

Density expansion of viscosity coefficient

A K HEBLEKAR

Physics Department, Centre of Post-Graduate Instruction and Research,
Panaji 403 001, India

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Abstract. The formalism developed earlier has been extended to obtain the density expansion of viscosity coefficient. The important role played by the Hartree average energy in obtaining an explicit temperature dependence for the density coefficients of the viscosity is demonstrated. The results obtained are compared with the available experimental data for the first density coefficient. A satisfactory agreement between theory and experiment is found.

Keywords. Density expansion; viscosity; Hartree energy; Green function.

1. Introduction

In an earlier paper (Heblekar *et al* 1982), henceforth referred to as I, a Green function approach to the shear viscosity coefficient using Kadanoff and Baym kinetic equations (*K* and *B* equations) was presented in a modified form. In this paper the formalism developed there to obtain the density expansion of the shear viscosity coefficient.

The problem of virial expansion of transport coefficients has been a matter of interest to a large section of workers in the kinetic theory of gases (Fujita 1966a; Hanley *et al* 1969; Kan and Dorfman 1977; Kestin *et al* 1980 and references therein). Many attempts have been made to obtain the expressions for the coefficients of the terms in the density expansion, however, none of them has been found to agree well with the experimental values (Kestin *et al* 1980 and references therein). Use of a generalised Boltzmann equation, obtained from Liouville equation, is an approach followed by some workers whereas others follow an approach which uses the time-correlation function method (Kan and Dorfman 1977 and references therein).

We propose in this paper a density expansion for viscosity coefficient using the equations derived in I and further calculating the coefficients using the potential as assumed in I. We obtain an exact temperature dependence for the first-order density coefficient and in doing so we demonstrate, for the first time, how the hitherto unknown Hartree term, plays an important role in obtaining the temperature dependence which agrees with the experimental results. All the experimental attempts have failed to recognise a \sqrt{T} temperature dependence in the first density coefficient as proposed in Chapman-Enskog method (Chapman and Cowling 1970; Kestin *et al* 1980). But our method proposes a $1/\sqrt{T}$ temperature dependence which seems to agree, if not conclusively, pretty well with the experimental results. The failure to obtain a conclusive evidence in support of $1/\sqrt{T}$ dependence is due to the inade-

quate experimental data (Hanley *et al* 1969; Kestin *et al* 1980 and references therein) available for comparison.

The earlier theoretical methods have reported a logarithmic term $\rho^2 \ln \rho$ of the second order besides the usual ρ^2 term in the density expansion which arises due to ternary and higher order collision processes (Kan and Dorfman 1977 and references therein). Our expansion treated here however does not contain this term but this does not deter us from obtaining a simple density expansion for the viscosity coefficient because so far all the experimentalists have reported failure to recognise existence of the logarithmic term upto the densities as high as nearly 10^8 amagats (Kestin *et al* 1980).

In § 2 a brief outline of the definitions and equation used to obtain the viscosity coefficient is given. In § 3 we use the kinetic effect term of K and B equation to evaluate the first density coefficient. Section 4 outlines the procedure for obtaining the higher order terms. In § 5, we apply it to obtain the next higher order terms. In § 6 we discuss the theoretical estimates in comparison with experimental results and draw conclusions.

2. Transport equation

As in I we consider a spinless system of quantum imperfect gas obeying the Maxwell-Boltzmann statistics. The transport equations for the viscosity problem are equations (17–20) (in I) which we reproduce here as

$$\left[\omega - \frac{p^2}{2m} - U \right] G_L^<(\mathbf{p}, \omega, \mathbf{R}) = \Phi_L^<(\mathbf{p}, \omega, \mathbf{R}) + K_L(\mathbf{p}, \omega, \mathbf{R}) \quad (1)$$

and

$$\left[\omega - \frac{p^2}{2m} - U \right] G_L^>(\mathbf{p}, \omega, \mathbf{R}) = \Phi_L^>(\mathbf{p}, \omega, \mathbf{R}) \quad (2)$$

with Φ_L^{\gtrless} and K_L given in terms of equilibrium and linear parts of the self energy $\sum_{L \neq q}^{\gtrless}$, \sum_L^{\gtrless} respectively by (19) and (20) of I.

