VISCOSITY OF DENSE FLUIDS

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Printed in the United States of America

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FOREWORD

The physical properties of fluids are perhaps among the most extensively investigated physical constants of any single group of materials. This is particularly true of the thermodynamic properties of pure substances since the condition of thermodynamic equilibrium provides the simplest considerations for experimental measurement as well as theoretical treatment. In the case of non-equilibrium transport properties, the situation is significantly complicated by the necessity of measurement of gradients in the experiment and the mathematical difficulties in handling non-equilibrium distribution functions in theoretical treatments. Hence, our knowledge of the transport properties of gases and liquids is perhaps one order of magnitude lower than for equilibrium thermodynamic properties. This situation is very much apparent when examining the available numerical data on the viscosity of fluids particularly at high pressures.

In this work, the authors have performed an outstanding contribution to the engineering literature by their critical evaluation of the pressure dependence of the available data on the viscosity of selected substances. The recommended values reported in the tables and figures also incorporate the saturated liquid and gas states as well as the data of the dilute gas in an attempt to integrate the present work with the recently published work by CINDAS/Purdue University on the viscosity of fluids at low pressures [166]. A deliberate effort was made to treat as many of the substances in the CINDAS volume as possible for which adequate high pressure data exist.

In these cases it was also attempted to establish internal consistency between the low pressure and saturation states data reported by CINDAS and the high pressure treatment presented herein. Unfortunately it was not possible to completely satisfy such internal consistency in all cases. Thus, these two works may well be considered complementary volumes particularly that there has been extensive cooperation between the two sets of authors.

While the primary goal of the present work is to present evaluated viscosity data at high pressures, the section on review of the state of theory and estimation techniques represents a significant contribution in its own right to the total volume. The skillfully prepared summary of these highly complex topics should prove to be a great assistance to those interested in having estimates of viscosity values for substances other than those reported herein. Similarly, the comprehensive list of references cited in both the textual part of the work as well as those reporting original data sources should provide the reader with a solid base for more extensive and in depth explorations.

The authors should be commended for their outstanding contribution in a most different and yet important area of thermophysics of vital interest to a wide spectrum of engineering applications.

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November 1978
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INTRODUCTION

This volume deals with the viscosity of gases and liquids at elevated pressures. Therefore, excluded from the discussion is the *dilute gas state* by which it is implied that the viscosity is independent of pressures. Defining the *dilute gas state* or alternatively the *states of elevated pressures*, in macroscopic terms, is not a simple task. No clear pressure limit can be given, but instead a bounding pressure-temperature curve, which is specific to each gas, must be specified as discussed by Childs and Hanley [1]. Thus the common assumption that at one bar pressure viscosity may be taken as that of a dilute gas, while correct in most cases, it is an incomplete statement. For example, for argon at 600 K, pressures up to 30 bar represent states that may still be considered in the dilute gas region, and for fluids with lower critical temperatures even higher pressures are allowed. On the other hand, even at very low pressures, a lower limit of dilution is reached, and the viscosity must be considered pressure dependent. This region, too, is not considered in this work. Therefore, the macroscopic pressure limits of coverage depend on the fluid and temperature considered. On the basis of molecular considerations the dilute gas region may best be defined as the state where binary collisions between molecules adequately define the transport properties of a gas. It is the region of the Boltzmann equation for the monatomic gas from which exact relations between the transport properties and the intermolecular pair potential may be found [2,3]. A vast literature exists concerning the viscosity of dilute gases, a comprehensive review of which may be found in [166] of the references to text.

