

Quantum Statistical Mechanical Formulations of Three-Body Problems via Non-Local Potentials

A. Maghari, V. H. Maleki

Abstract—In this paper, we present a quantum statistical mechanical formulation from our recently analytical expressions for partial-wave transition matrix of a three-particle system. We report the quantum reactive cross sections for three-body scattering processes $1+(2,3)\rightarrow 1+(2,3)$ as well as recombination $1+(2,3)\rightarrow 1+(3,1)$ between one atom and a weakly-bound dimer. The analytical expressions of three-particle transition matrices and their corresponding cross-sections were obtained from the three-dimensional Faddeev equations subjected to the rank-two non-local separable potentials of the generalized Yamaguchi form. The equilibrium quantum statistical mechanical properties such partition function and equation of state as well as non-equilibrium quantum statistical properties such as transport cross-sections and their corresponding transport collision integrals were formulated analytically. This leads to obtain the transport properties, such as viscosity and diffusion coefficient of a moderate dense gas.

Keywords—Statistical mechanics, Nonlocal separable potential, three-body interaction, Faddeev equations.

I. INTRODUCTION

THE three-particle problems have been extensively proved in a wide variety of problems in all area of physics, especially in quantum statistical mechanics of moderately dense gases. In the quantum theory of three-body systems, Faddeev [1] introduced a set of equations that is analogous to the Lippmann-Schwinger (LS) equation for two-body scattering. Faddeev showed that a well-behaved set of three-body equations involves the two-body T -matrix.

In a recent paper, we solved analytically the Faddeev equations for three-body scattering at arbitrary angular momentum and obtained the transition matrices for some transition processes, including scattering and recombination channels in terms of free-particle resolvent matrix. We used a generalized Yamaguchi rank-two nonlocal separable potential (NLSP) to obtain the analytical expressions for partial wave scattering properties of a three-particle system. The NLSPs have been widely used in many branches of physics, because of their extreme simplicity and yield algebraic solution in the LS equation [2]-[8]. Because of their extreme simplicity, these NLPS have been extensively used to theoretically describe the multiparticle problems, particularly in determination of three-body scattering properties using a two-body separable potential.

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The NLSP model can generally be written as

$$\hat{V}_{12} = \sum_{i=1}^n \sum_{\ell} (2\ell+1) v_i |\chi_i; \ell\rangle \langle \ell; \chi_i| \quad (1)$$

where n is the rank of the potential operator \hat{V}_{12} , v_i is the attractive (or repulsive) coupling strength and $|\chi_i; \ell\rangle$ is state of the system with angular momentum quantum number ℓ , which is a real number in the unitary case. The momentum representation of such potential is

$$\hat{V}_{12}(\mathbf{p}, \mathbf{p}') = \langle \mathbf{p} | \hat{V}_{12} | \mathbf{p}' \rangle = \sum_{i=1}^n \sum_{\ell} (2\ell+1) v_i \chi_i^{(\ell)*}(\mathbf{p}') \chi_i^{(\ell)}(\mathbf{p}) \quad (2)$$

where $\chi_i^{(\ell)}(\mathbf{p}) \equiv \langle \mathbf{p} | \chi_i; \ell \rangle$ is the momentum representation of form factor.

In the present work, our previous formulations of three-particle scattering properties [4] were used to obtain a new formulation for both equilibrium and non-equilibrium statistical mechanical properties of moderately dense gases. We formulated an analytic expression for equilibrium partition function of two and three-particle correlated states via NLSP. Moreover, in the framework of the non-equilibrium quantum-statistical mechanics and in the corresponding kinetic theory, we obtained the analytical expressions for three-particle collision cross-sections and their corresponding collision integrals, which leads to obtain the transport properties, such as viscosity and diffusion coefficient of a moderate dense gas.

