \quad (24) \]

and

\[ F = \frac{15k}{4m_0} E \quad (25) \]

The double subscripts \((i0)\) on \(\lambda\) and \(n\) refer to values for dilute pure species \(i\), given by equations \((12)\) and \((16)\).

In the case of a binary fluid, if the average species velocities \(\dot{u}_i\) are not equal, the species diffuse relative to one another. In the Chapman-Enskog theory, this difference in velocities serves as the basis for a definition of the diffusivity \(D_{12c}\). If the number average velocity \(\dot{u}_*\) is taken to be \(\dot{u}_s\), then the average peculiar velocities relative to \(\dot{u}\) are

\[ < \dot{C}_i* > = \frac{1}{n_i} \int f_i \dot{C}_i* d\dot{v}_i \quad (26) \]

\(D_{12co}\) and \(D_{1c}^{Tco}\) are defined by

\[ < \dot{C}_i* > - < \dot{C}_2* > = - \frac{n^2}{n_1n_2} \{ D_{12c}^{d12} + D_{1c}^{Tc} \frac{2}{\dot{\sigma} r} \ln T \} \quad (27) \]

where \(d_{12}\) is given by
The thermal diffusion ratio \( \frac{D_{12}^{\text{co}}}{D_{12}^{\text{co}}} \) is then given as the ratio

\[ D_{12}^{\text{co}} = \frac{3}{8n_{12}} \frac{kT(m_1+m_2)^{1/2}}{2\pi m_1 m_2} \quad (29) \]

the first approximation to the thermal diffusion ratio is

\[ k_T^{\text{co}} = 5(C-1) \frac{x_1 S_1 - x_2 S_2}{Q_1 x_1 / x_2 + Q_2 x_2 / x_1 + Q_{12}} \quad (30) \]

where for \( i \neq j \)

\[ S_i = M_i^2 E / \eta_{10} - 3M_j (M_j - M_i) - 4M_i M_j A \quad (31) \]

\[ Q_i = (M_i E / \eta_{10}) \{6M_j^2 + (5-4B)M_i^2 + 8M_i M_j A\} \quad (32) \]

\[ Q_{12} = 3(M_1 - M_2)^2 (5-4B) + 4M_1 M_2 A (11-4B) + 2E^2 M_1 M_3 / \eta_{10} \eta_{20} \quad (33) \]

The above derivation, due to Enskog and Chapman, is based on the assumption of property transport occurring due to molecular movement over distances. This assumption entered the derivation via the expression used to substitute for the right-hand side of equation (2).

For a dilute gas, the expression of \( \partial e / \partial t \) takes into account only the kinetic contribution to transport. Figure II.7 illustrates
Figure II.7

Kinetic vs. Collisional Transport
the kinetic and collisional contributions to transport. Molecule 1 travels from A to D where it collides with molecule 2. The kinetic contribution takes place via the actual motion of the molecule between collisions which corresponds to the arrow (BC). Collisional transport occurs over the distance between centers at collision (DE) for momentum and energy transfer. In a dilute gas, the distance BC is much greater than DE and therefore the assumption of only kinetic transport is valid.

Dense fluids, however, are subject to greater collisional transport because BC is on the order of DE. Therefore, Enskog extended the above derivation to include collisional effects in pure dense fluids.

For \( y = p/nkT - 1 \), the separate effects of collisional and kinetic contributions to thermal conductivity and viscosity can be expressed:

\[
\frac{\lambda_{\text{kinetic}}}{\lambda_0 b_0} = \frac{1}{y} + \frac{3}{5} \quad (34)
\]

\[
\frac{\lambda_{\text{collisional}}}{\lambda_0 b_0} = \frac{3}{5} \left( 1 + \frac{3}{5} y \right) + \frac{32y}{25\pi} \quad (35)
\]

\[
\frac{\eta_{\text{kinetic}}}{\eta_0 b_0} = \frac{1}{y} + \frac{2}{5} \quad (36)
\]

\[
\frac{\eta_{\text{collisional}}}{\eta_0 b_0} = \frac{2}{5} \left( 1 + \frac{2}{5} y \right) + \frac{48y}{25\pi} \quad (37)
\]

\( V \) is the total volume of the system and \( b_0 \) is the hard-sphere second virial coefficient. The total transport property is obtained by
summing the kinetic and collisional contributions. This particular form of expressing Enskog's results has the advantage that \( y \) has the significance of being expressed by the Pressure equation:

\[
y = \frac{2\pi n}{3} \sigma^3 g(\sigma)
\]  
(38)

The solution to the Boltzmann equation by Enskog's method has been generalized to dense binary hard-sphere fluids by H. H. Thorne. Although his complete work has never been published, a summary is given by Chapman and Cowling.³

For a binary mixture, there are three different pair interactions: 1-1, 1-2, and 2-2. For each interaction, there is a different radial distribution that is a function of composition. They are designated \( g_{11}, g_{22}, \) and \( g_{12} \).

For \( i \neq j \),

\[
g_{ij} = 1 + \frac{\pi}{12} n_1 \sigma_{11}^3 (8 - 3\sigma_{11}/\sigma_{12}) + \frac{\pi}{12} n_2 \sigma_{22}^3 (8 - 3\sigma_{22}/\sigma_{12}) + \ldots
\]  
(39)

where

\[
\sigma_{12} = (\sigma_{11} + \sigma_{22})/2
\]  
(40)

If \( \xi \) is the total molecular volume fraction,

\[
\xi = (n_1 \sigma_{11}^3 + n_2 \sigma_{22}^3) \pi/6
\]  
(41)
the pressure equation gives an expression for $g_{11}$

$$g_{11} = \left(1 + \frac{1}{2}\right) + \frac{3}{2} \frac{\pi}{6} n_j \sigma_{jj}^2 \left(\sigma_{11} - \sigma_{jj}\right) (1-\xi)^{-2} \tag{42}$$

and the Percus-Yevick approximation yields

$$g_{12} = (\sigma_{22} g_{11} + \sigma_{11} g_{22})/2 \sigma_{12} \tag{43}$$

The thermal conductivity to the first approximation is found to be

$$\lambda = \frac{75}{8} \frac{k^2 T}{g_{12}} \left(\frac{x_1 X_{\lambda}^2}{(a_{11-1} x_2 m_1^{-1/2})} - 2 \frac{a_{-1-1} X_{\lambda} Y_{\lambda}}{(m_1 m_2)^{1/2}} + a_{11} \frac{Y_{\lambda}^2 x_2}{x_1 (a_{11} a_{1-1} - a_{1-1}^2)} \right)$$

$$+ n^2 (\pi k^3 T)^{1/2} \left\{ m_1^{-1/2} x_1^2 g_{11} \sigma_{11}^4 + m_2^{-1/2} x_2^2 g_{22} \sigma_{22}^4 \right\}$$

$$+ 2(8M_1 M_2/m_0)^{1/2} x_1 x_2 g_{12} \sigma_{12}^{4/3} \tag{44}$$

where

$$X_{\lambda} = (1 + 2\pi n_1 \sigma_{11}^3 g_{11}/5 + 8M_1 M_2 \sigma_{12}^3 g_{12}/5) \tag{45}$$

and $Y_{\lambda}$ is similar with the subscripts reversed.

The a's are given by

$$a_{11} = a_{11} + \frac{x_1}{x_2} \frac{g_{11}}{g_{22}} a_{11}'' \tag{46}$$
for

\[ a_{11}' = \frac{5kT((6M_1^2 + 5M_2^2)/4 - 3M_2^2/5 + 4M_1M_2/5)/M_1E }{ (47) } \]

and

\[ a_{11}''' = \frac{5kT/2n_{10} }{ (48) } \]

\[ a_{-1-1} = 2_{-1-1}' + \frac{x_2 g_{22}}{x_1 g_{12}} a_{-1-1}'' \]

(49)

where \( a_{-1-1}' \) is given by equation (47) with the subscripts reversed and \( a_{-1-1}''' \) by equation (48) with \( n_{20} \) substituted for \( n_{10} \). Finally,

\[ a_{1-1} = -5(M_1M_2)^{1/2}kT(27/20)/E \]

(50)

Similarly, for viscosity,

\[ \eta = \frac{5kT}{2g_{12}} \frac{b_{-1-1}x_2 (x_1)^{-2}b_{1-1}x_1 y_n + b_{11}y_n (x_2)^2}{(b_{11}b_{-1-1} - b_{1-1}^2)} \]

+ \( n^2(\pi kT)^{1/2}m_1^{1/2}x_1^{2}g_{11}^{1/2}x_1^{4}m_2^{1/2}x_2^{2}g_{22}^{4} \)

+ \( 2(2m_0^{1/2}M_1M_2^{1/2}x_1x_2g_{12}^{4}g_{12}^{4})/15 \)

(51)

\[ X_{\eta} = (1 + 4\pi n_{10}g_{11}^{3}g_{12}/15 + 8M_2^{3}n_{2}g_{12}^{3}g_{12}/15) \]

(52)
and \( Y_n \) merely reverses the subscripts.

\[
\begin{align*}
\tilde{b}_{11} &= \hat{b}_{11} + \frac{x_{12} g_{11}}{x_{21} g_{12}} b_{11}'' \\
\end{align*}
\]  

(53)

where

\[
\begin{align*}
\hat{b}_{11} &= 5kT \left( \frac{2}{3} + \frac{2M_2}{5M_1} \right)/E \\
\end{align*}
\]  

(54)

and \( b_{11}'' = a_{11}'' \).

\[
\begin{align*}
\tilde{b}_{-1-1} &= \hat{b}_{-1-1} + \frac{x_{21} g_{22}}{x_{12} g_{12}} b_{-1-1}'' \\
\end{align*}
\]  

(55)

where \( b_{-1-1}'' = a_{-1-1}'' \) and \( b_{-1-1}'' \) corresponds to equation (54) with the species subscripts interchanged.

\[
\begin{align*}
\hat{b}_{-1-1} &= -4kT/3E \\
\end{align*}
\]  

(56)

The diffusion coefficient \( D_{12}^{c} \) is related to the dilute value \( D_{12}^{co} \)

\[
D_{12}^{c} = D_{12}^{co}/g_{12} 
\]  