The pressure dependence of a fluid is dramatic around its critical region, the derivative of viscosity with respect to pressure being infinite at the critical point itself. It is less pronounced far away from the critical point, yet by no means negligible. For most fluids reported in this volume the pressure effect represents an increase of viscosity between 10% and 20% per 100 bar in the liquid region far away from the critical point. In the gaseous region, the pressure dependence is a strong function of the temperature, and is influenced by the critical temperature. For temperatures high compared to the critical, and pressures which are not extremely high, the dilute gas state is approached and the pressure dependence fades away. This is the reason for the observed low pressure dependence at room temperature of the viscosity of fluids like helium, hydrogen, etc., which have low critical temperatures. On the basis of molecular considerations, the transport properties in the states considered in this volume are governed by higher order collisions and thus are beyond the scope of the original Boltzmann equation. The dynamics of many-body-collisions are not yet satisfactorily understood. Thus, contrary to the case of a monatomic dilute gas, no complete and rigorous theory has yet been developed for the dense fluid. Methods for the theoretical study of viscosity in dense fluids range from simplified models like Eyring's activated state theory and its successive modifications to the more formal but still idealized approaches like Enskog's hard sphere theory, and finally include the rigorous statistical mechanical theories in the form of the distribution function method or the time-correlation-function

method. Some excellent reviews have been published on the subject [4-10]. In addition to the theoretical treatments, a large number of empirical estimation techniques for the viscosity of fluids under pressure may be found in the literature [11]. They range from purely empirical ob- servations on the dependence of viscosity on temperature and density to the well-known group con- tribution methods that are recently studied successfully for equilibrium properties, and finally include correlations between viscosity and other fluid properties. A condensed, albeit incomplete summary of the more important developments in theory and estimation techniques is given in the introductory treatment of this volume.

Stuttgart, F.R.G., September 1978   Professor Dr.-Ing. K. Stephan

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NOTATION

b	$b = \frac{2}{3} \pi d^3$
d	hard sphere diameter
D	self-diffusion coefficient (Eq. 27)
E_o	activation energy of a molecule
ΔE_v	latent heat of vaporization
f	distribution function
$\bar{F}_{13}$	force exerted due to interaction of molecules 1 and 3 (with analogous meanings for other molecule pairs)
g(d)	equilibrium radial distribution function evaluated at distance d
g(R)	equilibrium radial distribution function (Eq. 5)
h	Planck's constant
J	microscopic stress tensor (Eq. 6, 7)
k	Boltzmann constant
m	molecular mass
M	molecular weight
n	number density
N	number of molecules (Eq. 18)
N_L	Loschmidt-number (Eq. 20)
p	equilibrium pressure
$\bar{p}_j$	the momentum of molecule j
p_{ix}	momentum of molecule i in x-direction
$\bar{\bar{P}}$	pressure tensor
q	partition function of a molecule per unit volume in the initial state
q*	same as q, except in activated state
r	distance of separation between two interacting molecules, (Eq. 14)
$\bar{r}$	the position considered in the system
$\bar{r}_j$	the position of molecule j
$\bar{r}_{kj}$	$\bar{r}_{kj} = \bar{r}_j - \bar{r}_k$
R	gas constant
T	absolute temperature
u	intermolecular potential (Eq. 14)
$\bar{u}$	the mass velocity
v	molar volume

V_f free volume

Z compressibility factor

Z^H compressibility factor value for the hard sphere model

Greek letters

β compressibility, (Eq. 37)

δ_{ij} Kronecker delta

$\delta(x)$ the delta-function

ε depth of potential-function well with the dimension of energy

$\bar{\bar{\varepsilon}}$ symmetric traceless part of the velocity gradient $\bar{\nabla}\bar{u}$, (Eq. 2)

ζ friction coefficient related to intermolecular force field (Eq. 5)

θ temperature function, (Eq. 34)

μ viscosity

μ_0 viscosity of the hard sphere molecule gas model in the low density limit

μ_v bulk viscosity (Eq. 2)

ξ scaling factor for viscosity (Eq. 19, 20)

π 3.1416

ρ density

σ molecular parameter in the potential-function model with the dimension of distance

τ time coordinate (Eq. 6, 7)

$\phi(r_{jk})$ potential function between molecule pairs j and k separated at distance r

χ transmission coefficient (Eq. 23)