II. FADDEEV EQUATIONS AND TRANSITION MATRICES

Let us consider three-particle system with the total Hamiltonian $\hat{H} = \hat{H}^0 + \hat{V}$, where \hat{H}^0 is the total kinetic energy operator and \hat{V} is the sum of pair interactions \hat{V}_i ($\hat{V}_i \equiv \hat{V}_{jk}$) of the three-body system, which treated on an equal footing. The kinetic energy \hat{H}^0 in the Jacobi coordinates may be written as

$$\hat{H}^0 = \frac{p_{bc}^2}{2\mu_{bc}} + \frac{p_a^2}{2\mu_{b,c-a}} \quad (3)$$

where

$$p_{bc} \equiv \frac{m_c \mathbf{k}_b - m_b \mathbf{k}_c}{m_b + m_c} \quad (4)$$

$$p_a \equiv \frac{(m_b + m_c) \mathbf{k}_a - m_a (\mathbf{k}_b + \mathbf{k}_c)}{m_a + m_b + m_c} \quad (5)$$

$$\mu_{bc} \equiv \frac{m_b m_c}{m_b + m_c} \quad (6a)$$

$$\mu_{b,c-a} \equiv \frac{m_b + m_c - m_a}{m_a + m_b + m_c} \quad (6b)$$

in which k_a , k_b and k_c denote the asymptotic momenta of three particles in cyclic order of a , b and c . In the Faddeev formulation, the total interaction potential energy \hat{V} among the three particles may be written as

$$\hat{V} = \hat{V}_a + \hat{V}_b + \hat{V}_c \quad (7)$$

The complete solution of the scattering problem is determined with known total transition operator $\hat{T}(z)$ given by

$$\hat{T}(z) = \hat{V} + \hat{V} \hat{G}_0(z) \hat{T}(z) \quad (8)$$

where the free particle Green function defined as $\hat{G}_0(z) \equiv (z - \hat{H}_0)^{-1}$, in which $z = E + i\epsilon$ is complex energy parameter and E is three-particle energy.

Faddeev has shown that the three-body transition operator can be conveniently a sum of separate terms corresponding to two-body interactions as [1]:

$$\hat{T}(z) = \hat{T}^{(1)}(z) + \hat{T}^{(2)}(z) + \hat{T}^{(3)}(z) \quad (9)$$

where $\hat{T}^{(i)}(z)$ can be represented in a matrix form:

$$\begin{pmatrix} \hat{T}^{(1)}(z) \\ \hat{T}^{(2)}(z) \\ \hat{T}^{(3)}(z) \end{pmatrix} = \begin{pmatrix} \hat{T}_1(z) \\ \hat{T}_2(z) \\ \hat{T}_3(z) \end{pmatrix} + \begin{pmatrix} 0 & \hat{T}_1(z) & \hat{T}_1(z) \\ \hat{T}_2(z) & 0 & \hat{T}_2(z) \\ \hat{T}_3(z) & \hat{T}_3(z) & 0 \end{pmatrix} \hat{G}_0(z) \begin{pmatrix} \hat{T}^{(1)}(z) \\ \hat{T}^{(2)}(z) \\ \hat{T}^{(3)}(z) \end{pmatrix} \quad (10)$$

in which the three-body transition matrix operator for two-body (b - c) bounded system with particle a as spectator and the three-body Green operator defined as $\hat{G}_a(z) = (z - \hat{H}_0 - \hat{V}_{bc})^{-1}$ may be given by

$$\hat{T}_a(z) = \hat{V}_{bc} + \hat{V}_{bc} \hat{G}_a(z) \hat{V} \quad (11)$$

Indeed, the transition matrix explicitly shows the contributions from the bound states, resonances and distant singularities in the complex-energy plane.