(57)

The thermal diffusion ratio \( k_T \) can be expressed

\[
k_T = (A_T X_T + B_T Y_T)/C_T 
\]  

(58)
where

\[ A_T = -10x_1 \left( \frac{M_2}{2M_1} \right) 3^{1/2} \beta + 8 \frac{x_2}{x_1} \frac{g_{22}}{g_{12}} \left( \frac{2r}{1+r} \right) \left( \frac{1}{M_1} \right)^{1/2} + \frac{M_1}{\sqrt{2}} \gamma \] (59)

\[ B_T = 10x_2 \left( \frac{M_1}{2M_2} \right)^{1/2} \alpha + 8 \frac{x_1}{x_2} \frac{g_{11}}{g_{12}} \left( \frac{2}{1+r} \right) \left( \frac{1}{M_2} \right)^{1/2} + \frac{M_2}{\sqrt{2}} \gamma \] (60)

and

\[ C_T = \alpha + 8 \frac{x_1}{x_2} \frac{g_{11}}{g_{12}} \left( \frac{2}{1+r} \right) \left( \frac{1}{M_1} \right)^{1/2} \beta + 8 \frac{x_2}{x_1} \frac{g_{22}}{g_{12}} \left( \frac{2r}{1+r} \right) \left( \frac{1}{M_2} \right)^{1/2} - \gamma^2 \] (61)

with

\[ X_T = 1 + \frac{12}{5} g_{11} x_1 \frac{V_1^*}{V} + \frac{6}{5} M_1 M_2 g_{12} x_2 (1+r)^3 \frac{V_1^*}{V} \] (62)

\[ Y_T = 1 + \frac{12}{5} g_{22} x_2 \gamma^3 \frac{V_1^*}{V} + \frac{6}{5} M_1 M_2 g_{12} x_1 (1+r)^3 \frac{V_1^*}{V} \] (63)

\[ \alpha = \frac{40}{M_1} \frac{1}{4} (6M_1^2 + 5M_2)^2 - \frac{3}{5} M_2^2 + \frac{4}{5} M_1 M_2 \left( \frac{M_1 M_2}{2} \right)^{1/2} \] (64)

\[ \gamma = \frac{54}{\sqrt{2}} \frac{M_1 M_2}{M_1 M_2} \] (65)

and \( \gamma \) is given by equation (64) with reversed subscripts.

The solution of the Boltzmann equation yields expressions for the mixing laws of the transport properties. A particular case of interest to which the Thorne equation might be applied is a dilute
suspension of macromolecules. For the viscosity of polymer solutions, there exists a considerable basis of theory from fluid mechanics, notably the Einstein equation. Before comparing the two results, a brief background in polymer solution theory is presented.
References


CHAPTER III. POLYMER SOLUTIONS

A. Einstein Equation Derivation

Although the major thrust of this work deals with the examination of kinetic theory as applied to the calculation of transport properties, much important work in this field has been done in fluid mechanics. The Einstein equation for viscosity of a dilute suspension of macroparticles is exactly such a result. A synopsis of its original derivation follows. 

A small region G in a liquid is considered such that linear terms in a Taylor's series are all that need be used.

The liquid in G is regarded as moving with the superposition of three simpler motions:

1. A parallel displacement of all the particles of the liquid without change of their relative position.
2. A rotation of the liquid without change of the relative position of the particles of the liquid.
3. A movement of dilatation in three directions at right angles to one another (the principle axes of dilatation).

Imagine a spherical particle being placed in G, its center at a place, which for convenience, we specify as the origin. Assuming negligible kinetic energy both for the sphere and the liquid bulk and assuming a no-slip condition, we see that the third motion is changed by the presence of the particle.

In its absence, the motion of the liquid could be expressed
where \((x, y, z)\) are the coordinates in the principle axes of dilata-
tion and \((u_0, v_0, w_0)\) the respective components of velocity of dilata-
tion. The constants \(A, B,\) and \(C\) due to the incompressibility of
the liquid, obey

\[
A + B + C = 0
\]  

At a large enough distance, the components of the liquid's velocities
must approach the velocities \((u_0, v_0, w_0)\). Therefore, if

\[
\begin{align*}
  u &= A \, x + u_1 \\
  v &= B \, y + v_1 \\
  w &= C \, z + w_1
\end{align*}
\]  

the velocities \((u_1, v_1, w_1)\) must vanish as the distance \(s\) from the
center as the sphere gets large relative to \(\frac{a}{2}\) the radius.

Using the equations of motion and continuity, we know

\[
\frac{\partial P}{\partial x} = \eta \nu^2 u; \quad \frac{\partial P}{\partial y} = \eta \nu^2 v; \quad \frac{\partial P}{\partial z} = \eta \nu^2 w
\]  

and
\[ \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0 \]  

(5)

Since \((u,v,w)\) and \((u_0,v_0,w_0)\) must both satisfy equations (4) and (5), the fact that the equations are linear implies \((u_1,v_1,w_1)\) must satisfy them as well.

This leads to a solution of the form

\[ p = -\frac{5}{3} \eta \left( \frac{g}{z} \right)^3 \left\{ \frac{a^2(1)}{s^2} + B \frac{a^2(1)}{s} + C \frac{a^2(1)}{z} \right\} + \text{const.} \]  

(6)

\[ u = A x - \frac{5}{3} \left( \frac{g}{z} \right)^3 A \frac{x}{s^3} - \frac{aD}{s^3} \]  

\[ v = B y - \frac{5}{3} \left( \frac{g}{z} \right)^3 B \frac{y}{s^3} - \frac{aD}{s^3} \]  

\[ w = C z - \frac{5}{3} \left( \frac{g}{z} \right)^3 C \frac{z}{s^3} - \frac{aD}{s^3} \]  

(7)

where

\[ D = A \left\{ \frac{5}{6} \left( \frac{g}{z} \right)^3 \frac{a^2 s}{ax^2} + \frac{1}{6} \left( \frac{g}{z} \right)^5 \frac{a^2(1)}{ax^2} \right\} \]

\[ + B \left\{ \frac{5}{6} \left( \frac{g}{z} \right)^3 \frac{a^2 s}{ay^2} + \frac{1}{6} \left( \frac{g}{z} \right)^5 \frac{a^2(1)}{ay^2} \right\} \]

\[ + C \left\{ \frac{5}{6} \left( \frac{g}{z} \right)^3 \frac{a^2 s}{az^2} + \frac{1}{6} \left( \frac{g}{z} \right)^5 \frac{a^2(1)}{az^2} \right\} \]  

(8)

Einstein then argues that this is the sole possible form of the
solution, a fact which we will accept without proof.

Next, postulate further a control volume spherical in shape with radius $R^5 \gg \sigma^5$. It is possible to calculate the mechanical work done per unit time on that control volume by the pressure in both cases—when the interior sphere is present and when it is not. The viscous dissipation of energy caused by the particle can then be calculated. Let the components of pressure exerted on the control volume $X, Y, Z$ be given by

$$
X = \frac{-1}{s} (X_1 x + X_2 y + X_3 z) \\
Y = \frac{-1}{s} (Y_1 x + Y_2 y + Y_3 z) \\
Z = \frac{-1}{s} (Z_1 x + Z_2 y + Z_3 z)
$$

where

$$
X_1 = P - 2n \frac{\partial u}{\partial x} \\
Y_2 = P - 2n \frac{\partial v}{\partial y} \\
Z_3 = P - 2n \frac{\partial w}{\partial z}
$$

$$
Y_3 = Z_2 = -n \left( \frac{\partial w}{\partial z} + \frac{\partial u}{\partial y} \right) \\
Z_1 = X_3 = -n \left( \frac{\partial w}{\partial x} + \frac{\partial u}{\partial z} \right)
$$

The work is then

$$
W = \int (Xu + Yv + Zw) \, dS
$$

where $dS$ is a differential element of the surface of the control volume and the integration is over the entire surface.
Evaluating the integrand and ignoring any terms in which the ratio \( \frac{\sigma}{2s} \) is raised to a power greater than three gives

\[
Xu + Yv + Zw = \frac{2n}{s} (A^2x^2 + B^2y^2 + C^2z^2)
\]

\[
- 5n \frac{\sigma^3}{8s^4} (A^2x^2 + B^2y^2 + C^2z^2)
\]

\[
+ 15n \frac{\sigma^3}{8s^6} (Ax^2 + by^2 + Cz^2)
\]

(12)

Performing the integration with the sphere yields

\[
W = 8\pi R^3 n \delta^2 + \frac{4}{3} \pi (\frac{\sigma}{2})^3 n \delta^2 = 2\delta^2 n (V + \phi)
\]

(13)

where \( \delta = A^2 + B^2 + C^2 \) and \( V \) and \( \phi \) represent the volume of the control volume and spherical particle respectively. With a unit total volume \( V \) becomes 1 and \( \phi \) becomes \( \phi \) the volume fraction. Without the sphere (\( \phi = 0 \))

\[
W = 2\delta^2 n V
\]

(14)

The difference, therefore, is \( \delta^2 n \phi \).