$\psi_2(R)$ a function represented by a differential equation with specified boundary conditions (Eq. 5)

Subscripts, superscripts and notations

$\bar{\bar{1}}$ unit tensor

$(\ )_R$ subscript R indicates a reduced (dimensionless) quantity. (See Eqs. 14-18)

$(\ )_{cr}$ subscript cr indicates values of the quantity at the critical point

c.p.   critical point

G   gas

L   liquid

n.b.p.   normal boiling point

n.m.p.   normal melting point

SL   saturated liquid

SV   saturated vapor

CONTENTS

THEORY AND ESTIMATION

THEORY AND ESTIMATION

THEORY OF THE VISCOSITY OF DENSE GASES AND LIQUIDS

INTRODUCTION

Under the heading of theory, we wish to summarize briefly and without detailed reference to the complicated mathematics involved, those theories of momentum transfer in dense fluids which are based on molecular theory in a rigorous or at least modelized way. Various different approaches widely differing in rigour, mathematical complexity, and practical utility are considered and the presentation is grouped under the subheadings referred to as: rigorous statistical mechanical theories, corresponding states theories and model theories.

RIGOROUS STATISTICAL MECHANICAL THEORIES

General Formal Theory

Two different approaches are available to derive formal expressions for the viscosity of dense fluids by rigorous statistical mechanical theory, namely; the older distribution-function method and the more recent time-correlation-function method. The basic idea which leads to a connection of viscosity with molecular properties is the identification of the microscopic conservation equation for momentum with the analogous equation from continuum mechanics which contains viscosity as an empirical transport coefficient. Averaging by means of the non-equilibrium distribution function all quantities in the microscopic conservation equation for momentum yields the corresponding macroscopic conservation law. Its identification with the momentum conservation equation from continuum mechanics gives the stress tensor in terms of averaged microscopic quantities like the momentum, the locus and the force field of the individual molecules.

$$\bar{\bar{P}} = \left\langle \sum_{j=1}^{N} m \left(\frac{\bar{p}_j}{m} - \bar{u} \right) \left(\frac{\bar{p}_j}{m} - \bar{u} \right) \delta(\bar{r}_j - \bar{r}) - \frac{1}{2} \sum_{j \neq k} \sum \bar{r}_{jk} \left(\frac{\partial \phi(r_{jk})}{\partial \bar{r}_{jk}} \right) \delta(\bar{r}_j - \bar{r}) \right\rangle \tag{1}$$

where $\bar{\bar{P}}$ is the pressure tensor, m the molecular mass, $\bar{p}_j$ the momentum of molecule j, $\bar{u}$ the mass velocity, $\delta(x)$ the Delta-function, $\bar{r}_j$ the position of molecule j, $\bar{r}$ the position considered in the system and $\bar{r}_{kj} = \bar{r}_j - \bar{r}_k$. The term $\phi(r_{jk})$ is the pair potential, Eq. (1) implying the approximation of pairwise additivity.

The corresponding phenomenological form of the pressure tensor including the viscosity μ as an empirical coefficient, reads

$$\overline{\overline{P}} = [p - \left[\mu_v - \frac{2}{3}\mu\right] (\overline{\nabla} \cdot \overline{u})]\overline{\overline{1}} - 2\mu\overline{\overline{\epsilon}}$$

with

$$\epsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) - \frac{1}{3}(\overline{\nabla} \cdot \overline{u})\delta_{ij} \tag{2}$$

where μ_v is the bulk viscosity, p the equilibrium pressure, $\overline{\overline{1}}$ the unit tensor, $\overline{\overline{\epsilon}}$ the symmetric traceless part of the velocity gradient $\overline{\nabla}\cdot\overline{u}$, and δ_{ij} the Kronecker delta.

