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Moderately dense gas transport coefficients via time correlation functions. II. Shear viscosity and thermal conductivity

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An equation for a moderately dense gas transport coefficient, derived in the preceding article from time correlation function theory, is specialized to the estimation of the coefficients of viscosity and thermal conductivity. These equations include the first order in density correction to the transport coefficient, but are restricted to being valid only for repulsive potentials. It is shown that the resulting expressions are, within a series of analogous approximations, identical to those obtained by solving the generalized Boltzmann equation. © *1999 American Institute of Physics.*
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I. INTRODUCTION

In the preceding article,[1] henceforth referred to as I, a general formalism was introduced for deriving density corrections for transport coefficients from their general expressions as time correlation functions. The transport coefficient was first expressed in terms of a combination of matrix elements of appropriately projected resolvent operators. The matrix elements were then estimated by applying the binary collision expansion to the resolvents and keeping terms up to first order in density. In this article, these matrix elements are explicitly evaluated for systems with repulsive intermolecular forces. The assumption of a repulsive potential prevents the formation of bound states and makes the integrals over binary collisions finite. The calculation is carried out for the shear viscosity and thermal conductivity coefficients. For the shear viscosity, the momentum flux is a second rank symmetric traceless tensor, and so the contractions in the general formalism are written as doubledot contractions. The heat flux for the thermal conductivity calculation is a vectorial quantity and so contractions in the formalism are reduced to simple dot products. The matrix elements in I are expressed in terms of contractions of flux vectors, with resolvents and Liouville operators still in their general forms. In this work, the operator combinations that appear in the matrix elements are specialized in each case to lead to binary collision operators, Møller operators and time-evolution operators. This leads to the matrix elements being expressed in terms of binary collision parameters.

The presently used standard for the calculation of moderately dense gas transport coefficients is the method of Rainwater and Friend.[2,3] This is based on the work of Bogoliubov[4] and Green[5] on the nonlocal properties of the Boltzmann collision operator, as developed by Snider and Curtiss,[6,7] an estimation of the effect of termolecular collisions by Hoffman and Curtiss,[8] and an adaptation of the work of Stogryn and Hirschfelder[9] on the contribution of the presence of bound states to transport coefficients. Clearly

this method is based on combining a number of different developments, but all of which are based on the Boltzmann equation. The present work is based on time correlation function theory, an alternative for calculating transport coefficients, which is by nature based on the evaluation of a single quantity, Eq. (1) of Paper I, which thus implies that the calculation of all contributions is to be carried out in a unified manner. As developed so far, the expressions are restricted to repulsive potentials, so that the difficulty of taking bound states into account in a unified manner has not been required, as have various associated problems of separating interacting two particle dynamics into the dynamics of bound and metastable states versus the dynamics of isolated binary collisions.

The expressions, as simplified by Snider and McCourt[7] and extended with the incorporation of the Hoffman–Curtiss correction, are equivalently written: for the shear viscosity,

$$\eta = \frac{kT}{\langle v \rangle \mathfrak{S}(20)} \left[1 + nB(T) - \frac{4n\sigma^3}{15\pi^{1/2}} F_\eta \right.$$
$$\left. - \frac{4n\sigma^3\pi^{1/2}}{15} N_\eta - \frac{n\sigma^2 R(T)}{10\pi\mathfrak{S}(20)} \right]; \qquad (1)$$

and for the thermal conductivity,

$$\lambda = \frac{3k(kT)}{4m\langle v \rangle \mathfrak{S}(20)} \left[5 + 5nB(T) - \frac{20n\sigma^3}{3\pi^{1/2}} F_\lambda - \frac{4n\pi^{1/2}\sigma^3}{3} \right.$$
$$\left. \times N_\lambda - \frac{7n}{3} T \frac{dB}{dT} - \frac{5n}{3} T^2 \frac{d^2B}{dT^2} - \frac{n\sigma^2 R(T)}{10\pi\mathfrak{S}(20)} \right]. \qquad (2)$$

All these quantities appear later in this work and are defined as they arise. It is the object of the present work to obtain comparable expressions for the first order density corrections from the time correlation function formulae, as developed in I using projection operators.