For the case of multiple spheres in suspension, the situation is more complicated. If the center of the sphere \( i \) is represented \((\xi_i, T_i, \zeta_i)\) then translating the axes to the sphere's center gives
Now if there are $n$ spheres in a unit volume such that their volume fraction $\phi$ is small, we can obtain expressions for $(u,v,w)$, neglecting higher order terms, by summing contributions:

$$
x_i = x - \xi_i
$$
$$
y_i = y - \tau_i \tag{15}
$$
$$
z_i = z - \zeta_i
$$
$$
S_i = x_i^2 + y_i^2 + z_i^2
$$

Now if there are $n$ spheres in a unit volume such that their volume fraction $\phi$ is small, we can obtain expressions for $(u,v,w)$, neglecting higher order terms, by summing contributions:

$$
u = Ax - \sum_{i=1}^{n} \left( \frac{5}{2} \frac{\sigma_3}{8S_i^2} \frac{x_i(Ax_i^2 + By_i^2 + Cz_i^2)}{S_i^3} + \frac{\sigma_5}{32S_i^4} \frac{Ax_i}{S_i} \right)$$

$$
v = By - \sum_{i=1}^{n} \left( \frac{5}{2} \frac{\sigma_3}{8S_i^2} \frac{y_i(Ax_i^2 + By_i^2 + Cz_i^2)}{S_i^3} + \frac{\sigma_5}{32S_i^4} \frac{By_i}{S_i} \right) \tag{16}
$$
\[ w = Cz - \sum_{i=1}^{n} \left\{ \frac{5}{2} \frac{\sigma_i^3}{8S_i^2} \frac{z_i (A_{x_i}^2 + B_{y_i}^2 + C_{z_i}^2)}{S_i^3} \right\} \]

\[ - \frac{5}{2} \frac{\sigma_i^5}{32S_i^4} \frac{z_i (A_{x_i}^2 + B_{y_i}^2 + C_{z_i}^2)}{S_i^3} + \frac{\sigma_i^5}{32S_i^4} \frac{C_{z_i}}{S_i} \]

We can see that each sphere contributes to the work loss and a generalization of equation (13) gives the work \( W^* \) of the mixture.

\[ W^* = 2\sigma^2 \eta (1 + \phi/2) \] (17)

If the mixture is then considered as a pseudo-homogeneous liquid, we can speak of its principle dilatation \( A^*, B^*, C^* \) different from those of the suspending liquid \( A, B, C \). Rewriting equations (16) in the form

\[ u = Ax + \sum u_i \]

\[ v = By + \sum v_i \] (18)

\[ z = Cz + \sum z_i \]

then, considering only \( A^* \) for the moment,

\[ A^* = \left( \frac{\partial u}{\partial x} \right)_{x=0} = A + \sum \left( \frac{\partial u_i}{\partial x} \right)_{x=0} = A - \sum \left( \frac{\partial u_i}{\partial \xi_i} \right)_{x=0} \] (19)
Assuming that we are not close to the sphere, the expression for \( u \) simplifies and

\[
\frac{5}{2} \frac{1}{8r_i^2} \frac{\epsilon_i (A \epsilon_i^2 + B T_i^2 + C \zeta^2)}{r_i^2}
\]  

(20)

and analogous expressions for \( v_i \) and \( w_i \) with

\[
r_i^2 = \epsilon_i^2 + T_i^2 + \zeta^2
\]

(21)

Approximating the summation by an integration, we obtain

\[
A^* = A - n \int \frac{\partial u_i}{\partial \epsilon_i} \frac{d\epsilon_i}{dT_i} \frac{dT_i}{d\epsilon_i}
\]

\[
= A - n \int \frac{u_i \epsilon_i}{r_i} dS
\]

(22)

Performing the integration over the surface of a control volume of radius \( R \) gives

\[
A^* = A - \frac{5}{2} \frac{1}{8R^6} n \int x_0^2 (A x_0^2 + B y_0^2 + C z_0^2) dS
\]

\[
= A (1-\phi)
\]

(23)

and

\[
B^* = B (1-\phi)
\]

\[
C^* = C (1-\phi)
\]
analogously. If we consider once again our mixture to be a liquid, we have shown

\[ \bar{W}^* = 2\delta^* n^* \]  

(24)

where \( n^* \) is the viscosity of the mixture and \( \delta^* \) is given as the sum of the squares of the dilatations \( A^*, B^*, \) and \( C^* \).

In approximation, therefore, \( \delta^* \) can be given from equation (23)

\[ \delta^2 = \delta^2 (1 - 2\phi) \]  

(25)

A combination of equations (17), (24), and (5.25) yields an expression for \( n^* \) in terms of \( n \) and \( \phi \). Neglecting higher order terms

\[ n^*/n = 1 + 2.5\phi \]  

(26)

This is the Einstein viscosity equation.
References

B. Molecular Dimensions and Masses

The primary use of the Einstein viscosity equation is in the analysis of polymer solutions. We therefore take a brief look at polymers.

Most polymers are made with processes that are unable to produce a product of uniform molecular size and weight. Therefore, for any unfractionated sample of polymers, there will be a distribution of weights. The average molecular weight of such a group is non-unique in its definition. Measuring the total mass and the total number of moles yields the number average mass. Alternatively, some experiments have results that measure the contribution of individual molecules as a function of their mass. These methods, e.g. sedimentation, produce a weight average molecular mass. A third method, in which we are the most interested, is the measurement of the viscosity of dilute solutions of polymers. As can be seen from Figure III.1, these methods can produce different results for molecular weight in a distributed sample.

Often, there are several size parameters of interest. The fully extended length of polymer chain is called its contour length. The mean square radius of gyration $s^2$ is defined as the average distance of all parts of the polymer from its center of gravity. The mean square of the distance between the ends is denoted $\zeta^2$.

The above definitions apply to any conditions for the polymer molecules. Of particular interest is the situation when the polymer is unperturbed (i.e. the arrangement of the polymer follows a random distribution). $s_0^2$ refers to the mean square radius of gyration in
Figure III.1
Molecular Weight Averages

Number Average
Viscosity Average
Weight Average

Weight
Chain Length
an unperturbed state. If $x$ refers to the number of monomer segments in the polymer chain, then

$$s_0^2 \propto x$$  \hspace{1cm} (1)$$

This, in turn implies that

$$\overline{s_0^2} \propto m$$  \hspace{1cm} (2)$$

or that $s_0^2/m$ is a characteristic constant for a given polymer independent of outside factors.

The typical polymer solution is not ideal. There are thermodynamic effects of mixing which come about from the interaction of the solvent with the polymer. These interactions cause an elongation of a polymer chain from its unperturbed or random state. The expansion factor $\alpha$ is defined

$$\alpha^2 = \frac{s^2}{s_0^2}$$  \hspace{1cm} (3)$$

Assuming a good solvent, the expansion occurs because the chain can extend preferentially from its center into areas where the polymer chain is not. Therefore, there is an "excluded-volume" associated with the polymer chain in non-ideal situations. $\beta$, the excluded volume, can be given by the integral

$$\beta = 4\pi \int_0^\infty [1 - g(s)] s^2 ds$$  \hspace{1cm} (4)$$
Where $s$ is, for this equation, the separation distance between polymer segment pairs.
References

C. Thermodynamic Effects and Theta Temperature

In an ideal solution, the partial pressure is proportional to the molar fraction. This means that the Gibb's free energy of mixing is

\[ \Delta G_{\text{mix}} = NkT(x_1 \ln x_1 + x_2 \ln x_2) \]   \hspace{1cm} (1)

And since \( \Delta H_{\text{mix}} = 0 \) for an ideal solution, the entropy of mixing is given

\[ \Delta S = -Nk(x_1 \ln x_1 + x_2 \ln x_2) \]   \hspace{1cm} (2)

Since this is always positive, the mixing should always occur spontaneously.

In the Flory-Krigbaum\textsuperscript{3} theory to model actual polymer solutions, the partial molar enthalpy, entropy, and free energy of the intermolecular interactions take into account the effects of excluded volume. It can be shown that the excess partial molar properties of the solvent (above the ideal) are dependent on the volume fraction of the polymer \( \phi_2 \) to the second and greater powers. The application to a dilute solution allows one to neglect the higher order terms to arrive at the expressions

\[ \Delta H_1 = RT \kappa_1 \phi_2^2 \]   \hspace{1cm} (3)

\[ \Delta S_1 = R \psi_1 \phi_2^2 \]   \hspace{1cm} (4)
\[ \Delta G_1 = (\mu_1 - \mu_1^0)_E = R \, T \, (\kappa_1 - \psi_1) \, \phi_2^2 \]  

(5)

where the terms on the left are partial molar quantities, \( \mu \) is the chemical potential where \( \mu_1^0 \) refers to the pure solvent and the subscript \( E \) refers to the excess quantity and \( \kappa_1 \) and \( \psi_1 \) are constants.

If \( \Theta \) is defined as the "ideal" temperature:

\[ \Theta = \frac{\kappa_1 \, T}{\psi_1} \]  

(6)

then

\[ \kappa_1 - \psi_1 = \psi_1 \left( \frac{\Theta}{T} - 1 \right) \]  

(7)

Therefore, at \( T = \Theta \) the excess chemical potential of mixing is zero and the solution behaves as if it were ideal. At this Theta temperature, molecular interactions causing excluded volume effects (e.g. perturbing \( s_0^2 \)) are non-existent.
 References


D. Intrinsic Viscosity

One of the methods of characterization of a dilute polymer solution is by the value of its intrinsic viscosity \([\eta]\) which is a measure of the contribution of individual polymer molecules to the viscosity.

If \(\eta\) represents the viscosity of the solution and \(\eta_1\) the viscosity of the pure solvent, the specific viscosity \(\eta_{sp}\) is given

\[
\eta_{sp} = \frac{\eta}{\eta_1} - 1
\]

which can be used to define the intrinsic viscosity

\[
\lim_{c_2 \to 0} \frac{\eta_{sp}}{c_2} = \lim_{c_2 \to 0} \frac{\eta}{c_2} = [\eta]
\]

To obtain the intrinsic viscosity from this definition, some function of specific viscosity must be plotted versus concentration \(c_2\) and extrapolated to zero concentration.

One relationship between the viscosities and concentration was given by Huggins:

\[
\frac{\eta_{sp}}{c_2} = [\eta] + k' [\eta]^2 c_2
\]

The slope constant \(k'\) typically varies between 0.3 and 0.5 and is a characteristic of a given polymer system. For flexible chain polymers, the plot is usually linear and the extrapolation presents no problem. In other cases, another equation is used, sometimes in conjunction
with equation (3)

\[
\frac{\ln \left( \frac{n}{n_1} \right)}{c_2} = [\eta] - \beta'[\eta]^2 c_2
\]  

(4)

The two can be plotted on the same graph since the same intercept should result for \( \eta_{sp}/c_2 \) or \( \frac{\ln \left( \frac{n}{n_1} \right)}{c_2} \). Equation (4) is sometimes preferred since the slope is less steep.