Proceeding further in line of the distribution function method, a kinetic equation has to be established for the non-equilibrium distribution function which is contained in the averaged microscopic quantities of the stress tensor [12]. Starting from the Liouville equation, which the N-body non-equilibrium distribution function must satisfy, it is possible to set up a hierarchy of equations for the lower order non-equilibrium functions, the BBGKY-hierarchy (Bogoliubov-Born-Green-Kirkwood-Yvon). If pairwise additivity of the intermolecular forces is assumed, such that the total potential energy of the intermolecular forces may be replaced by the sum of the potential energies of all molecular pairs, only the first and the second order distribution functions are important. The first two members of the hierarchy give coupling equations between the first order, the second order and the third order distributions.

$$\frac{\partial f_1}{\partial t} + \frac{\overline{p}_1}{m}\frac{\partial f_1}{\partial \overline{r}_1} = -\int F_{12} \left(\frac{\partial f_2}{\partial \overline{p}_1}\right)d\overline{r}_2 d\overline{p}_2 \tag{3}$$

$$\frac{\partial f_2}{\partial t} + \frac{\overline{p}_1}{m}\left(\frac{\partial f_2}{\partial \overline{r}_1}\right) + \frac{\overline{p}_2}{m}\left(\frac{\partial f_2}{\partial \overline{r}_2}\right) + \overline{F}_{12}\left(\frac{\partial f_2}{\partial \overline{p}_1}\right) + \overline{F}_{21}\left(\frac{\partial f_2}{\partial \overline{p}_2}\right) = -\int\left[F_{13}\left(\frac{\partial f_3}{\partial \overline{p}_1}\right) + F_{23}\left(\frac{\partial f_3}{\partial \overline{p}_2}\right)\right]d\overline{r}_3 d\overline{p}_3 \tag{4}$$

Here the index to the distribution function f indicates its order. $\overline{F}_{13}$ is the force exerted on molecule 1 due to its interaction with molecule 3, $\overline{F}_{23}$ has an analogous meaning.

In order to get a closed form kinetic equation for the second order non-equilibrium distribution function, some truncation or decoupling has to be effected in the hierarchy. This can only be done by introducing specific assumptions. For the dilute gas, the most important assumption is that of completely random molecular distribution, which transforms the coupling equation between the first order and the second order distribution function into a kinetic equation for the single particle distribution function, the Boltzmann equation (3).

For dense gases and liquids, Kirkwood's Brownian Motion Theory leads to Fokker-Planck-type equations for the time-smoothed first order and second order non-equilibrium distribution functions [13-15,17,18]. The equation for viscosity is [16,19]

$$\mu = \frac{nmkT}{2\zeta} + \frac{\pi\zeta}{15kT}n^2\int_0^\infty R^3\left(\frac{d\phi}{dR}\right)g(R)\psi_2(R)dR \tag{5}$$

Here ζ is a friction coefficient related to the intermolecular force field, for which various theoretical expressions exist, all of which are not fully satisfactory. This quantity may also be obtained from experimental data for the selfdiffusion coefficient. The quantity ϕ is the pair

potential, $g(R)$ the equilibrium radial distribution function, $\psi_2(R)$ a function for which a differential equation along with boundary conditions has been specified. Comparison with experimental results reveals discrepancies in the order from one to several hundred percent depending on the values used for $g(R)$ and ζ [16,19]. This, in addition to the complicated numerical evaluation, makes this approach unattractive for practical application.

Rice and Allnatt [20,21] have modified the Kirkwood theory. They have idealized the repulsive part of the intermolecular potential as a hard core. The change of the distribution function due to hardcore collisions is treated by means of an Enskog-type collision term, whereas the rate of change due to motion in the attractive fields of surrounding molecules between hard core collisions is treated by Kirkwood's approach. This theory, too, contains the friction coefficient ζ which must be obtained by some method. The resulting expressions are too complicated to be cited here. Many workers have discussed this approach [22-26]. Various other approaches to a theory of transport in dense media on the basis of distribution functions have been made [27-36]. Comparison of calculated viscosities to experimental data have been carried out. None of these approaches appears to be in good agreement with experiment for a large region of states.