The N-particle resolvent in a general time correlation expression for a transport coefficient has been simplified in I by application of a binary collision expansion and an assessment made as to which terms need to be kept for the reten-

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tion of the first order density corrections to the transport coefficients. Those results are presented in Sec. II together with a review of various definitions introduced in I and those to be used in the rest of the article. Sections III and IV expand these expressions for the viscosity and thermal conductivity. It is demonstrated that within a comparable set of approximations, the present theory gives density corrections consistent with those derived from the Boltzmann equation by Snider and Curtiss[6] and by Hoffman and Curtiss.[8] This article concludes with a short discussion, Sec. V. Appendix A summarizes those aspects of the dynamics of a binary collision needed for the evaluation of the quantities arising from the binary collision expansion. Appendixes B, C, and D identify certain integrals arising from the matrix elements in terms of the temperature dependent functionals $F_\eta, F_\lambda, N_\eta$, and N_λ of the intermolecular potential, which arose when solving the generalized Boltzmann equation.

II. DEFINITIONS AND STARTING EQUATIONS

This section organizes the general expressions derived in I for calculating moderately dense gas transport coefficients and introduces a variety of definitions and notation that is used throughout this article.

The first order density correction for a transport coefficient σ can be obtained by the evaluation of Eq. (88) of Paper I,

$$\sigma = \lim_{\substack{\epsilon \to 0^+ \\ }} \lim_{\substack{N, V \to \infty \\ N/V = \text{const}}} \frac{NnB}{\mathbb{K}_{KK}}\left[A_K^2 - A_K A_V\left(\frac{\mathbb{V}_{VK}}{\mathbb{V}_{VV}} + \frac{i}{N}\mathbb{K}_{KV}^L\right)\right]. \tag{3}$$

This has involved the separation of the physically defined flux $\mathbf{J}$ into orthogonal and normalized kinetic, $\mathbf{J}_K$, and potential, $\mathbf{J}_V$, parts, with scale factors A_K, A_V defined so that

$$\mathbf{J} = A_K \mathbf{J}_K + A_V \mathbf{J}_V. \tag{4}$$

The normalization and orthogonal conditions are stated as

$$\langle\langle \mathbf{J}_K | \mathbf{J}_K \rangle\rangle = \langle\langle \mathbf{J}_V | \mathbf{J}_V \rangle\rangle = N\mathbf{E}^{(\alpha)}, \tag{5}$$

$$\langle\langle \mathbf{J}_K | \mathbf{J}_V \rangle\rangle = \langle\langle \mathbf{J}_V | \mathbf{J}_K \rangle\rangle = 0, \tag{6}$$

where $\langle\langle | \rangle\rangle$ denotes a thermal average for N particles in a volume V. $\mathbf{J}$ and its components belong to the $(2\alpha + 1)$-dimensional irreducible representation of the rotation group, whose 2α rank tensor $\mathbf{E}^{(\alpha)}$ is the identity for this representation. B is a scale factor appropriate for the particular transport coefficient, while $\mathbb{K}_{KK}, \mathbb{V}_{VK}, \mathbb{V}_{VV}$, and $\mathbb{K}_{KV}^L$ are particular scalar matrix elements of the resolvents of particular projected Liouville superoperators, see I for their detailed definition and low density estimation.

For each of the viscosity and thermal conductivity, it is necessary to identify and/or calculate all the above mentioned quantities within a binary collision approximation. A number of variables that arise in all evaluations are now presented. The momenta $\mathbf{p}_1$ and $\mathbf{p}_2$, and positions $\mathbf{r}_1$ and $\mathbf{r}_2$ for a pair of particles are organized into center of mass

$$\mathbf{P} \equiv \mathbf{p}_1 + \mathbf{p}_2, \quad \mathbf{R} \equiv \tfrac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2) \tag{7}$$

and relative

$$\mathbf{p} \equiv \tfrac{1}{2}(\mathbf{p}_2 - \mathbf{p}_1), \quad \mathbf{r} \equiv \mathbf{r}_2 - \mathbf{r}_1 \tag{8}$$

momenta and positions. It is convenient to use the reduced momenta of particle 1,