In 1930, Staudinger\(^4\) originally proposed that the reduced viscosity \( \eta_r = \frac{n}{n_1} \) of a polymer is proportional to its molecular weight. This has been modified slightly

\[
[\eta] = K'm^a
\]  

(5)

where \( K' \) and \( a \) are constants for a given polymer. They are determined from double logarithmic plots of \([\eta]\) vs. \( m \). \( a \) is typically between 0.5 and 1.0. Equation (5) is used to obtain viscosity average molecular weights \( \bar{m}_v \):

\[
\bar{m}_v = \left[ \sum_{i=1}^{\infty} w_i m_i^a \right]^{1/a}
\]  

(6)

where \( w_i \) is the weight fraction of molecules with mass \( m_i \). Since the number average, weight average, and viscosity average masses are all approximately equal for a fractionated sample (\( \bar{m}_n = \bar{m}_w = \bar{m}_v \)) the constants in equation (5) can be evaluated with any average mass calculated from a fractionated sample.
References


In a system obeying the Einstein equation, the specific viscosity \( \eta_{sp} \) is given by

\[
\eta_{sp} = 2.5 \phi_2
\]  

(1)

which, if the polymer is regarded as a hard sphere, can be written

\[
\eta_{sp} = 2.5 \left( \frac{\pi}{6} n_2 \sigma_{22}^3 \right)
\]  

(3)

This is true assuming no molecular void space is associated with the macromolecule. If \( c_2 = n_2 m_2 \), then

\[
\eta_{sp}/c_2 = \frac{2.5 \pi}{6} \sigma_{22}^3 / m_2 = [\eta]
\]  

(3)

It should be noticed that the intrinsic viscosity for an Einstein fluid can be given by the simple ratio \( \eta_{sp}/c_2 \) since it is constant with respect to \( c_2 \) as \( c_2 \) approaches zero.

If we assume that the macromolecules in question all have the same density then \( m_2 \propto \sigma_{22}^3 \) and \([\eta]\) is totally independent of molecular size. For the case of macromolecules that are straight chain polymers in a Theta solvent we have seen\(^3,4\) that

\[
\frac{\sigma_{22}^2}{m_2} = \frac{\sigma^2}{m_2} = \text{a constant for a particular polymer} \equiv k
\]  

(4)
If we identify the mean square radius of gyration $s^2$ with the square of the radius of our spherical macromolecule, $\sigma_{\text{22}}^2/4$, the result for the intrinsic viscosity is as follows:

$$[\eta] \propto m_2^{1/2}$$

which is of the same form as equation (III.D.5). In addition, it can be shown that for a Theta solvent the exponent of mass should be 0.5. Therefore, a correspondence exists between the behavior of an Einstein fluid and a polymer solution in a Theta solvent.

The following tables give some intrinsic viscosity results for a Theta-temperature solvent and for some biological macromolecules exhibiting roughly spherical shape.

### Table III.1

<table>
<thead>
<tr>
<th>Protein</th>
<th>$[\eta]/(\text{ccg}^{-1})$</th>
<th>$M/(\text{g mole}^{-1})$</th>
<th>$\sigma_{\text{22}}^{\text{\AA}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ribonuclease</td>
<td>3.3</td>
<td>13,683</td>
<td>36</td>
</tr>
<tr>
<td>$\beta$-Lactoglobulin</td>
<td>3.4</td>
<td>35,000</td>
<td>54</td>
</tr>
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<td>Serum Albumin</td>
<td>3.7</td>
<td>65,000</td>
<td>72</td>
</tr>
<tr>
<td>Hemoglobin</td>
<td>3.6</td>
<td>67,000</td>
<td>62</td>
</tr>
<tr>
<td>Catalase</td>
<td>3.9</td>
<td>250,000</td>
<td>104</td>
</tr>
</tbody>
</table>

Aqueous salt solutions

### Table III.2

**Polystyrene in cyclohexane at 35.01°C**

<table>
<thead>
<tr>
<th>$\eta$</th>
<th>$M/(\text{g mole}^{-1})$</th>
<th>$\sigma_{\text{22}}^{\text{\AA}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>39.2</td>
<td>208,000</td>
<td>195</td>
</tr>
<tr>
<td>59.0</td>
<td>465,000</td>
<td>270</td>
</tr>
<tr>
<td>86.5</td>
<td>1,013,000</td>
<td>419</td>
</tr>
</tbody>
</table>
It can be seen from the experimental results in the two tables that intrinsic viscosity is not, in fact, a constant for either case.

The biological polymers exhibit nearly constant density (i.e. \( m_2 = \sigma_{22}^3 \)) but the intrinsic viscosity has a linear dependence on \( \sigma_{22} \). Alternatively, in the case of the polystyrene at its Theta temperature, although the mass goes up roughly as the square of the diameter, the dependence of intrinsic viscosity on diameter is once again linear.

The Einstein equation, a good first approximation to the behavior of polymer solutions, clearly leaves out a functionality of polymer dimensions. The previous analysis tends to suggest that the coefficient of the volume fraction in the Einstein equation should be linear with respect to macromolecular diameter.
References


CHAPTER IV. RESULTS

A. Mixing Laws and Excess Properties

By substitution of the Percus-Yevick approximation into the contact pair distribution terms in the Thorne equations, the Thorne equations can be solved to yield mixing laws for the transport properties. The results for this section deal with a comparison of experimental data and theoretical predictions of viscosity and thermal conductivity behavior.

In Chapter I, excess properties were defined, and Figure I.1 shows some typical results for thermal conductivity. Excess properties will be the basis for comparison between experimental and theoretical findings.

Firstly, let us examine the form that the mixing laws for viscosity and thermal conductivity can take. The full Thorne equations for thermal conductivity and viscosity, respectively, are given in equations (II.C.44) and (II.C.49). It was shown by Dahler\(^1\) that the first term of equation (II.C.44) arises from the distortion of the velocity distribution from the Maxwellian result while the second term is the contribution of the locally Maxwellian distribution to the collisional contribution to thermal conductivity. He likewise showed that the Longuet-Higgins,\(^2\) et al. result, given by the following:

\[
\lambda_{\text{mix}} = \sigma k n (k T / \pi)^{1/2} [x_1^2 m_1^{-1/2} + 4x_1 x_2 (2m_1 m_2 / (m_1 + m_2)^3)^{1/2} + x_2 m_2^{-1/2}] \tag{1}
\]

was generalized by Kandiyoti and McLaughlin\(^3\) by using the second term of the Thorne equation. Their result, for disparate size molecules is given by:
where $g_i^0$ represents the radial contact pair distribution for pure species $i$.

An analogue for viscosity to the expression for thermal conductivity was also proposed by Kandiyoti and McLaughlin:

$$
\frac{\eta_{\text{mix}}}{\eta_1} = \left(\frac{v_1^0}{v}\right)^2 \frac{1}{g_1^0} \left[ x_1^2 g_{11}^0 + \left(\frac{R}{8(1+R)}\right)^{1/2} x_1 x_2 g_{12}^0 (1 + r)^4 + R^{-1/2} x_2^2 g_{22}^0 r^4 \right]
$$

If a volume fraction $\phi_i$ is defined by $\phi_i = x_i v_i^*/v \xi_i$, where $\xi_i$ refers to the volume fraction taken up by the molecules in a system of pure species $i$, and $G_i = g_{ij}/g_{i}^0$, equations (1) and (2) can be re-arranged into pseudo-quadratic mixing laws:

$$
\lambda_{\text{mix}} = G_1 \phi_1^2 \lambda_1 + 2 \phi_1 \phi_2 \lambda_{12} + G_2 \phi_2^2 \lambda_2
$$

$$
\eta_{\text{mix}} = G_1 \phi_1^2 n_1 + 2 \phi_1 \phi_2 n_{12} + G_2 \phi_2^2 n_2
$$

This definition of $\phi_i$, arising naturally from equations (2) and (3), corresponds to volume fractions based on the volumes of the pure fluids rather than the partial molecular volumes--another possible definition. The cross-term coefficients are given by:
The values for the pure components, \( \lambda_i \) and \( n_i \), can be calculated using equations (6) and (7) with all of the molecules identically species i. \( n_i^0 \) is the number density of pure species i.

Although quadratic in appearance, there is a hidden compositional dependency in the \( G_i \)'s which prevents equations (4) and (5) from being truly quadratic. However, they do indicate why, particularly for liquids, a quadratic type formula might fit the experimental data well.

In actual fact, when equation (1.1) is applied to the thermal conductivity of a \( \text{C}_4\text{H}_4 - \text{C}_6\text{H}_6 \) mixture at 20°C, the cross-term coefficient, \( \lambda_{12} \), varies from .811 to .997 when the mole fraction of \( \text{C}_6\text{H}_6 \) varies from 0.8551 to 0.1359. It is clear that a purely quadratic mixing law is not adequate to describe experimental behavior.

Before comparing the results of Kandiyoti and McLaughlin with experimental results, let us examine another proposed mixing law.

Moelwyn-Hughes\(^7\) proposed a compositional formula that, for a strictly regular solution, can be written

\[
Q_{\text{mix}} = (x_1 q_1 + x_2 q_2)(1 - x_1 x_2 \frac{w}{kT})
\]

where \( w \) is the "interchange energy." The interchange energy is one-half the change in potential energy occurring when two molecules, one each from two pure lattices (liquid or crystalline) are interchanged.\(^8\)
For the particular case of thermal conductivity, the excess property is given by

\[ \lambda_{xs} = (x_1 \lambda_1 + x_2 \lambda_2)(-x_1 x_2 \frac{W}{kT}). \]  

(9)

Given this mixing law, the excess thermal conductivity should exhibit the same arithmetic sign as the interchange energy. Yet, there are various solutions which show positive and negative deviations from Raoult's Law--therefore, positive and negative interchange energies--but which all have negative excess thermal conductivities. In fact, a review\(^5\) of experimental work done by Jamieson and Hastings\(^9\) reveals that of the fifty-nine mixtures tested, fifty showed negative excess thermal conductivities. The nine that were positive could also have been negative within experimental error.