Instead of non-equilibrium distribution functions, the viscosity can be related to the way in which spontaneous fluctuations regress in an equilibrium system. This idea leads to the time-correlation-function expression for viscosity, in which the viscosity is connected with the time-correlation-function of a dynamical phase function proportional to the microscopic stress tensor. The resulting expression for the viscosity of pure fluids [8] is

$$\mu = \frac{1}{VkT} \int_0^\infty \left\langle J^{xy}(0) J^{xy}(\tau) \right\rangle d\tau \tag{6}$$

with

$$J^{xy} = \sum_{i=1}^N \left(\frac{p_{ix} p_{iy}}{m} - \frac{1}{2} \sum_{j \neq 1}^N r_{ij}^y \frac{d\phi}{dr_{ij}^x} \right) \tag{7}$$

where p_{ix} is the momentum of molecule i in x-direction. The angular brackets in Eq. (6) indicate averaging over an equilibrium ensemble.

The time-correlation function, which is the integrand in Eq. (6), measures the extent to which the value of a dynamical variable at a given time is affected by its value at some earlier time, and is therefore obviously a function of time. Various methods have been used to relate transport coefficients, especially the viscosity, to time-correlation functions [37-40]. Again the microscopic analog of the usual macroscopic momentum flux is used to identify the time-correlation function formula for viscosity. The resulting expression, Eq. (6), is valid irrespective of density. Special discussions have been given for the region close to the critical point [41, 42]. Of course, the time correlation expression for viscosity is purely formal. Solutions of the N-body problem are required before a rigorous evaluation can be completed. For dilute gases, where the main dynamical events are taken to be isolated binary encounters, the time-correlation-function expressions for the transport properties have been evaluated [37,43]. The results coincide with the results of the Chapman-Enskog solution of the Boltzmann equation. Calculations with

the assumption of a hard sphere potential and a decaying exponential for the autocorrelation of the stress tensor lead to close agreement with Enskog's theory [44]. A general discussion on the connection between the kinetic approach and the time-correlation approach is given in [45]. A computer simulation solution of the time-correlation-function expression for viscosity by molecular dynamics has been given in [46]. Using the Lennard-Jones-potential, a comparison of the thus calculated values with experimental data for the viscosity of liquid argon reveal deviations in the order of 10%, which is by far better than the results of any other statistical calculation for viscosity in the liquid region without fitting of data. As molecular dynamics calculations are not practical as a tool to compute viscosity, theoretical solutions of the time-correlation-functions are needed. Such solutions for viscosity are discussed in [47-51].

A formal approach to the solution of the rigorous statistical mechanical formulae for the transport coefficients is the density expansion method. In equilibrium statistical mechanics, such a procedure yields the virial series. Similar efforts for the transport coefficients may either start from the BBGKY-hierarchy or from the time-correlation functions, whereby equivalent results are obtained. Due to successive correlated collisions, the density expansion is divergent, re-summation introducing logarithmic terms. The first density correction to the Chapman-Enskog dilute gas results requires the detailed analysis of triple collision events and is very involved [52-57].

The Enskog-Theory

Long before the general formal theory discussed above was developed, D. Enskog proposed a method for extending the Boltzmann equation to higher densities for the special case of a fluid consisting of hard spheres [9]. The assumption of hard spheres means that the forces between the molecules on collision are impulsive, i.e., the collision time goes to zero. Therefore, ternary and higher order collisions are neglected. Taking only static correlations into account and neglecting all successive binary collision events, by the assumption of molecular chaos for the momenta, leads to a modified Boltzmann equation for a dense fluid of hard spheres. It can be solved analogous to the case of a dilute gas, yielding the following expression for viscosity

$$\frac{\mu}{\mu_o} = \frac{1}{g(d)} + 0.800 \ bn + 0.761 \ b^2 n^2 g(d) \tag{8}$$

Here μ_o is the viscosity of the hard sphere gas in the low density limit, $g(d)$ is the equilibrium radial distribution function evaluated at a distance d, the hard sphere diameter $b = (2/3)\pi d^3$, and n is the number density. Equation (8) has been tested by comparison with molecular dynamics calculations [58,59]. As the hard sphere potential model has been used in these computations, the results serve to test primarily the molecular chaos assumption for momenta. It can be concluded that for viscosity the error of the Enskog formula for hard spheres lies within 20%. Good agreement is also found between the first density correction of the dilute gas viscosity taken from the Enskog equation and more accurate calculations for this quantity including triple collisions [60].