$$\mathbf{W}_1 \equiv \frac{\mathbf{p}_1}{\sqrt{2mkT}}, \tag{9}$$

and also of the center of mass and relative motion of the 12 pair

$$\mathcal{G} \equiv \frac{\mathbf{P}}{\sqrt{4mkT}} = \frac{1}{\sqrt{2}}(\mathbf{W}_1 + \mathbf{W}_2),$$

$$\boldsymbol{\gamma} \equiv \frac{\mathbf{p}}{\sqrt{mkT}} = \frac{1}{\sqrt{2}}(\mathbf{W}_2 - \mathbf{W}_1). \tag{10}$$

The detailed binary collision calculations will be carried out using classical mechanics, so that the reduction of the general formulae, which are expressed in a quantum language, involves the replacement of the quantum trace [Tr_1 for particle 1] by the corresponding phase space integration [$h^{-3}\int\int d\mathbf{p}_1 d\mathbf{r}_1$]. When transforming into center of mass and relative coordinates, the Jacobian is unity, but more usefully

$$\mathrm{Tr}_{12}\varphi_1\varphi_2 = \frac{1}{h^6}\int \cdots \int \varphi_1\varphi_2 d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{r}_1 d\mathbf{r}_2$$

$$= \frac{1}{\pi^3}\int \cdots \int e^{-\mathcal{G}^2 - \gamma^2}d\boldsymbol{\gamma} d\mathcal{G} d\mathbf{r} d\mathbf{R}, \tag{11}$$

also serves to get rid of a number of mass, m, and temperature, T, factors. $\varphi_1 = (h/\sqrt{2\pi mkT})^3 \exp(-W_1^2)$ is the Maxwellian momentum distribution function for particle 1. Lastly, the classical Liouville superoperators for a pair of particles, as used here and defined so that they are Hermitian are, for kinetic motion

$$\mathcal{K}_{12} = -i\frac{\mathbf{p}_1}{m}\cdot\frac{\partial}{\partial\mathbf{r}_1} - i\frac{\mathbf{p}_2}{m}\cdot\frac{\partial}{\partial\mathbf{r}_2} = -i\frac{\mathbf{p}}{m/2}\cdot\frac{\partial}{\partial\mathbf{r}} - i\frac{\mathbf{P}}{2m}\cdot\frac{\partial}{\partial\mathbf{R}} \tag{12}$$

and for potential interaction

$$\mathcal{V}_{12} = -i\mathbf{F}\cdot\frac{\partial}{\partial\mathbf{p}}. \tag{13}$$

Some of the matrix element calculations require a detailed knowledge of the whole collision trajectory, not just its asymptotic behavior. This is covered in Appendix A.

III. SHEAR VISCOSITY

For a dense gas, the transverse momentum flux tensor $\mathbf{J}$, has both a kinetic and a potential part, specifically[10]

$$\mathbf{J} = \sum_j \frac{1}{m}[\mathbf{p}_j\mathbf{p}_j]^{(2)} - \sum_{j<l}\frac{du(r_{jl})}{dr_{jl}}\frac{1}{r_{jl}}[\mathbf{r}_{jl}\mathbf{r}_{jl}]^{(2)}$$

$$= \sum_j 2kT[\mathbf{W}_j]^{(2)} + \sum_{j<l}[\mathbf{F}_{jl}\mathbf{r}_{jl}]^{(2)}. \tag{14}$$

The $[\ ]^{(2)}$ designates the symmetric traceless part of the second rank tensor, while if the same vector appears more than once inside the square brackets, the expression is simplified by writing the repeated vector only once. The kinetic

contribution has been expressed both in terms of the momentum and in terms of its reduced form $\mathbf{W}_j$. The potential contribution is written both in terms of the derivative of the potential u_{jl} between particles j and l, and in terms of the equivalent force. As developed by Green[11] and Kubo,[12] the factor B appearing in Eq. (3) needs to be set to $1/(2kT)$ to yield the viscosity coefficient.