Equation (4) was analyzed\(^5\) to see whether a model taking only size and mass into account and considering only the collisional contribution to transport could successfully predict this result. Because volume fraction is the compositional variable in equation (4), it was convenient to define the excess thermal conductivity in terms of the volume rather than the mole fraction:

\[ \lambda_{xs} = \lambda_{mix} - \phi_1 \lambda_1 - \phi_2 \lambda_2. \]  

(10)

Two cases were considered, restricting \(r\), the size ratio, to unity, and bounding all variables within a region.
Case 1  \( r = 1 \)

Because the sizes of the molecules are the same, the radial contact pair distribution functions are the same and the \( G_i \)'s are unity. To further simplify matters, a positive constant was factored from each term in the equation giving the excess thermal conductivity. The result is a "reduced" excess thermal conductivity \( \lambda_{xsr} \) which has the same arithmetic sign as \( \lambda_{xs} \) and which is given by the following:

\[
\lambda_{xsr} = 2^{5/2} \frac{R}{(R+1)^{3/2}} - R^{1/2} - 1
\]  

(11)

Every physical mass ratio is represented when \( R \) varies from zero through unity. Values for \( \lambda_{xsr} \) were computed starting with \( R = 0.05 \) and for every increment of 0.05 through unity. All were negative.

Case 2

For the purposes of this analysis, macromolecules were excluded from consideration. Consequently, a reasonable range of variables was felt to be as follows: \( r \) from zero to one, \( R \) from one-fifty to five, \( x_1 \) from zero to one, and \( p v_1^*/kT \) from one to five.

Because \( r \) is not restricted to unity, certain factors constant in the previous case must appear as variables here. Simplifying as much as possible, another "reduced" excess thermal conductivity can be expressed as follows:

\[
\lambda_{xsr} = \phi_1 (G_1 \phi_1 - 1) \left( \frac{n_1^0}{n_2^0} \right) g_1^0 R^{1/2} + \phi_2 (G_2 \phi_2 - 1) (n_2^0/n_1^0) g_2^0 r^4 + 2^{5/2} \phi_1 \phi_2 g_{12} (\frac{r+1}{2}) \frac{4R}{(R+1)^{3/2}}
\]  

(12)
Once again, $\lambda_{xs}$ is of the same arithmetic sign as $\lambda_{xs}$, and for all calculated values, within computer accuracy, $\lambda_{xs}$ was non-positive.

In the above situations, only the collisional contribution has been considered. The full Thorne equations have been solved with the Percus-Yevick approximations giving results that can be non-dimensionalized to yield

$$\frac{\lambda_{\lambda}}{\lambda_1} = \frac{1}{5g_{12}} \left[ \frac{A_{\lambda 1} x_1^2 + A_{\lambda 12} x_1 x_2 + A_{\lambda 2} x_2^2}{B_{\lambda 1} x_1^2 + B_{\lambda 12} x_1 x_2 + B_{\lambda 2} x_2^2} \right] + \frac{Q_{\lambda} (C_{\lambda 1} x_1^2 + C_{\lambda 12} x_1 x_2 + C_{\lambda 2} x_2^2)}{g_1} + \frac{1}{5} \left( \frac{v_1^*}{v_0} \right)^2 + 16 \left( \frac{9\pi + 32}{25\pi} \right) g_1^0 \left( \frac{v_1^*}{v_0} \right)^2$$

(13)

and

$$\frac{n_{\eta}}{\eta_1} = \frac{1}{5g_{12}} \left[ \frac{A_{\eta 1} x_1^2 + A_{\eta 12} x_1 x_2 + A_{\eta 2} x_2^2}{B_{\eta 1} x_1^2 + B_{\eta 12} x_1 x_2 + B_{\eta 2} x_2^2} \right] + \frac{Q_{\eta} (C_{\eta 1} x_1^2 + C_{\eta 12} x_1 x_2 + C_{\eta 2} x_2^2)}{g_1} + \frac{1}{5} \left( \frac{v_1^*}{v_0} \right)^2 + \frac{16 + 16}{25\pi} g_1^0 \left( \frac{v_1^*}{v_0} \right)^2$$

(14)

where

$$A_{\lambda 1} = \alpha_{\lambda 1}\alpha_{\lambda 12} \left( \frac{r+1}{2} \right)^2 \left( \frac{1}{2R(1+R)^5} \right)^{1/2}$$

(15)
for

\[ \alpha_{\lambda 1} = \frac{(6R^2 + 5)}{4} - \frac{3}{5} + \frac{4R}{5} \]  
(16)

\[ \alpha_{\lambda 12} = 1 + 12 x_1 g_{11} \left( \frac{v_1^*}{v} \right)/5 + 48 x_2 g_{12} \left( \frac{v_1^*}{v} \right) R/5(1 + R)^2 \]  
(17)

Also,

\[ A_{\lambda 2} = \alpha_{\lambda 2} \alpha_{\lambda 21}^2 \left( \frac{r+1}{2} \right)^2 \left( \frac{1}{2R(1+R)^5} \right)^{1/2} \]  
(18)

\[ \alpha_{\lambda 2} = (6 + 5R^2)/4 - \frac{3R^2}{5} + \frac{4R}{5} \]  
(19)

where \( \alpha_{\lambda 21} \) corresponds to \( \alpha_{\lambda 12} \) with interchanged subscripts and \( g_{21} = g_{12} \).

\[ A_{\lambda 12} = \frac{g_{22} r^2}{5 g_{12} R^{1/2}} \alpha_{\lambda 12}^2 + 2 \frac{27}{20} \left( \frac{r+1}{2} \right)^2 \left( \frac{R}{2(1+R)^5} \right)^{1/2} \alpha_{\lambda 12} \alpha_{\lambda 21} \]

\[ + \frac{g_{11}}{5 g_{12} R} \alpha_{\lambda 21}^2 \]  
(20)

In addition,

\[ B_{\lambda 1} = \frac{g_{11}}{5 g_{12}} \alpha_{\lambda 1} \left( \frac{1}{1+R} \right)^3 \left( \frac{r+1}{2} \right)^2 \left( \frac{R+1}{2R} \right)^{1/2} \]  
(21)

\[ B_{\lambda 12} = \frac{g_{11} g_{22} r^2}{25 g_{12} R^{1/2}} + \frac{\alpha_{\lambda 1} \alpha_{\lambda 2}}{2} \left( \frac{1}{1+R} \right)^5 \left( \frac{r+1}{2} \right)^4 \]

\[ - \frac{R^2}{2(1+R)^5} \left( \frac{27}{20} \right)^2 \left( \frac{r+1}{2} \right)^4 \]  
(22)
\[ B_{\lambda 2} = \frac{g_{22}}{5g_{12}} \alpha_{\lambda 2} \left( \frac{R}{2(1+R)^5} \right) \left( \frac{r+1}{2} \right) \left( \frac{r^2}{R^{1/2}} \right) \]  

(23)

and

\[ Q_{\lambda} = \frac{512}{25\pi} \left( \frac{v_1^*}{v} \right)^2 / (1 + R)^{1/2} \]  

(24)

\[ C_{\lambda 1} = (1 + R)^{1/2} g_{11} \]  

(25)

\[ C_{\lambda 12} = 2 \left( \frac{8R}{(1+R)^2} \right)^{1/2} g_{12} \left( \frac{r+1}{2} \right)^4 \]  

(26)

\[ C_{\lambda 2} = g_{22} r^4 \left( \frac{1+R}{R} \right)^{1/2} \]  

(27)

For viscosity, the various functions are given as

\[ A_{\eta 1} = \alpha_{\eta 1} \alpha_{\eta 12} \left( \frac{r+1}{2} \right)^2 \left( \frac{R}{2(1+R)^3} \right)^{1/2} \]  

(28)

with

\[ \alpha_{\eta} = \left( \frac{2}{3} + \frac{2}{5R} \right) \]

\[ \alpha_{\eta 12} = \{1 + 8x_1 g_{11} \left( \frac{v_1^*}{v} \right)/5 + 16x_2 \left( \frac{r+1}{2r} \right)^3 \]

\[ \left( \frac{R}{1+R} \right) g_{12} \left( \frac{v_2^*}{v} \right)/5 \]  

(29)

\[ A_{\eta 2} \] is equivalent to \[ A_{\eta 1} \] but with interchanged species numbers and with the other constants:
\[
\alpha_{n2} = \left( \frac{2}{3} + \frac{2R}{5} \right) 
\]  (30)

\[
\alpha_{n21} = \{1 + 8x_{2}g_{22} \left( \frac{v_{*}}{v} \right)/5 + 16x_{1} \left( \frac{r+1}{2} \right)^{3} \left( \frac{1}{1+R} \right) 
\]

\[g_{12} \left( \frac{v_{*}}{v} \right)/5 \} 
\]  (31)

\[
A_{n12} = \frac{g_{22}}{5g_{12}} \frac{r^{2}}{R^{1/2}} \alpha_{n12}^{2} + \frac{8}{15} \left( \frac{r+1}{2} \right)^{2} \left( \frac{R}{2(1+R)} \right)^{1/2} \alpha_{n12}^{2} \alpha_{n21} 
\]

\[+ \frac{g_{11}}{5g_{12}} \alpha_{21}^{2} 
\]  (32)

\[
B_{n1} = \frac{g_{11}}{5g_{12}} A_{n1}/\alpha_{n12}^{2} 
\]  (33)

\[
B_{n12} = \alpha_{n1} \alpha_{n2} \left( \frac{r+1}{2} \right)^{4} \left( \frac{R}{2(1+R)} \right)^{3} + \frac{g_{11}g_{22}}{(5g_{12})^{2}} \frac{r^{2}}{R^{1/2}} 
\]

\[- \left( \frac{4}{15} \right)^{2} \left( \frac{r+1}{2} \right)^{4} \left( \frac{R}{2(1+R)} \right)^{3} \]  (34)

\[
B_{n2} = \frac{g_{22}}{5g_{12}} \frac{r^{2}}{R^{1/2}} A_{n2}/\alpha_{n21}^{2} 
\]  (35)

and finally,

\[
Q_{n} = \frac{768}{25\pi} \frac{v_{*}^{2}}{(v)} \]  (36)

\[
C_{n1} = g_{11} 
\]  (37)

\[
C_{n12} = 2\left( \frac{2R}{1+R} \right)^{1/2} \left( \frac{r+1}{2} \right)^{4} g_{12} 
\]  (38)
\[ c_{n2} = R^{1/2} r^4 g_{22} \]  

The Thorne equations were derived for dense fluids. However, in order to test their ability to predict excess quantities (both positive and negative) data from dilute fluids was also used. The Thorne equations are applicable to low density fluids since they reduce to the Chapman-Enskog\[12\] expressions for dilute gas mixtures. This is easily seen because at low density \( v^*/v \) approaches zero and the radial contact pair distribution approaches unity reducing equation (II.A.21) to the virial equation of a dilute hard sphere gas.