The Enskog formula for viscosity has also been used to predict the viscosity of dense real fluids. Various methods have been considered. From a theoretical viewpoint the most satisfactory

approach is the one using high density-high temperature p-v-T data to obtain a temperature dependent value for the hard sphere diameter d [61]. Simple perturbation theory for the thermodynamic equation of state yields the compressibility factor Z as an expansion in terms of the reciprocal temperature around the hard sphere value Z^H

$$Z = Z^H + \frac{a_1(v)}{T} + O\left(\frac{1}{T^2}\right) \tag{9}$$

Experimental data for Z, plotted as isochores against 1/T, in fact give straight lines in the limit of high temperatures. Extrapolation to $(1/T) \to 0$ an "experimental" value for Z^H is obtained, which is in good agreement with the theoretical equation of state for hard spheres, e.g., the Carnahan-Starling equation [62]. From interpretation of the slight curvature of the isochores at lower temperatures as the effect of a temperature dependent hard sphere diameter, a method may be developed to determine such values for d(T) from p-v-T data. In addition to that, g(d) is calculated by the well-known hard sphere radial distribution function and μ_o from the well-known dilute gas viscosities of hard spheres. Computed viscosities for the heavy noble gases agree well with experimental data at high temperatures and high densities. For densities below the critical, the discrepancies become large. This is an expected result, as the hard sphere model appears to be realistic only for high densities and high temperatures. For more complicated fluids, this approach gives less satisfactory results. Typical errors are between 10% at high densities and 40% at zero density [63]. Another method to determine the hard sphere diameter is fitting viscosity data at high densities and different temperatures to the theoretical Enskog curve. For monatomic substances, such d values agree with those from p-v-T data [64]. For simple polyatomic fluids, the viscosity is also predicted quite satisfactorily over a wide range of states by this method [63]. Another way to apply Enskog's theory to real fluids uses p-v-T data to determine an empirical expression for the equilibrium radial distribution function

$$g(d) = \frac{1}{bn}\left[\frac{1}{nk}\left(\frac{\partial p}{\partial T}\right)_v - 1\right] \tag{10}$$

When d is chosen to fit the experimental dilute gas viscosity, reasonable agreement is obtained with experimental data for simple gases, for densities up to and somewhat above the critical, provided that the temperature is sufficiently above the critical temperature [63,65].

The Enskog approach has been extended to a fluid of molecules interacting with a square-well potential [66-69]. This potential model takes attractive forces into consideration and at the same time retains the desirable feature of repulsive forces, now at two distinct separations. Again molecular chaos for the momenta is assumed. The resulting expression for viscosity is

$$\mu = \frac{5}{16\sigma^2}\left(\frac{mkT}{\pi}\right)^{1/2}\left\{\frac{\{1 + (2bn/5)[g(\sigma) + R^3 g(R\sigma)A]\}^2}{g(\sigma) + R^2 g(R\sigma)[B + (1/6)(\varepsilon/kT)^2]} + \frac{48}{25\pi}(bn)^2[g(\sigma) + R^4 g(R\sigma)B]\right\} \tag{11}$$

with

$$A = 1 - e^{-\varepsilon/kT} + \frac{\varepsilon}{2kT}\left\{1 + \frac{4}{\sqrt{\pi}}e^{\varepsilon/kT}\int_{(\varepsilon/kT)^{1/2}}^{\infty} e^{(-x^2)}x^2 dx\right\} \tag{12}$$