As stated, the kinetic and potential contributions are separated into orthogonal, normalized parts, $\mathbf{J}_K$ and $\mathbf{J}_V$. These are

$$\mathbf{J}_K \equiv \sqrt{2}\sum_j [\mathbf{W}_j]^{(2)} \quad \text{and} \quad \mathbf{J}_V \equiv \frac{1}{A_V}\sum_{j<l}[\mathbf{F}_{jl}\mathbf{r}_{jl}]^{(2)}. \quad (15)$$

The normalized kinetic combination standardly appears in modern dilute gas kinetic theory,[13,14] so that setting $A_K = \sqrt{2}kT$ satisfies Eqs. (4) and (14). To find the normalization factor A_V, it is necessary to use Eq. (5). A doubledot contraction of both sides of the equation for $\mathbf{J}_V$ gives

$$5NA_V^2 = \frac{N(N-1)}{3V}\int d\mathbf{r}\left(\frac{du}{dr}\right)^2 r^2 g(r) \equiv 5Nn\Gamma_\eta, \quad (16)$$

where $g(r)$ is the radial distribution function. Thus $A_V = \sqrt{n\Gamma_\eta}$ where Γ_η is seen to be

$$\Gamma_\eta = \frac{1}{15}\int d\mathbf{r}\left(\frac{du}{dr}\right)^2 r^2 g(r). \quad (17)$$

Integration by parts, along with the use of the lowest order in density approximation for the radial distribution function, $g(r) = e^{-\beta u}$ relates this integral to the shear modulus at infinite frequency, G_∞ derived by Zwanzig and Mountain,[15]

$$G_\infty = nkT + \frac{2\pi n^2}{15}\int_0^\infty dr\, e^{-\beta u}\frac{d}{dr}\left[r^4\frac{du}{dr}\right]$$

$$\approx nkT + \frac{1}{2}n^2\Gamma_\eta. \quad (18)$$

These kinetic and potential components of the transverse momentum flux are easily shown to be orthogonal, so they satisfy all the requirements for the use of Eq. (3) for the calculation of the viscosity.

The matrix elements appearing in Eq. (3) are now evaluated. Binary collision expansions of the resolvents in the matrix elements have been given in I and the lowest order contributions to these are presently calculated. Explicitly this implies that only terms that contribute up to a first order density correction to the viscosity are retained, but also it is assumed that it is sufficient to ignore more complex terms that arise from successive binary collisions and are interpretable[16] as equivalent to the higher Sonine correction terms in the analogous Boltzmann equation calculation of a transport coefficient. The latter approximation will often be referred to as the *one-moment approximation*.

A. Expansion of $\mathbb{K}_{KV}^L$

The lowest order in density contribution of $\mathbb{K}_{KV}^L$ is, from Eq. (I.51), given in the one-moment approximation by

$$\mathbb{K}_{KV}^L = \frac{1}{5}\mathrm{Tr}_{12}\mathbf{J}_{K1}:\mathcal{V}_{12}\frac{i}{z-\mathcal{L}_{12}}\mathbf{J}_{V12}\rho_{12}^{(2)}$$

$$= \frac{nN\Lambda_r^3}{5\sqrt{2}A_V}\mathrm{Tr}_{\mathrm{rel}}[\gamma]^{(2)}\mathcal{V}:\frac{i}{z-\mathcal{L}_{\mathrm{rel}}}[\mathbf{rF}]^{(2)}e^{-\gamma^2-\beta u}, \quad (19)$$

where the individual particle's momentum has been expanded into center of mass and relative momentum, with the subsequent trace over the center of mass carried out. A factor of V from the trace has changed one n to N and the thermal deBroglie wavelength that remains is for relative motion, $\Lambda_r = h/\sqrt{\pi mkT}$. Evaluation of the result is aided by expressing the resolvent in terms of the associated time evolution superoperator,

$$\mathbb{K}_{KV}^L = \frac{nN\Lambda_r^3}{5\sqrt{2}A_V}\mathrm{Tr}_{\mathrm{rel}}[\gamma]^{(2)}\mathcal{V}:\int_0^\infty dt\, e^{i(z-\mathcal{L}_{\mathrm{rel}})t}[\mathbf{rF}]^{(2)}e^{-\gamma^2-\beta u}. \quad (20)$$