In this work, the two-particle potential interaction is considered as a 3D rank- two NLSP given by:

$$\begin{aligned} \hat{V}_{bc}(\mathbf{p}_a, \mathbf{p}_{bc}; \mathbf{p}'_a, \mathbf{p}'_{bc}) &= \langle \mathbf{p}_a, \mathbf{p}_{bc} | \hat{V}_{bc} | \mathbf{p}'_a, \mathbf{p}'_{bc} \rangle \\ &= \sum_{i=1}^2 \sum_{\ell} (2\ell + 1) v_{i,\ell} \chi_i^{(\ell)*}(\mathbf{p}_a, \mathbf{p}_{bc}) \chi_i^{(\ell)}(\mathbf{p}'_a, \mathbf{p}'_{bc}) P_{\ell}(\hat{\mathbf{p}}_a \cdot \hat{\mathbf{p}}_a) P_{\ell}(\hat{\mathbf{p}}_{bc} \cdot \hat{\mathbf{p}}_{bc}) \end{aligned} \quad (12)$$

where $P_{\ell}(\hat{\mathbf{p}} \cdot \hat{\mathbf{p}}')$ is Legendre function with orbital angular momentum quantum number ℓ in which $\hat{\mathbf{p}}$ and $\hat{\mathbf{p}}'$ are unit

vectors, $v_{i,\ell}$ is the attractive (or repulsive) coupling strength and $\chi_i^{(\ell)}(\mathbf{p}_a, \mathbf{p}_{bc})$ is the form factor, which we assumed as the generalized Yamaguchi-type model [4]:

$$\begin{aligned} \chi_i^{(\ell)}(\mathbf{p}_a, \mathbf{p}_{bc}) &= \frac{1}{\pi^{3/4}} \left[\frac{2^{2\ell} \ell! (2\ell + 1) a_i^{2\ell+1}}{\Gamma(\ell + 1/2)} \right] \\ &\times \frac{(p_a p_{bc})^{\ell}}{[(a_i^2 + p_a^2)(a_i^2 + p_{bc}^2)]^{\ell+1}} \quad (i = 1, 2) \end{aligned} \quad (13)$$

where $\Gamma(m)$ is the Gamma function and the attractive (or repulsive) inverse range a_i plays the role of a scale factor.

In our previous work [4], we calculated the ℓ th partial-wave off-shell transition operators $\hat{\tau}_{a1}^{(\ell)}(z)$ for the scattering (with $a = 1$) and recombination (with $a = 2$) processes in the reduced momentum representation as

$$\begin{aligned} \langle \tilde{\mathbf{p}}_a, \tilde{\mathbf{p}}_{bc} | \hat{\tau}_{11}^{(\ell)}(z) | \tilde{\mathbf{p}}'_a, \tilde{\mathbf{p}}'_{bc} \rangle &= \\ \langle \tilde{\mathbf{p}}_a, \tilde{\mathbf{p}}_{bc} | (\hat{V}_{ab} + \hat{V}_{ca}) [1 - (\hat{V}_{ab} + \hat{V}_{ca}) G_1(z)]^{-1} | \tilde{\mathbf{p}}'_a, \tilde{\mathbf{p}}'_{bc} \rangle & \quad (14a) \\ &= \sum_{i=1}^2 \sum_{m=1}^2 \sum_{n=1}^2 \sum_{m'=1}^2 \sum_{n'=1}^2 \gamma_{mn} \gamma_{m'n'} (\tilde{v}_{i,ab} + \tilde{v}_{i,ca}) B_{mn}^{(\ell)} \\ &\times \chi_i^{(\ell)}(\tilde{\mathbf{p}}_a, \tilde{\mathbf{p}}_{bc}) \chi_n^{(\ell)}(\tilde{\mathbf{p}}'_a, \tilde{\mathbf{p}}'_{bc}) [B_{im}^{(\ell)} - V \hat{Q}_{im}^{(\ell)}] \hat{Q}_{n'm}^{(\ell)-1} \end{aligned}$$