The perturbation solution $G_L^<$ of these equations is given by (39) of I, of which $G_L^{<(0)}$ is the lowest order Green function linear in q_{xy} , the velocity gradient. It is noted that $G_L^{<(0)}$ is rendered density-independent by taking rigid-sphere particle density n_0 , defined by (47) and (48) of I. Up to the first order of perturbation we considered the contribution due to the first two terms in (39) of I to obtain the dilute gas viscosity coefficient η_1 (for the momentum transfer part only) as

$$\eta_1 = a \sqrt{T} + b = \eta_{(0)}, \quad (3)$$

where $\eta_{(0)}$ is used to indicate the density independence. Of the right side terms of (3), the first is of the zeroth order perturbation and b comes from the first order perturbation. When we consider the other terms in the expansion of $G_L^<$ we get higher

order density terms also the first among them being the kinetic effect term K_L which we treat in a little more detail in the next section.

3. First density term

At this stage we may write the term K_L explicitly, by expanding the Poisson brackets in (20) of I. Equation (20) of I being:

$$\begin{aligned}
 K_L(\mathbf{p}, \omega, \mathbf{R}) = & \frac{1}{2} [\nabla_{\mathbf{R}} \Sigma^>(\mathbf{p}, \omega, \mathbf{R}) \cdot \nabla_{\mathbf{p}} G^<(\mathbf{p}, \omega, \mathbf{R}) \\
 & - \nabla_{\mathbf{R}} G^<(\mathbf{p}, \omega, \mathbf{R}) \cdot \nabla_{\mathbf{p}} \Sigma^>(\mathbf{p}, \omega, \mathbf{R}) \\
 & + \nabla_{\mathbf{R}} G^>(\mathbf{p}, \omega, \mathbf{R}) \cdot \nabla_{\mathbf{p}} \Sigma^<(\mathbf{p}, \omega, \mathbf{R}) \\
 & - \nabla_{\mathbf{R}} \Sigma^<(\mathbf{p}, \omega, \mathbf{R}) \cdot \nabla_{\mathbf{p}} G^>(\mathbf{p}, \omega, \mathbf{R})] \quad (4)
 \end{aligned}$$

in accordance with the definition of Poisson brackets given by (13) of I. The linear terms in q_{xy} are obtained by the operation of the gradient on the functions involved. The functions in (4) essentially the local equilibrium Green functions (Kadanoff and Baym 1963) and therefore they involve the actual particle density n which makes them the first order terms in the density expansion. When one actually carries out the differential operations on the self energy parts Σ^{\lessgtr} and G^{\lessgtr} in (4) one obtains for the lowest order in λ ,

$$\begin{aligned}
 K_{L0}(\mathbf{p}, \omega, \mathbf{R}) = & (-\pi m) \beta p_x p_y \int d\mathbf{k} \frac{[v(\mathbf{k})]^2}{k} \\
 & \times 2\pi \delta\left[\omega - \frac{p^2}{2m}\right] \exp\left(2\alpha - \beta \frac{p^2}{2m}\right) (2q_{xy}). \quad (5)
 \end{aligned}$$

And this when substituted in the viscosity formula, (37) of I, gives the first-order density term for the viscosity as

$$\eta_1^{(1)} = n \left(\frac{m}{8\pi k_B T} \right)^{1/2} \int d\mathbf{k} \frac{\{[v(\mathbf{k})]^2/k\}}{|\bar{v}|} \quad (6)$$

where the superscript (1) on the left side indicates the first order in density. Equation (6) may be written in the form

$$\eta_1^{(1)} = \rho \eta_{(1)}, \quad (7)$$

$$\text{where } \rho = mn \quad (8)$$

is the density and $\eta_{(1)}$ is the first density coefficient of the viscosity given by

$$\eta_{(1)} = \left(\frac{1}{8\pi k_b} \right)^{1/2} \frac{\int dk \{ [v(\mathbf{k})]^2 / k \}}{|\bar{V}|} \frac{1}{T^{1/2}} = \frac{b'}{T^{1/2}} \quad (9)$$

This term is of the same order in λ as the density independent term b in (3), but one order higher in the density, n (cf I).