The calculation of the time integral is carried out using classical mechanics, by following a binary collision trajectory according to

$$\lim_{z\to 0}\int_0^\infty dt\, e^{i(z-\mathcal{L}_{\mathrm{rel}})t}[\mathbf{rF}]^{(2)}$$

$$\to \int_0^\infty dt[\mathbf{r}(-t)\mathbf{F}(-t)]^{(2)}$$

$$= -\lim_{s_0\to\infty}\left\{[\mathbf{r}(-t)\mathbf{p}(-t)]^{(2)}\Big|_0^{s_0} + \int_0^{s_0}dt\frac{[\mathbf{p}(-t)]^{(2)}}{m/2}\right\}$$

$$= \lim_{s_0\to\infty}\left\{[\mathbf{rp}]^{(2)} - [\mathbf{r}(-s_0)\mathbf{p}(-s_0)]^{(2)} - \frac{2s_0}{m}[\mathbf{p}(-s_0)]^{(2)}\right.$$

$$\left. + \frac{2}{m}\int_0^{s_0}dt([\mathbf{p}(-s_0)]^{(2)} - [\mathbf{p}(-t)]^{(2)})\right\}. \quad (21)$$

Note that, since the time parameter is $-t$, which appears because the evolution is calculated essentially by using the Heisenberg picture for the evolution of an observable, Newton's second law reads $F(-t) = -d\mathbf{p}(-t)/dt$, and as well, $\mathbf{p}(-t) = -(m/2)d\mathbf{r}(-t)/dt$. The time integral contribution to Eq. (20) is thus,

$$\mathbb{K}_{KV}^L(\text{time}) = \frac{\sqrt{2}NnkT}{5\pi^{3/2}A_V}\int d\mathbf{r}\, d\gamma[\gamma]^{(2)}\mathcal{V}:\int_0^{s_0}dt$$

$$\times\{[\gamma(-s_0)]^{(2)} - [\gamma(-t)]^{(2)}\}e^{-\gamma^2-\beta u}. \quad (22)$$

The remaining time integrated terms in Eq. (21) represent nonlocal aspects of a collision,

$$\mathbb{K}_{KV}^L(\text{nonlocal}) = \frac{i\sqrt{2}Nn\Lambda_r^3}{5A_V}\mathrm{Tr}_{\mathrm{rel}}[\gamma\mathbf{F}]^{(2)}:\{[\mathbf{r}\gamma]^{(2)}$$

$$- [\mathbf{r}'\gamma_0]^{(2)}\}e^{-\gamma^2-\beta u}, \quad (23)$$

where

$$\mathbf{r}' \equiv \lim_{s_0\to\infty}\mathbf{r}(-s_0) + 2s_0\mathbf{p}(-s_0)/m. \quad (24)$$

The first integral simplifies to a multiple of the second virial coefficient,

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$$\frac{\Lambda_r^3}{5}\text{Tr}_{\text{rel}}[\,\boldsymbol{\gamma}\mathbf{F}]^{(2)}{:}[\mathbf{r}\boldsymbol{\gamma}]^{(2)}e^{-\gamma^2-\beta u}=kTB(T), \tag{25}$$

while the second integral is evaluated in detail in Appendix B,

$$-\Lambda_r^3\,\text{Tr}_{\text{rel}}[\,\boldsymbol{\gamma}\mathbf{F}]^{(2)}{:}[\mathbf{r}'\,\boldsymbol{\gamma}_0]^{(2)}e^{-\gamma^2-\beta u}=\frac{-4kT\sigma^3}{3\,\pi^{1/2}}F_\eta \tag{26}$$

in terms of the quantity F_η defined by Snider and McCourt.[7] Therefore, to the lowest order in density,

$$\mathbb{K}_{KV}^L=\frac{i\sqrt{2}NnkT}{A_V}\left[B(T)-\frac{4\sigma^3}{15\pi^{1/2}}F_\eta\right]+\mathbb{K}_{KV}^L(\text{time}). \tag{27}$$

B. Evaluation of $\mathbb{K}_{KK}$

The binary collision expansion of the resolvent in $\mathbb{K}_{KK}$ is given in I. The contributions up to the first density correction are separated there into three terms, namely $\mathbb{K}_{KK}^2$, $\mathbb{K}_{KK}^3$, and $\Delta\mathbb{K}_{KK}^3$ depending on the number of particles that participate in the dynamics. The explicit form of these contributions for the shear viscosity are now calculated.