$$\begin{aligned} \langle \tilde{\mathbf{p}}_a, \tilde{\mathbf{p}}_{bc} | \hat{\tau}_{21}^{(\ell)}(z) | \tilde{\mathbf{p}}'_a, \tilde{\mathbf{p}}'_{bc} \rangle &= \\ \langle \tilde{\mathbf{p}}_a, \tilde{\mathbf{p}}_{bc} | (\hat{V}_{ab} + \hat{V}_{ca}) [1 + G_1(z)(\hat{V}_{ab} + \hat{V}_{ca})] & \\ \times [1 - (\hat{V}_{ab} + \hat{V}_{ca}) G_1(z)]^{-1} | \tilde{\mathbf{p}}'_a, \tilde{\mathbf{p}}'_{bc} \rangle & \quad (14b) \end{aligned}$$

$$= \sum_{i,j=1}^2 \sum_{m,n=1}^2 \sum_{m',n'=1}^2 \sum_{m'',n''=1}^2 \left\{ \begin{aligned} &\gamma_{mn} (\tilde{v}_{i,ab} + \tilde{v}_{i,ca}) B_{mn}^{(\ell)} \chi_i^{(\ell)}(\tilde{\mathbf{p}}_a, \tilde{\mathbf{p}}_{bc}) \chi_n^{(\ell)}(\tilde{\mathbf{p}}'_a, \tilde{\mathbf{p}}'_{bc}) \\ &\times \left[\delta_{ij} + \gamma_{m'n'} \gamma_{m''n''} (\tilde{v}_{j,ab} + \tilde{v}_{j,ca}) \right] \\ &\times (B_{jm}^{(\ell)} - V \hat{Q}_{jm}^{(\ell)}) \hat{Q}_{n'm,\ell}^{-1} \hat{Q}_{m'',\ell} \end{aligned} \right\}$$

where

$$B_{mn}^{(\ell)} \equiv \langle \chi_m^{(\ell)} | \chi_n^{(\ell)} \rangle = \frac{2^{2\ell} \ell!}{i\pi^{1/2}} \left(\frac{\sqrt{\tilde{a}_{m,bc}} \tilde{a}_{n,bc}}{\tilde{a}_{m,bc} + \tilde{a}_{n,bc}} \right)^{2\ell+1} \quad (15a)$$

$$\begin{aligned} \chi_i^{(\ell)}(\tilde{\mathbf{p}}_a, \tilde{\mathbf{p}}_{bc}) &= \frac{1}{\tilde{a}^3 \pi^{3/4}} \left[\frac{2^{2\ell} \ell! (2\ell + 1) \tilde{a}_i^{2\ell+1}}{\Gamma(\ell + 1/2)} \right] \\ &\times \frac{(\tilde{p}_a \tilde{p}_{bc})^{\ell}}{[(\tilde{a}_i^2 + \tilde{p}_a^2)(\tilde{a}_i^2 + \tilde{p}_{bc}^2)]^{\ell+1}} \end{aligned} \quad (15b)$$

and γ_{mn} are parameters that must be satisfied by:

$$\begin{aligned} \sum_{m=1}^2 \sum_{n=1}^2 \gamma_{mn} \left[\frac{\tilde{a}_m \tilde{a}_n}{(\tilde{a}_m + \tilde{a}_n)(\tilde{a}_i + \tilde{a}_m)(\tilde{a}_j + \tilde{a}_n)} \right]^{-2\ell+1} & \\ = -\frac{\pi}{2^{4\ell} (\ell!)^2} \frac{1}{(\tilde{a}_i + \tilde{a}_j)^{2\ell+1}} & \quad (16) \end{aligned}$$

The reduced parameters and variables are defined as $\tilde{p} \equiv p/\tilde{a}$, $\tilde{v}_i \equiv Mv_i/a_i^2$, $\tilde{a}_i \equiv a_i/\tilde{a}$, where $\tilde{a} \equiv (a_1 + a_2)/2$.