4. Higher order terms

Higher order perturbation (and also in density) terms for viscosity are obtained by substituting higher order terms involving $\Phi_{L1}^<, K_{L1}$, etc., from (39) of I, in the viscosity formula. To write the expressions for $\Phi_{L1}^<, \Phi_{L2}^<$, etc., one may make use of the connected diagram techniques described by Fujita (1966b, 1971). However, the same techniques cannot be used for obtaining terms like K_{L1}, K_{L2} , etc., due to the differentiation operations involved. But since in K_{Li} ($i = 1, 2, 3, \dots$) the equilibrium functions are involved, the perturbation expansion of equilibrium Green functions described in I may be used to obtain the higher order terms in K_{Li} . In each of these cases K_{Li} has the same order of perturbation as the corresponding Φ_{Li} but one order higher in density.

We note that there are two ways of 'dressing up' the diagrams to obtain the diagram expansions as described by Fujita (Fujita 1966b, 1971). One is by using the Hartree loops which increases the order of both perturbation and density by 1 and the other by self energy parts which increases the order of both perturbation and density by 2. These processes are shown in figure 2. Figure 1 depicts the $\Phi_{L0}^<$ (see *e.g.* Wagh 1978) and figure 2 depicts $\Phi_{Li}^<$ ($i = 1, 2$) obtained by dressing up $\Phi_{L0}^<$ in different ways. It can be shown by numerical estimates that a term dressed up by two Hartree loops contributes more than the term dressed up by a self-energy part.

The next higher order terms for η_1 (equivalent to λ^2) are obtained by using $\Phi_{L1}^<$ and K_{L1} . Of these $\Phi_{L1}^<$ is obtained as in figure 2 (a) by dressing up $\Phi_{L0}^<$ by one Hartree loop. K_{L1} is obtained by using

$$\phi_1 = n \bar{V} \quad (10)$$

as given by (29) of I.

As mentioned earlier, there is a basic difference between these two terms. Contribution to η_1 due to $\Phi_{L1}^<$ obtained by dressing up $\Phi_{L0}^<$ is of first order in density (since $\Phi_{L0}^<$ is independent of density) but second order in λ . That due to K_{L1} is of second order in both density and λ , (since it is obtained from K_{L0} which is first order in n as well as λ). The contribution of a term obtained by either dressing up by a Hartree loop or by expanding local equilibrium Green function can be written simply by multiplying the basic contribution by a factor $\beta n |\bar{V}|$. *e.g.*

the contribution to viscosity due to $\Phi_{L1}^< = \beta n |\bar{V}| \times$ that due to $\Phi_{L0}^< = \beta n |\bar{V}| \cdot b$.
(11a)

Similarly

the contribution due to $K_{L1} = \beta n |\bar{V}| \times$ contribution due to K_{L0} (11b)

Thus one may proceed to write the higher order terms. In this process we get two

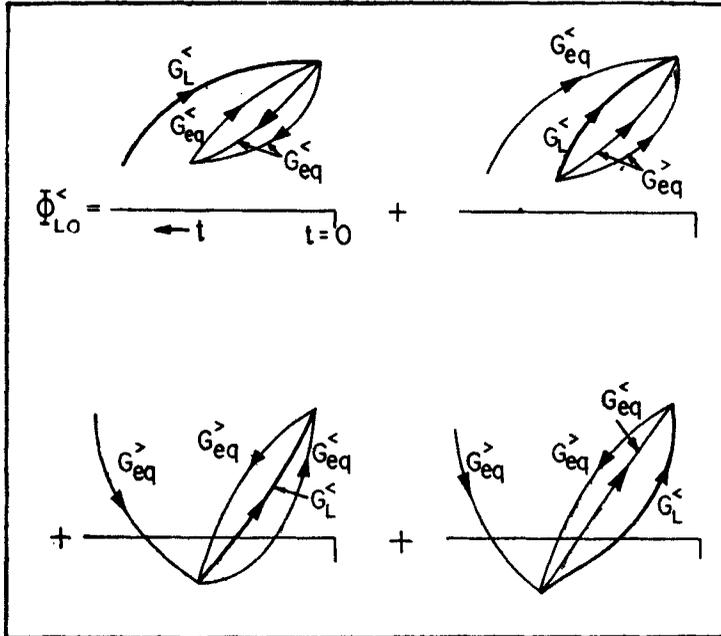


Figure 1. The four linear terms contributing to $\Phi_{L0}^<$ in the density independent part $\eta_{(0)}$ of the viscosity coefficient η_1 . Thick lines represent $G_L^<$ and thin ones represent $G_{eq}^>$.