1. The 2-particle collision contribution to $\mathbb{K}_{KK}$

With the inclusion of the equilibrium pair correlations, $\mathbb{K}_{KK}^2$ is identified as the modified Boltzmann collision integral used by Hoffman and Curtiss[8] for estimating the effect of a third particle on the bimolecular Boltzmann collision operator in their generalization of the Enskog collision integral to soft potentials. Their method for the approximate evaluation of this collision integral is followed here. The evaluation is based on assuming that the factor $Y_{[0]}$, which includes the effect of the presence of a third particle on the colliding pair, defined in Eq. (38) of Paper I changes little during the collision dynamics, so it can be moved to the left of the resolvent. Since it is also only a function of the position, it can also be moved to the left of $\mathcal{V}_{12}$. With these approximations and also using the one-moment approximation, $\mathbb{K}_{KK}^2$ is rewritten as

$$\mathbb{K}_{KK}^2\approx\frac{n^2\Lambda^6}{10}\text{Tr}_{12}\mathbf{J}_{K1}{:}Y_{[0]}(\mathbf{r}_{12})\mathcal{V}_{12}e^{-\beta H_{12}^{(2)}}$$

$$\times\frac{i}{z-\mathcal{L}_{12}}\mathcal{V}_{12}\sqrt{2}[\,\boldsymbol{\gamma}]^{(2)}, \tag{28}$$

which recognizes that $\mathbf{J}_{K1}+\mathbf{J}_{K2}$ can be expressed in terms of center of mass and relative momenta, of which only the (reduced) relative momentum $\boldsymbol{\gamma}$ is affected by $\mathcal{V}_{12}$. A subsequent rewriting of the remaining $\mathbf{J}_{K1}$ in terms of center of mass and relative coordinates and integration over the center of mass position and momentum reduces $\mathbb{K}_{KK}^2$ to a trace only over relative motion, so the particle labels can be dropped. Furthermore, the combination of operators

$$\lim_{\epsilon\to 0}\frac{1}{z-\mathcal{L}_{\text{rel}}}\mathcal{V}_{\text{rel}}=\Omega'-1 \tag{29}$$

is identified in the limit as a restricted form of the Møller superoperator, with the prime denoting the restricted appli-

cability, namely that this operator identity is only valid when acting on a function of the momentum. This implies that

$$\mathbb{K}_{KK}^2=\frac{iNn\Lambda_r^3}{5}\text{Tr}_{\text{rel}}[\,\boldsymbol{\gamma}]^{(2)}{:}Y_{[0]}(\mathbf{r})\mathcal{V}e^{-\beta H_{\text{rel}}}(\Omega'-1)[\,\boldsymbol{\gamma}]^{(2)}$$

$$=-\frac{iNn\Lambda_r^3}{5}\text{Tr}_{\text{rel}}[\,\boldsymbol{\gamma}]^{(2)}{:}Y_{[0]}(\mathbf{r})\mathcal{K}\Omega'e^{-\beta K_{\text{rel}}}[\,\boldsymbol{\gamma}]^{(2)}. \tag{30}$$

In the final form, the ''-1'' term vanishes since it is odd in position and momentum directions. The Møller superoperator satisfies the intertwining relation

$$H_{\text{rel}}\Omega'=\Omega'K_{\text{rel}}, \tag{31}$$

which immediately implies that

$$e^{-\beta H_{\text{rel}}}\Omega'=\Omega'e^{-\beta K_{\text{rel}}}. \tag{32}$$

A second intertwining relation is $\mathcal{L}\Omega'=\Omega'\mathcal{K}$ which, combined with the first gives the useful relation

$$\mathcal{V}\Omega'e^{-\beta K_{\text{rel}}}[\,\boldsymbol{\gamma}]^{(2)}=-\mathcal{K}\Omega'e^{-\beta K_{\text{rel}}}[\,\boldsymbol{\gamma}]^{(2)}$$

$$=-\mathcal{K}e^{-\gamma_0^2}[\,\boldsymbol{\gamma}_0]^{(2)}, \tag{33}$$

on the basis that the operator on which Ω' acts has zero $\mathcal{K}$ eigenvalue and defining $\boldsymbol{\gamma}_0\equiv\Omega'\boldsymbol{\gamma}$ as the reduced momentum before the collision began.