To compare\[11\] the experimental results with the predictions of the equations, a value for \( r \) must be chosen. To do this, viscosities from experiment, when available, were equated to the Chapman-Enskog hard sphere gas viscosity expression. This expression was then solved for the diameters at the temperature of interest. If experimental data were unavailable, viscosities were first calculated from the Chapman-Enskog expression with 12:6 force constants. Then hard sphere diameters were calculated to give the same values as if the viscosities were actual instead of calculated.

The results for the viscosity equation were disappointing in that no consistent correlation with experimental behavior was observed overall.\[11\] The data of Trautz, et al.\[13\] agree qualitatively with the excess viscosities predicted by equation (14). These data (primarily for mixtures of hydrogen with other gases--all in the dilute phase) all exhibit positive excess viscosities as do the calculations.
However, no simple mathematical restrictions in the R/r plane resulted in exclusively positive excess viscosities.

For the dense fluid, the equation predicts and the data exhibit both positive and negative excess viscosities. Unfortunately, there is no correlation between the two. Therefore, the size and mass ratios are inadequate to predict even qualitatively the excess viscosities of dense fluid mixtures.

For thermal conductivity, the results do correlate. When $R < r^2 < 1$, the excess thermal conductivities as calculated by equation (13) are all negative, seemingly for all values of pressure. In the dilute gas phase, those mixtures quoted by Hirschfelder, Curtiss, and Bird$^{14}$ all exhibit negative excess thermal conductivity.$^{11}$ As previously mentioned, the mixtures studied by Jamieson and Hastings$^9$ in the liquid phase exhibit primarily negative excess thermal conductivities.

Therefore, there is a high degree of qualitative correspondence between experimental data and theoretical calculations of excess thermal conductivity as outlined in this work.
References


B. The Einstein Analogue

In Section III.A, the Einstein viscosity equation was derived. Because of its dependence on the assumption that the suspending fluid is a continuum, obviously the Einstein equation is true only in the limit as the molecular size of species 2 increases without bound. Alternatively, if the suspended particles were identical to those of the suspending fluid, no intrinsic viscosity effect would be noticeable. Unfortunately, for fluid mechanics there is no "in-between." The Thorne equation for viscosity provides an alternative approach to the same problem in which the relative size of the particles plays an important role.

Equation (III.A.26), the Einstein equation, gives the dependence of viscosity on volume fraction to the first order approximation. It is obvious from its derivation that equation (III.A.26) is but the truncation of a power series in volume fraction which can be written

\[
\frac{n}{n_1} = 1 + \sum_{i=1}^{\infty} K_i \phi_2^i
\]  

(1)

The Einstein result shows \( K_1 \) to be 2.5 and later work suggests that \( K_2 \) is of the order of \( K_1^2 \).

The questions which this work sets out to answer are "Do the Thorne equations provide a counterpart to the Einstein equation, and, if so, what form might it take?"
The Einstein equation has been derived for a system in which the macromolecular size is large, but the volume fraction of the macromolecules is small—-at least this is a statement of the assumptions for a real system composed of discrete particles. Those two assumptions translate mathematically into the following stipulations:

\[ r \gg 1 \]  

Equation (2) is equivalent to specifying a suspension of macromolecules.

The second stipulation, corresponding to small macromolecular volume fraction, is dependent on the definition of volume fraction. We will use a generalization of the definition in section IV.A.

\[ \phi_i = \frac{x_i v_i^*}{\xi v} = \frac{x_i v_i^*}{x_1 v_1^* + x_2 v_2^*} \]  

For constant \( \xi \), equation (3) reduces to that definition in section IV.A. This is not the exact definition used by Einstein in deriving his equation, since some void space between molecules (not recognized in fluid mechanics) is associated with each molecule.

With this definition, the macromolecular volume fraction is on the order of \( x_2 r^3 \), so for the dilute solution,

\[ x_2 r^3 \ll 1 \]
specifies\textsuperscript{4,5} the necessary degree to which the Thorne equation must be simplified.

Given equations (2), (3), (II.C.42) and (II.C.43) one can obtain approximations for the radial pair distributions, $g_{ij}$'s:\textsuperscript{5}

\begin{align*}
g_{11} &= (1 + \frac{\xi}{2}) - \frac{3}{2} \xi \phi_2 (1 - \xi)^{-2} \\
g_{22} &= (1 + \frac{\xi}{2}) + \frac{3}{2} (1 - \phi_2) \xi r (1 - \xi)^{-2}
\end{align*}

and

\begin{equation}
g_{12} = (1 + 2\xi - 3\xi \phi_2) (1 - \xi)^{-2}
\end{equation}

Finally, in order to simplify equation (IV.A.14), $R$ must be assigned some functionality of $r$ because of its explicit appearance. This procedure is deemed less artificial than further constraining $R$ in a manner similar to equations (3) and (4).

A physically reasonable situation might be the assumption that each molecule had the same mass density. In that case,

\begin{equation}
R = \frac{m_2}{m_1} = \frac{\sigma_{22}^3}{\sigma_{11}^3} = r^3
\end{equation}

Therefore, the first simplifications of the full Thorne viscosity equation will assume equation (8).
Combining equations (IV.A.14), (3) and (5) with inequality (4) will yield an expression for the viscosity of a dilute solution of macromolecules. Because all terms smaller than $x_2r^3$ have been discarded, the equation is accurate to the first order in $\phi_2$. What cannot be stated for the resultant equation is that the remainder of the equation (the truncated terms) are of the order of $\phi_2^2$. This occurs because $\phi_2^2 \propto x_2r^6$ and terms such as $x_2r^2$ are truncated. Only if $x_2r^3$ and the reciprocal of $r$ have the same order do the two truncations share the same order. The resulting equation can be expressed by

$$\frac{n}{\eta} = \left\{ \frac{1}{g_{11}} \left[ \alpha_{n12}^2 \right] + \frac{768}{25\pi} \left( \frac{1}{v} \right)^{2} \left[ x_1^2 g_{11} + 2(\frac{2R}{1+R})^{1/2} x_1 x_2 g_{12} \left( \frac{r+1}{2} \right)^4 \right] \right\}$$

$$\left[ \frac{1}{g_{1}} + \frac{16}{5} \left( \frac{1}{v} \right)^{2} + \left( \frac{64\pi + 768}{25\pi} \right) g_{1}^{0} \left( \frac{1}{v} \right)^{2} \right]$$

(9)

Substitution for $\alpha_{n12}$ and defining $\phi_i$ as in equation (3) yields

$$\frac{n}{\eta} = \left\{ \frac{1}{g_{11}} \left[ \left\{ 1 + \frac{8}{5} \phi_1 \xi g_{11} + \frac{16}{5} \left( \frac{r+1}{2r} \right)^3 \phi_2 \xi g_{12} \left( \frac{R}{1+R} \right)^2 \right\} \right] \right. $$

$$+ \left. \frac{768}{25\pi} \left( \frac{1}{v} \right)^{2} \left[ x_1^2 g_{11} + 2(\frac{2R}{1+R})^{1/2} x_1 x_2 g_{12} \left( \frac{r+1}{2} \right)^4 \right] \right\}$$

$$\left[ \frac{1}{g_{1}} + \frac{16}{5} \xi_1 + \left( \frac{64\pi + 768}{25\pi} \right) g_{1}^{0} \xi_1 \right]$$

(10)

where $\xi_1 = \xi$ at $x_i = 1$. 

The addition of equation (8) and inequality (2) will result in the following approximation:

\[
\frac{n}{n_1} = \frac{1}{g_{11}} \left[ 1 + \frac{16}{5} \xi g_{11} + \frac{64}{25} \xi^2 g_{11}^2 + \frac{768}{25\pi} \xi^2 g_{11}^2 - \frac{16}{5} \xi g_{11} \phi_2 
+ \frac{4}{5} \xi g_{12} \phi_2 + \frac{32}{25} \xi^2 g_{11} g_{12} \phi_2 - \frac{32}{25} \xi^2 g_{11} g_{12} \phi_2^2 
- \frac{128}{25} \xi^2 g_{11} \phi_2 + \frac{64}{25} \xi^2 g_{11} \phi_2 - \frac{4}{25} \phi_2^2 \xi^2 g_{12}^2 \right] 
+ \frac{768}{25\pi} \left[-2\xi^2 g_{11} \phi_2 + \xi^2 g_{11} \phi_2 - 2\xi^2 \phi_2 g_{12} \xi^2 (\frac{r}{g_1} + \frac{1}{4}) \right] 
- 2^{3/2} \phi_2^2 g_{12} \xi^2 \left(\frac{r}{g_1} + \frac{1}{4}\right) \right] \left[ \frac{1}{g_{11}} + \frac{16}{5} \xi_1 + \left(\frac{64}{25} + \frac{768}{25\pi}\right) g_1 \xi_1^2 \right] 
\]

(11)

At this point substitutions for the various radial contact pair distributions need to be made. They can be expressed as a power series expansion as illustrated for \( g_{11} \).

\[
\frac{1}{g_{11}} = \frac{1 - \xi^2}{(1 + \xi)^2} = \frac{2(1-\xi)^2}{(2+\xi)} \left( \frac{1}{1 - \frac{3\xi_2}{2+\xi}} \right) 
= \frac{2(1-\xi)^2}{(2+\xi)} \sum_{i=0}^{\infty} \left( \frac{3\xi_2}{2+\xi} \right)^i 
\]

(12)