The expression of free-particle motion $Q_{ik}^{(\ell)}(q)$, appeared in (15) can be obtained as

$$Q_{ik}^{(\ell)} = \frac{2^{2\ell+2} \pi^{1/2} \ell! (\tilde{a}_{i,bc} \tilde{a}_{k,bc})^{(2\ell+3)/2}}{\Gamma(\ell+1/2) (\tilde{a}_{i,bc} + \tilde{a}_{k,bc})^{2\ell+1}} \frac{\Lambda^{(\ell)}(\tilde{a}_{i,bc}, \tilde{a}_{k,bc}, \tilde{q})}{(\tilde{q} + i\tilde{a}_{i,bc})^{\ell+1} (\tilde{q} + i\tilde{a}_{k,bc})^{\ell+1}} \quad (17)$$

The analytic expression for $\Lambda^{(\ell)}(\tilde{a}_{i,bc}, \tilde{a}_{k,bc}, \tilde{q})$ is essentially the same as that of two-body problem, which has been described in detail in our previous work (see appendix A of [3]).

The above analysis is a unique method for dealing with scattering via the rank-two separable potentials and allows calculating the analytical expression for transition matrix elements in terms of free motion resolvent matrix elements.

III. RESULTS AND DISCUSSION

A. Equilibrium Statistical Mechanical Properties

In thermal equilibrium the grand canonical partition function can be written as

$$\Xi \equiv \sum_{N=0}^{\infty} \zeta^N \text{Tr} \left(e^{-\beta \hat{H}_N} \right) = 1 + \zeta \text{Tr} \left(e^{-\beta \hat{H}_0} \right) + \zeta^2 \text{Tr} \left(e^{-\beta \hat{H}_2} \right) + \dots \quad (18)$$

where $\beta \equiv 1/kT$ and $\zeta \equiv e^{\beta\mu}$ is the absolute activity, in which μ is the chemical potential. Moreover, the grand characteristic function is given by

$$\frac{PV}{kT} = \ln \Xi = \zeta \text{Tr} \left(e^{-\beta \hat{H}_0} \right) + \zeta^2 \left\{ \text{Tr} \left(e^{-\beta \hat{H}_2} \right) - \frac{1}{2} \left[\text{Tr} \left(e^{-\beta \hat{H}_0} \right) \right]^2 \right\} + \zeta^3 \left\{ \text{Tr} \left(e^{-\beta \hat{H}_3} \right) - \text{Tr} \left(e^{-\beta \hat{H}_0} \right) \text{Tr} \left(e^{-\beta \hat{H}_2} \right) + \frac{1}{3} \left[\text{Tr} \left(e^{-\beta \hat{H}_0} \right) \right]^3 \right\} + \dots \quad (19)$$

Using the absolute activity expansion $\frac{P}{kT} \equiv \sum_{n=1}^{\infty} b_n \zeta^n$ and comparing with (19), the coefficients b_n are obtained as

$$b_1 = \frac{1}{V} \text{Tr} \left(e^{-\beta \hat{H}_0} \right) \quad (20a)$$

$$b_2 = \frac{1}{V} \left\{ \text{Tr} \left(e^{-\beta \hat{H}_2} \right) - \frac{1}{2} \left[\text{Tr} \left(e^{-\beta \hat{H}_0} \right) \right]^2 \right\} \quad (20b)$$

$$b_3 = \frac{1}{V} \left\{ \text{Tr} \left(e^{-\beta \hat{H}_3} \right) - \text{Tr} \left(e^{-\beta \hat{H}_0} \right) \text{Tr} \left(e^{-\beta \hat{H}_2} \right) + \frac{1}{3} \left[\text{Tr} \left(e^{-\beta \hat{H}_0} \right) \right]^3 \right\} \quad (20c)$$