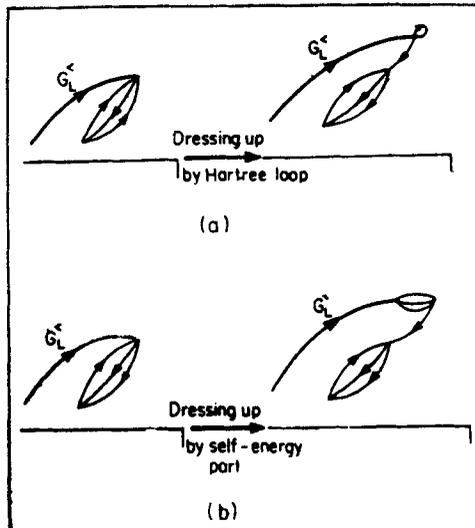


Figure 2. Dressing up of $\Phi_{L0}^>$. The first of the four diagrams in figure 1 is dressed up (a) by a Hartree loop to get $\Phi_{L1}^>$ (b) by a self energy part.

strings of terms (i) those with lower orders of n than that of λ ; (ii) those with same orders of n as that of λ . The first category will arise due to the diagram expansion of $\Phi_{L_0}^{\leq}$ and the second category is obtained due to expansion of the local equilibrium Green functions in K_{L_0} .

The terms obtained from the diagram expansion of $\Phi_{L_0}^{\leq}$ arising solely due to 'dressing up by Hartree loops' can be grouped up to give a closed sum, (this we shall show in the next section). However such is not the case for the terms coming from perturbation expansion of K_{L_0} and hence cannot be grouped to give a closed expression. Therefore, they will have to be treated individually.

There may be a second series of terms coming from the dressing up of $\Phi_{L_0}^{\leq}$ by self-energy parts which are smaller in magnitude as compared to those obtained from Hartree loops of the corresponding order. We shall neglect those as insignificant and not useful for our present discussion.

We write the second order contribution coming from K_{L_1} to be

$$\eta_1^{(2)} = \beta n |\bar{V}| \eta_1^{(1)} = \rho^2 \eta_{(2)}, \quad (12)$$

where

$$\eta_{(2)} = \left(\frac{1}{8\pi m^2 k_B^3} \right)^{1/2} |\bar{V}| \frac{\int d\mathbf{k} \{ [v(\mathbf{k})]^2 / k \}}{|\bar{V}|} \frac{1}{T^{3/2}}. \quad (13)$$

We shall not treat the contributions arising from K_{L_2} , etc., since those are insignificant. However, one can easily write them when required.

5. Diagram expansion of $\Phi_{L_0}^{\leq}$

As stated earlier the diagram expansion of $\Phi_{L_0}^{\leq}$ is obtained by using the techniques of Fujita (1966b, 1977) and Wagh (1978). Dressing up each G_L^{\leq} or G_{eq}^{\leq} by Hartree loops one can obtain the higher order terms (figure 1). Eight different diagrams are obtained from $\Phi_{L_0}^{\leq}$ by dressing up each G_L^{\leq} or G_{eq}^{\leq} by one Hartree loop to get $\Phi_{L_1}^{\leq}$. There are 16 different ways to get $\Phi_{L_2}^{\leq}$ (dressing by two Hartree loops) and so on. The contribution due to each $\Phi_{L_1}^{\leq}$ to the viscosity coefficient can be written down by merely multiplying that due to $\Phi_{L_0}^{\leq}$ by a factor $\beta n |\bar{V}|$. Therefore, the net contribution of the term $\Phi_{L_1}^{\leq}$ to η_1 is $8 \beta n |\bar{V}| b$. Similarly one can write contribution due to

$$\Phi_{L_2}^{\leq} \text{ to } \eta_1 = 16 (\beta n |\bar{V}|)^2 b. \quad (14)$$

Contribution due to

$$\Phi_{L_3}^{\leq} \text{ to } \eta_1 = 24 (\beta n |\bar{V}|)^3 b. \quad (15)$$

and so on.