Substitution gives the following equation:
\[
\frac{n}{n_1} = \left[ \frac{2(1-\xi)}{2+\xi} \right]^2 \sum_{i=0}^{\infty} \frac{3\xi \phi_2}{2+\xi}^i + \frac{16}{5} \xi + \left( \frac{64}{25} + \frac{768}{25\pi} \right) \xi^2 \frac{(2+\xi - 3\xi \phi_2)}{2(1-\xi)^2} \\
+ \frac{8}{15} (1 + 2\xi - 3\xi \phi_2) \sum_{i=1}^{\infty} \frac{3\xi \phi_2}{2+\xi}^i + \left[ \frac{32}{25} \xi^2 \frac{(1+2\xi - 3\xi \phi_2)}{(1-\xi)^2} - \frac{16\xi}{5} \right] \\
- \frac{128}{25} \xi^2 \frac{(2+\xi - 3\xi \phi_2)}{2(1-\xi)^2} - \frac{768}{25\pi} \xi^2 \frac{(2+\xi - 3\xi \phi_2)}{(1-\xi)^2} \\
+ \frac{768}{25\pi} 2^{5/2} \xi^2 \phi_2 \frac{(1+2\xi - 3\xi \phi_2)}{(1-\xi)^2} + \frac{768}{25\pi} 2^{-1/2} \frac{(1+2\xi - 3\xi \phi_2)}{(1-\xi)^2} \xi^2 \phi_2 \\
+ \frac{8}{225} (1+2\xi - 3\xi \phi_2)^2 \frac{(2+\xi)}{(1-\xi)^2} \sum_{i=2}^{\infty} \frac{3\xi \phi_2}{2+\xi}^i \\
+ \left[ \frac{768}{25\pi} \xi^2 \frac{(2+\xi - 3\xi \phi_2)}{2(1-\xi)^2} - \frac{32}{25} \xi^2 \frac{(1+2\xi - 3\xi \phi_2)}{(1-\xi)^2} \right] \\
- \frac{768}{25\pi} 2^{5/2} \xi^2 \phi_2 \frac{(1+2\xi - 3\xi \phi_2)}{(1-\xi)^2} - \frac{768}{25\pi} 2^{-1/2} \xi^2 \frac{(1+2\xi - 3\xi \phi_2)}{(1-\xi)^2} \phi_2^2 \right] \\
+ \frac{1}{g_1^0} + \frac{16}{5} \xi \phi_1 + \left( \frac{64}{25} + \frac{768}{25\pi} \right) g_1^0 \xi^2 \phi_1^2 \tag{13}
\]

in which indices have been shifted and terms rearranged.

Finally, \( \xi \) is assumed to be constant. This means that the initial term in the series expansion for \( \frac{1}{g_1} \) is equivalent to \( \frac{1}{g_1^0} \) and \( \xi = \xi_1 \). Consequently, equation (13) can be rearranged in the following form:
\[
\frac{n}{n_1} = 1 + \left( \frac{6\xi(1-\xi)^2}{(2+\xi)^2} + \frac{8\xi}{5} \frac{(1+2\xi)}{2+\xi} + \frac{32}{25} \xi^2 \frac{(1+2\xi)}{(1-\xi)^2} - \frac{16\xi}{5} \right) \\
- \frac{64}{25} \xi^2 \frac{(2+\xi)}{(1-\xi)^2} - \frac{768}{25\pi} \xi^2 \frac{(2+\xi)}{(1-\xi)^2} + 2^{-5/2} \xi^2 r \left( \frac{1+2\xi}{(1-\xi)^2} \right)^2 \frac{768}{25\pi} \\
+ \left( \frac{768}{25\pi} \right)^2 \left( \frac{1+2\xi}{(1-\xi)^2} \right)^2 \phi_2 \\
+ \left[ \frac{64}{25} \left( \frac{3\xi^3}{(1-\xi)^2} \right) + \frac{768}{25\pi} \left( \frac{3\xi^2}{(1-\xi)^2} \right) - \frac{24}{5} \left( \frac{\xi^2}{2+\xi} \right) - \frac{32}{25} \left( \frac{3\xi^2}{(1-\xi)^2} \right) \right] \\
- 2^{-5/2} \left( \frac{768}{25\pi} \right)^2 \left( \frac{3\xi^2}{(1-\xi)^2} \right) r - 2^{-1/2} \left( \frac{3\xi^2}{(1-\xi)^2} \right)^2 \left( \frac{768}{25\pi} \right)^2 + \left( \frac{768}{25\pi} \right)^2 \xi^2 \frac{(2+\xi)}{2(1-\xi)} \\
- \frac{32}{25} \xi^2 \frac{(1+2\xi)}{(1-\xi)^2} - 2^{-5/2} \xi^2 r \left( \frac{1+2\xi}{(1-\xi)^2} \right)^2 \frac{768}{25\pi} \\
- \frac{768}{25\pi} \xi^{-1/2} \xi^2 \left( \frac{1+2\xi}{(1-\xi)^2} \right)^2 \phi_2^2 \\
+ \left[ \frac{32}{25} \left( \frac{3\xi^3}{(1-\xi)^2} \right) + 2^{-5/2} \left( \frac{3\xi^3}{(1-\xi)^2} \right)^2 \frac{768}{25\pi} \right] \\
+ \left( \frac{768}{25\pi} \right)^2 \xi^{-1/2} \left( \frac{3\xi^3}{(1-\xi)^2} \right)^2 \left( \frac{768}{25\pi} \right)^2 \phi_2^3 \\
+ \left[ \frac{2(1-\xi)^2}{2+\xi} + \frac{8}{15} (1 + 2\xi - 3\xi\phi_2) + \frac{8}{225} \frac{(1+2\xi-3\xi\phi_2)^2}{(1-\xi)^2} \right].
\]

Equation (14) is patently inaccurate for terms higher than first order - second order contributions have already been discarded. However, it does show that \( \frac{n}{n_1} \) can be expressed as
\[
\frac{n}{\eta} = \sum_{i=0}^{\infty} a_i \phi^i 
\]  \hspace{1cm} (15)

where the \(a_i\)'s are functions of \(r\) and \(\xi\) \((a_0 = 1)\).

A comparison of equations (1) and (15) shows that an analog to the Einstein result has been derived. Further, values of \(r\) and \(\xi\) can be chosen (e.g. 16.88 and 0.5 respectively) such that \(a_1\) is 2.5, the Einstein result. In fact, \(a_1\) is given by

\[
a_1 = \left[ \frac{6\xi(1-\xi)^2}{(2+\xi)^2} + \frac{8\xi}{5} \frac{(1+2\xi)}{(2+\xi)} + \frac{32}{25} \frac{\xi^2}{(1-\xi)^2} - \frac{16\xi}{5} \right.

\left. - \frac{64}{25} \frac{\xi^2}{(1-\xi)^2} \right] - \frac{768}{25\pi} \frac{\xi^2}{(1-\xi)^2} \left[ \frac{1}{\xi} + \frac{16}{5} \xi_1 + \frac{64}{25} + \frac{768}{25\pi} \xi_0 \xi_1 \right] \]

\hspace{1cm} (16)

and is therefore of the form:

\[
a_1 = a_1^i + a_1^r \]

(17)

- a linear relation with respect to size ratio for a given void space fraction.

If the specific viscosity, \(n/\eta - 1\), of an Einstein solution is divided by the macromolecular volume fraction, \(\phi_2\), a constant (2.5) results. For the Thorne equation, the linear function \(a_1\) results.
These two appear to be in direct contradiction. The Thorne result does not approach (asymptotically or otherwise) the Einstein result. What significance, then, does equation (17) have?

Firstly, for convenient values of $\xi$, $r$ can be made large enough to recover the Einstein equation. Secondly, in the pure solvent, there is no intrinsic viscosity effect, i.e., for molecules the same size ($r$ equal unity) the ratio of $\eta/\eta_1$ is unity. For a given value of $\xi$, $r$ can be found such that $\alpha_1$ is zero. Clearly, then, the applicability of equation (17) should lie in the transitional region between macromolecular effects and solutions of equally sized molecules. Figure IV.1 is illustrative of this proposition.

There are several arguments for belief in such a model. There must be some intermediate region where, for $r$ rising from unity, the intrinsic viscosity rises from zero to the Einstein value. Although it is highly unlikely that a true linear transition occurs, equation (17) provides a first approximation.

A closer look at the data in Tables III.1 and III.2 indicates some qualitative differences between the two tables. In Table III.2, the molecules exhibit an increase in mass proportional to the square of the radius. As the Einstein equation predicts, its intrinsic viscosity is proportional to the square root of the mass and hence to the first power of the size ratio $r$. Note that not only is the intrinsic viscosity linear in $r$ but also proportional to $r$ as the Einstein equation predicts (when in the form of equation (III.E.5)).

In Table III.1, the intrinsic viscosity exhibits a linear dependence on molecular size, but the mass is proportional to the volume. This is clearly not predicted by the Einstein equation.
Figure IV.1

Interpretation of Equation (17)
If 6.093 Å and 2.73 Å are used as the diameters of cyclohexane and water respectively, the diameter ratios for polystyrene in cyclohexane vary between roughly thirty-two and sixty-nine while the ratios of sizes for the biological polymers in aqueous salt solutions vary from approximately thirteen to thirty-eight. Given these differing spans for \( r \), does equation (17) indicate that a difference in behavior would be expected from the different systems? To determine the answer to this question requires the evaluation of points A and B on Figure IV.1 which further requires a value of the void space fraction. Equation (17) gives the following results:

- point A \((\xi, r, a_1) = (.5, 4.4, 0)\)
- point B \((\xi, r, a_1) = (.5, 16.9, 2.5)\)

It is easily seen that for these two experimental systems, if a reasonable choice (e.g. 0.5) is made for \( \xi \), equation (17) indicates different resultant behavior. Although the biological polymer solutions are not modeled accurately by equation (17), they do exhibit what is now an understandable deviation from the Einstein result because they are close to the limit of its range of applicability. Alternatively, the polystyrene/cyclohexane solutions have size ratios considerably greater and should do a better job of exhibiting Einstein behavior. They do, as illustrated in Figures IV.2 and IV.3, since their mass is proportional to \( a_{22}^2 \) and the Einstein equation predicts the proportionality to \( r \) of their intrinsic viscosity.
Figure IV.2
Intrinsic Viscosity
of Biopolymers/Water

\[ \frac{[n]}{ccg^{-1}} \]

\[ r \]

- 10 20 30 40
Figure IV.3

Intrinsic Viscosity of Polystyrene/Cyclohexane

\([\eta]/\text{ccg}^{-1}\)
For these reasons, the use of equation (17) is proposed as a first approximation to behavior in a transition zone between mixtures of particles of approximately equal sizes and dilute solutions of particles large enough that fluid mechanics is a more reasonable approximation.