These coefficients are related to the ordinary virial coefficients:

$$B = -\frac{b_2}{b_1^2}, \quad C = -\frac{2b_3}{b_1^3} \quad (21)$$

where B is the second virial coefficient and C is third virial coefficient. Furthermore, the N -particle statistical operator

$e^{-\beta \hat{H}_N}$ and the N -particle resolvent operator $\hat{G}_N(z) \equiv (z - \hat{H}_N)^{-1}$ are related by [9], [10]:

$$\exp(-\beta \hat{H}_N) = \frac{1}{2\pi i} \int_C dz \exp(-\beta z) \hat{G}_N(z) \quad (22)$$

where the contour C encircles all singularities of $\hat{G}_N(z)$. For two and three-particle scattering ($N=2$ and 3), it is possible to express the grand canonical partition function as well as the second and third virial coefficients in terms of two- and three-particle transition operators. Substituting (22) into (20) and (21) gives the second and third virial coefficients in terms of two- and three-particle transition matrices (14a) and (14b).

Fig. 1 shows the reduced second and third virial coefficients as a function of reduced temperature for d-wave scattering via NLSP with the reduced parameters. All examples of this work, that are second and third virial coefficients, collision cross-sections and collision integrals are used the potential parameters as the following:

$\tilde{a}_{1,12} \equiv 0.35, \tilde{a}_{1,13} \equiv 1.80, \tilde{a}_{1,23} \equiv 1.60, \tilde{v}_{1,12} \equiv -20, \tilde{v}_{2,12} \equiv 30, \tilde{v}_{1,13} \equiv -10, \tilde{v}_{2,13} \equiv 50, \tilde{v}_{1,23} \equiv -1$ and $\tilde{v}_{2,23} \equiv 50$. The reduced second and third virial coefficients are defined as $B^* \equiv B/(h/\bar{a})^3$ and $C^* \equiv C/(h/\bar{a})^6$, respectively and the reduced temperature is defined as $T^* \equiv \mu k_B T / \bar{a}^2$.

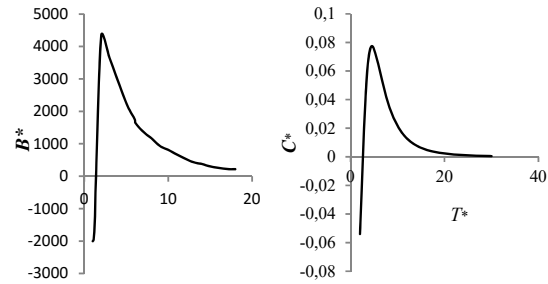


Fig. 1 Reduced second and third virial coefficients as a function of reduced temperature for d-wave scattering

B. Non-Equilibrium Statistical Mechanical Properties

The transport properties such as diffusion, viscosity, heat conductivity and thermal diffusion are described by the corresponding transport coefficients or, equivalently, by the collision transport cross sections. These cross sections are related to the so-called transport collision integrals, which are integrals of transport cross sections. Fig. 2 shows the partial-wave three-particle collision cross-sections for ℓ -waves.

The two- and three-particle collision cross sections $Q_n(E)$ can be written in terms of partial-wave scattering amplitude $f_\ell(\tilde{E})$ as

$$\tilde{Q}_n(\tilde{E}) = \frac{\pi}{\tilde{E}} \sum_{\nu>0} \sum_{\ell=0}^{\infty} a_{n\nu}^\ell \left| \frac{f_{\ell+\nu}^*(\tilde{E})}{f_{\ell+\nu}(\tilde{E})} - \frac{f_\ell^*(\tilde{E})}{f_\ell(\tilde{E})} \right|^2 \quad (23)$$

where

$$f_i(E) = -(2\pi)^2 \lim_{\varepsilon \rightarrow 0} \langle \mathbf{p}_a, \mathbf{p}_{bc} | \hat{\tau}_{12}^{(i)}(E + i\varepsilon) | \mathbf{p}_a, \mathbf{p}_{bc} \rangle \quad (24)$$