One may sum up all these contributions due to all the $\Phi_{L_i}^{\leq}$ to give the net contribution to

$$\eta' = \sum_{p=0}^{\infty} 8b \cdot \rho x^p \quad (16)$$

$$\text{where } x = \beta n |\bar{V}|. \quad (17)$$

Rewriting (16) we get

$$\eta' = \frac{8 b \beta n |\bar{V}|}{[1 - \beta n |\bar{V}|]^2} \quad (18)$$

Combining equations (3), (7), (12) and (18), we find the density expansion (up to λ^2 order of perturbation) of the viscosity coefficient to be

$$\eta_1 = \eta_{(0)} + \eta_{(1)} \rho + \eta_{(2)} \rho^2 + \eta'_{(1)} \frac{C \rho}{[1 - C' \rho]^2} \quad (19)$$

where C and C' are constants of which C' is a function of temperature. The temperature dependences of $\eta_{(1)}$, $\eta_{(2)}$ and $\eta'_{(1)}$ are $1/T^{1/2}$, $1/T^{3/2}$ and $1/T$ respectively. Of the terms on the right side of (19), the second term is of order λ^1 , the third and the fourth are of order λ^2 . The factor $\beta n |\bar{V}|$ at moderate densities is approximately of the order of magnitude $10^{-2}/T$. Each successive higher order perturbation term is smaller than the previous term by the same order of magnitude.

This is the expression for the momentum transfer term which Kan and Dorfman 1977 call 'Kinetic-Kinetic term'. The potential dependent part (cf. I) is again neglected being insignificant, (see also Kan and Dorfman 1977).

6. Discussions and conclusions

The experimental researchers have reported failure to recognize terms beyond the first order density term in the viscosity measurements. Therefore there is no evidence to support a $1/T^{3/2}$ temperature dependence for $\eta_{(2)}$. The logarithmic term in the earlier works also has not been recognized experimentally (Kestin *et al* 1980 and references therein). The last term on the right side of (19) is much smaller than the $\eta_{(1)}$ term, but for the same order of magnitude as $\eta_{(2)}$, we have no experimental evidence for comparison. Therefore we concentrate only on $\eta_{(1)}$. Hanley *et al* (1969) have collected all the experimental data available for $\eta_{(1)}$ analysing them and presenting the estimates in what they call '95% confidence' range, within the 'realistic error' brackets.

We compare the experimental data (Hanley *et al* 1969) for $\eta_{(1)}$ with our theoretical predictions of (9), in table 1. The value of $\eta_{(1)}$ has been fixed at 298.15°K for each gas and the others analysed with respect to formula 9. The agreement between the experimental values and theoretical predictions of (9) are fairly within what Hanley *et al* (1969) call the 'realistic error' brackets. One may agree with Kestin *et al* (1980) that the experimental data are not extensive to reach any definite conclusion regarding a specific temperature dependence for $\eta_{(1)}$. However, the available data seem to support $1/T^{1/2}$ dependence for $\eta_{(1)}$.

Hanley *et al* (1969) report that the first density coefficient changes sign at some temperatures, becoming even zero, for some gases (*e.g.* H₂, He). This indicates that one more term containing the first order density may be present in the expansion.

Table 1. The experimental and theoretical values of $\eta_{(1)}$ are shown. The values are calculated by fitting the average of all the values of $\eta_{(1)}$ at 298.15 to the formula (9).