Finally, to clear up certain non-rigorous portions of this deviation, account must be taken of the fact that $R$ can be a function of $r$ other than $r^3$. Indeed, use has already been made of equation (17) to attempt to model behavior for $R = r^2$.

Examination of equation (10) shows that as long as $R$ is greater than or equal to $r$, equation (16) results. There is also a hidden dependence on $R$ in going from equation (IV.A.14) to equation (9). For $R$ in the closed interval $[r, r^3]$, equation (16) is always the result. Therefore, the application of equation (17) to analyze the experimental systems is justified.

In summary, simplification of the Thorne equation for viscosity to that for a dilute suspension of macromolecules results in an analogue to the Einstein viscosity equation. Application to two specific systems indicates that the result is a first approximation to the transitional behavior wherein the intrinsic viscosity climbs from zero to the Einstein result as $r$ increases from unity. It also indicates a range of values for $r$ in which that transition might take place.
References


C. Thermal Diffusion Ratio

In Chapter I, various diffusion coefficients were given as examples resulting from different diffusive fluxes and driving forces. A summary of the Thorne results is given in Chapter II. The Thorne diffusion coefficient is based on a number velocity difference \((\langle C_1^* \rangle - \langle C_2^* \rangle)\) and a diffusive flux \(d_{12}\) given in equation (II.C.28). Neglecting other terms, \(d_{12}\) is the concentration gradient.

There has recently been a considerable research effort explaining the discrepancies between the Thorne results and results for diffusivities based on other premises. In fact, it has been shown that the Thorne result fails to obey the Onsager reciprocity relation (i.e. \(D_{12} \neq D_{21}\)) a violation of irreversible thermodynamics.\(^3\) Al-Chalabi and McLaughlin\(^5\) suggested using a diffusion coefficient \(D_{12}\) based on chemical potential which, from equation (I.C.9) can be shown,\(^5\) for ordinary diffusion, to equal

\[
D_{12} = (\frac{\partial \ln a_1}{\partial \ln x_1})_{T,p} D_{12}
\]

Since the Thorne result \(D_{12}^C\) corresponds to a concentration gradient, the "correct" coefficient to use, given \(D_{12}^C\), would be one corrected by \((\frac{\partial \ln a_1}{\partial \ln x_1})_{T,p}\).

Barajas, Garcia-Colin, and Pina\(^6\) have shown that the diffusion flux \(d_{12}\) differs from that calculated for irreversible thermodynamics \(d_{12}^{(H)}\) by an amount dependent on the order of density included in the...
calculations. They then derived an expression to relate the Thorne diffusivity $D_{12}^c$ to the diffusivity $D_{12}^\text{(H)}$ based on the proper diffusive force $d_{12}^\text{(H)}$. (The H refers to Hirschfelder.)

$$D_{12}^\text{(H)} = D_{12}^c \left( \frac{3kT}{\rho} \right) \frac{3}{\rho} \left( \frac{\partial \mu}{\partial w_1} \right)_{T,p}$$

(2)

Where $w_1$ is the weight fraction of species 1 and $\mu$ is the chemical potential defined by

$$\mu = \frac{\mu_1}{m_1} - \frac{\mu_2}{m_2}$$

(3)

for $\mu_i$ the chemical potential per molecule of species $i$.

What relationship $D_{12}^\text{(H)}$ has to $D_{12}$ is a question arising naturally from the above discussion. To evaluate equation (2), $\left( \frac{\partial \mu}{\partial w_1} \right)$ is expressed as $\left( \frac{\partial \mu}{\partial x_1} \right) \left( \frac{\partial x_1}{\partial w_1} \right)$. The initial term is given by

$$\left( \frac{\partial \mu}{\partial x_1} \right) = \frac{1}{m_1} \frac{\partial \mu_1}{\partial x_1} - \frac{1}{m_2} \frac{\partial \mu_2}{\partial x_1}$$

(4)

The Gibbs-Duhem equation for a binary mixture can be written

$$\left( \frac{\partial \mu_2}{\partial x_1} \right) = - \frac{x_1}{x_2} \left( \frac{\partial \mu_1}{\partial x_1} \right)$$

(5)

Therefore,

$$\left( \frac{\partial \mu}{\partial x_1} \right) = \left( \frac{\partial \mu}{\partial x_1} \right) \left( \frac{m}{x_2 m_1 m_2} \right)$$

(6)
where \( m = x_1 m_1 + x_2 m_2 \).

The chemical potential per molecule \( \mu_1 \) can be expressed

\[
\mu_1 = \mu_1^0 + kT \ln a_1
\]

which means

\[
\frac{\partial \mu_1}{\partial x_1} = \frac{kT}{x_1} \frac{\partial \ln a_1}{\partial x_1},
\]

Also, since

\[
W_1 = \frac{x_1 m_1}{x_1 m_1 + x_2 m_2}
\]

the partial derivative \( \frac{\partial w_1}{\partial x_1} \) is given by

\[
\frac{\partial w_1}{\partial x_1} = \frac{m_1 m_2}{m^2}
\]

Combining equations (2), (6), (8) and (10) and simplifying, the following equation results:

\[
D_{12}^{(H)} = \frac{\partial \ln a_1}{\partial \ln x_1} T, p D_{12}^c
\]

Therefore,

\[
D_{12}^{(H)} = D_{12}
\]
The correction term originally proposed by Al-Chalabi and McLaughlin is sufficient to modify the Thorne diffusion coefficient to obtain a thermodynamically consistent diffusion coefficient.

Given the use of the above diffusion force, Barajas, et. al.\(^6\) give a correction for the thermal diffusion ratio \(k_T^{(H)}\).

\[
k_T^{(H)} = \left[ (\frac{\rho_1^2}{\rho_1^2}) D_{12}^{(H)} / (n_2 / n_1 n_2) D_{12} \right] k_T^C
\]  

Kandiyoti\(^7\) has calculated the thermal diffusion coefficient, \(k_T^C\), as defined by Thorne.

To obtain the corrected thermal diffusion coefficient, one need only evaluate the following equation:

\[
k_T^{(H)} = (\rho_1^2 n_1 n_2 / \rho_1^2) (\frac{\partial \ln \alpha_1}{\partial \ln x_1})_{T,p} k_T^C
\]

It should be noted that the correction term is not identically unity except in such trivial cases as for mixtures of perfect gases with identical masses. Table IV.1 and Figure IV.4 show the calculated values of Kandiyoti for \(k_T^C\) where \(\rho_1^* v_1^*/kT = 1\), \(R = .5\), and \(r = 1\).
Table IV.1

\[ k_T^{(H)} / \left[ \left( \rho_1 n_1 n_2 / \rho_1^2 \rho_2 \right) \left( \frac{\partial \ln n_1}{\partial \ln x_1} \right) \right] \rho = k_T^C \]

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<th>( k_T^{(H)} )</th>
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</tbody>
</table>
Figure IV.4

Compositional Dependence of Thorne's Thermal Diffusion Ratio
References


D. Summary

This work has been concerned with the transport properties: viscosity, thermal conductivity, and thermal diffusion. By extending the Chapman-Enskog\textsuperscript{1-3} theory of statistical mechanics, H. H. Thorne\textsuperscript{4} derived expressions for these transport properties which had lain "dormant", unevaluated, for decades. Recent advances had enabled McLaughlin, et. al.\textsuperscript{5-8} to arrive at evaluations for some of these properties from the Thorne theory. Diffusion, in particular, had been exhaustively examined.\textsuperscript{5-7}

There have been certain further applications of the Thorne theories which had not been addressed and with which this work is concerned. The full mixing laws for viscosity and thermal conductivity were evaluated and special cases of each were analyzed with reference to excess properties.\textsuperscript{9}

The viscosity equation was simplified in order to apply it to a dilute suspension of macromolecules.\textsuperscript{10} This resulted in an equation analogous to that proposed by Einstein.\textsuperscript{11} The differences between the two lie in the route of derivation (statistical versus fluid mechanics) and the explicit size dependence of intrinsic viscosity to which the Thorne equation leads. It was proposed that this result, because of its form and derivation, approximates the behavior in a "transition" region for molecules large enough to show intrinsic viscosity effects but not large enough to conform to the Einstein behavior.

Finally, thermal diffusion had been solved by McLaughlin, et. al.\textsuperscript{5,12} Recent research, however, had indicated that the Thorne theory in the case of diffusion violates irreversible thermodynamics.\textsuperscript{13}
Revisions to the Thorne theory were proposed. This thesis shows that the proposed revisions simplify to a correction factor first proposed by Al-Chalabi and McLaughlin.

In conclusion, there are several research directions which may be taken from the results of this work. One possibility is the duplication of this work using a more realistic molecular potential function than that of hard spheres. Also, experimental work to verify the accuracy of the expression for the thermal diffusion ratio needs to be done. Finally, data should be obtained in the transition region of molecular size to further corroborate the applicability of the Einstein Equation analogue.
References


VITA

Bill McElhannon (a Jr.) was born, with premeditation, on April 5, 1951, in Houston, Texas. He lived most of his life in Baytown, Texas, where he went to Robert E. Lee high school from which he graduated magna cum laude in 1969. Not content with such accolades, he pursued and obtained a Bachelor of Science in mathematics from Louisiana State University, graduating magna cum laude in 1972. He was awarded a Master of Science in Chemical Engineering in 1975. Exxon Production Research in Houston, Texas, is Bill's current employer. As a man driven, he is pursuing with reckless lethargy, a doctorate of Philosophy in Chemical Engineering.

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