Moreover, the reduced collision integrals are determined from an average over a Maxwell-Boltzmann distribution as [11]:

$$\tilde{\Omega}^{(n,s)}(\tilde{T}) = \frac{F(n,s)}{2\tilde{T}^{s+2}} \int_0^\infty e^{-\tilde{E}/\tilde{T}} \tilde{E}^{s+1} \tilde{Q}_n(\tilde{E}) d\tilde{E} \quad (25)$$

where the factor $F(n,s)$ is defined as

$$F(n,s) = \frac{4(n+1)}{\pi(s+1)! [2n+1 - (-1)^n]} \quad (26)$$

The superscripts n and s appearing in the collision integral denotes weighting factors that account for the mechanism of transport by molecular collision. The calculated values of three-particle reduced collision integrals $\tilde{\Omega}^{(n,s)}$ as a function of reduced temperature are shown in Fig. 3. To calculate the collision integrals, the potential parameters are selected as those obtained the virial coefficients.

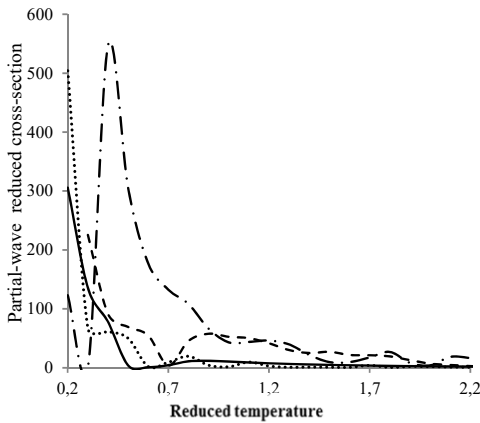


Fig. 2 Partial-wave reduced cross-sections versus reduced energy for: s -wave (—), p -wave (•••), d -wave (— —) and f -wave (— • —)

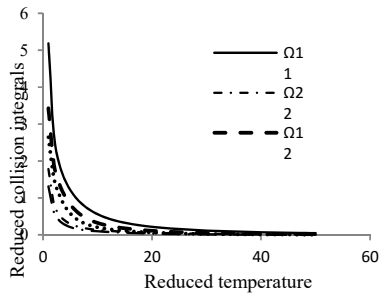


Fig. 3 Calculated values of three-particle reduced collision integrals $\tilde{\Omega}^{(n,s)}$ as a function of reduced temperature with different n and s

The collision integrals $\tilde{\Omega}^{(1,1)}$ and $\tilde{\Omega}^{(2,2)}$ are used to obtain the principal transport coefficients, i.e. diffusion, viscosity and

thermal conductivity from (26)-(28), whereas the collision integral $\tilde{\Omega}^{(1,2)}$, $\tilde{\Omega}^{(1,3)}$ and $\tilde{\Omega}^{(2,3)}$ can be used to obtain the coupled transport coefficients, such as thermal diffusion factor and diffusion thermo-effect. The Chapman- Enskog kinetic theory of a dilute gas leads to the expressions for single processes, i.e. viscosity η , diffusion D and the thermal conductivity λ as [12]:

$$\eta(T) = \frac{5}{16} \frac{(2\pi\mu k_B T)^{1/2}}{\Omega^{(2,2)}(T)} f_\eta \quad (27)$$

$$D(T, \rho) = \frac{3}{32} \frac{(2\pi k_B T / \mu)^{1/2}}{\rho \Omega^{(1,1)}(T)} f_D \quad (28)$$

$$\lambda(T) = \frac{75}{64} \frac{(2\pi\mu k_B^3 T)^{1/2}}{2\mu \Omega^{(2,2)}(T)} f_\lambda \quad (29)$$

where ρ is the number density. The values of f_η , f_D and f_λ typically differ from unity by about 1%, and can be determined from ratios of collision integrals [12].

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