Gas	Temperature (K)	Experimental value of $\eta_{(1)} \times 10^7$ (Poise/amagat) (Hanley <i>et al</i> 1969)	Theoretical value of $\eta_{(1)} \times 10^7$ (Poise/amagat) (equation 9)
Krypton	293.15	3.47 ± 0.64	3.39
	298.15	3.36 ± 0.41	3.36
	298.16	3.13	3.36
		(Kestin <i>et al</i> 1980)	
	323.15	4.81 ± 0.76	3.23
	348.15	3.69 ± 0.67	3.11
Argon	223.0	2.48 ± 2.15	2.57
	248.0	2.13 ± 2.15	2.43
	293.17	2.03 ± 0.22	2.24
	298.15	2.20 ± 0.12	2.22
	298.15	2.14 ± 1.29	2.22
	298.15	2.31 ± 0.46	2.22
	298.16	2.0*	2.22
	298.17	2.15 ± 0.3	2.22
	323.15	2.74 ± 0.92	2.13
	348.15	2.80 ± 0.34	2.05
Neon	223.15	0.76 ± 0.89	0.70
	248.15	0.68 ± 0.20	0.66
	293.15	0.48 ± 0.19	0.61
	298.15	0.55 ± 0.14	0.605
	298.15	0.66 ± 0.50	0.605
	323.15	0.43 ± 0.13	0.58
	348.15	0.48 ± 0.14	0.56
	373.15	0.52 ± 0.64	0.54
Nitrogen	223.15	1.95 ± 0.13	1.68
	248.15	2.10 ± 1.29	1.59
	293.15	1.36 ± 0.59	1.46
	298.15	1.18 ± 0.36	1.45
	298.15	1.48 ± 0.32	1.45
	298.15	1.70 ± 0.14	1.45
	323.15	1.61 ± 1.29	1.39
	373.15	2.08 ± 1.90	1.30

*Kestin *et al* 1980

If we 're-expand' the terms on the right side of (18), the first term will be of first order in density and negative in sign due to b . However this term may contribute for some \bar{V} which may make the change of sign a potential dependent phenomenon. Since the experimental data for these two gases are very limited, a satisfactory agreement could not be tried.

The expression in (18) displays a singularity which will affect only when densities are larger by several orders of magnitude or temperatures are in the range of fractions. Therefore, the singularity appears to be of only academic interest since in both these extreme cases there may be phase changes.

At this stage a note is in order regarding the absence of logarithmic term in our expansion. The presence of a logarithmic term in the density expansion of viscosity has been demonstrated by several authors (Kan and Dorfman 1977). These terms arise due to collision processes. As noted by Kadanoff and Baym (1963), the self-energy parts Σ^{\geq} contain the information regarding the collisions. To get ternary and higher order collisions one may dress up $\Phi_{L_0}^{\leq}$ in our formalism by self-energy parts and then try to obtain the required term from grouping some of the terms so obtained. Here we have tried to demonstrate within the framework of theory developed in I, that we can obtain a density expansion using our formalism which can satisfactorily explain the available experimental results. However, we may note at this stage that the lowest terms, when obtained in our formalism from self-energy dressing will be of λ^3 and higher orders and therefore smaller by orders of magnitude $10^{-3}/T$ and below than the $\eta_{(1)}$ obtained above; hence insignificant. We have attempted to satisfactorily establish a case for the Green function approach to transport problem and emphasize the need to reconsider the position of average energy like Hartree energy in calculating transport coefficients. Our formalism has again succeeded in giving a simple temperature relation for viscosity coefficient of dense gases as well as dilute gases.

A comparison with the prevalent theoretical methods like the ones proposed by Kan and Dorfman (1977 and references therein) is not possible since our method essentially uses a coupled density cum perturbation expansion and there is no one-to-one correspondence between our terms and theirs. However, we feel our method may be considered on its own merit as an independent approach.

References

- Chapman S and Cowling T G 1970 *The mathematical theory of non-uniform gases* (Cambridge: University Press)
- Fujita S 1966a *Proc. Natl. Acad. Sci.* **56** 16
- Fujita S 1966b *Nonequilibrium quantum statistical mechanics* (Philadelphia: Saunders)
- Fujita S 1971 *Phys. Rev.* **A4** 1114
- Hanley H J M, McCarty R D and Sengers J V 1969 *J. Chem. Phys.* **50** 857
- Heblekar A K, Wagh A S and Boswarva I M 1982 *Pramana* **18** 405
- Kadanoff L P and Baym G 1963 *Quantum statistical mechanics* (New York: Benjamin)
- Kan Y and Dorfman J R 1977 *Phys. Rev.* **A16** 2447
- Kestin J, Korfali O and Sengers J V 1980 *Physica* **A100** 335
- Wagh A S 1978 *Physica* **A90** 137