Substituting these relations into Eq. (30) and performing an integration by parts with the position variable gives

$$\mathbb{K}_{KK}^2=\frac{-2Nn}{5m\pi^{3/2}}\int\int d\Sigma\cdot\mathbf{p}\,d\boldsymbol{\gamma}[\,\boldsymbol{\gamma}]^{(2)}{:}e^{-\gamma_0^2}[\,\boldsymbol{\gamma}_0]^{(2)}$$

$$+\frac{2Nn}{5m\pi^{3/2}}\int\int d\mathbf{r}\,d\boldsymbol{\gamma}[\,\boldsymbol{\gamma}]^{(2)}{\cdot}\mathbf{p}\cdot\frac{\partial Y_{[0]}}{\partial\mathbf{r}}{:}e^{-\gamma_0^2}[\,\boldsymbol{\gamma}_0]^{(2)}. \tag{34}$$

The surface integral ($Y_{[0]}=1$ as $r\to\infty$) is proportional to the Chapman–Cowling omega integral[17,18] $\Omega^{(2,2)}$, and/or the kinetic cross section for viscosity $\mathfrak{S}(20)$,[13,14]

$$\frac{16Nn(\pi kT)^{1/2}}{5m^{1/2}}\int_0^\infty\int_0^\infty b\,db\,d\gamma\,\gamma^7(1-\cos^2\chi)e^{-\gamma^2}$$

$$=\frac{8Nn}{5}\Omega^{(2,2)}=Nn\langle v\rangle\mathfrak{S}(20), \tag{35}$$

where χ is the angle of deflection and b is the impact parameter.

Finally, the $Y_{[0]}$ dependent term is related to the Hoffman–Curtiss[8] $R(T)$ function

$$\int\int d\mathbf{r}\,d\boldsymbol{\gamma}\,\boldsymbol{\gamma}\cdot\frac{\partial Y_{[0]}}{\partial\mathbf{r}}(\boldsymbol{\gamma}\cdot\boldsymbol{\gamma}_0)^2e^{-\gamma^2-\beta u}=n\sigma^2R(T). \tag{36}$$

Thus up to terms including linear in density corrections, $\mathbb{K}_{KK}^2$ is approximated by

$$\mathbb{K}_{KK}^2=Nn\langle v\rangle\mathfrak{S}(20)\left[1+\frac{n\sigma^2R(T)}{10\pi\mathfrak{S}(20)}\right]. \tag{37}$$

The $\mathbb{K}_{KK}^2$ term involves the standard kinetic cross section for the viscosity together with a correction for the static presence of a third particle on this cross section. The result depends on

three approximations, the first being that only binary collisions are considered, the second that the effect of successive collisions is neglected, equivalently that the one-momentum approximation is sufficient and third, that the $Y_{[0]}$ term is assumed constant during a collision.

2. The 3-particle collision contributions to $\mathbb{K}_{KK}$

The 3-particle contributions to the kinetic matrix element $\mathbb{K}_{KK}$ were seen in I to be $\mathbb{K}^3_{KK}(B) + \Delta\mathbb{K}^3_{KK}$. The $\mathbb{K}^3_{KK}(B)$ term is the 3-particle collision contribution with Bogoliubov's form for the triple collision operator. To our knowledge, the evaluation of such terms have only been considered for rigid spheres[19] and the present work will not investigate this further.

$\Delta\mathbb{K}^3_{KK}$ is determined within the one-moment approximation by Eqs. (78) and (79) of Paper I, where the appropriate kinetic cross section for the viscosity is $\mathfrak{S}(20)$. Putting in the appropriate kinetic flux for the viscosity, Eq. (15), and carrying out the trace over the center of mass gives

$$\Delta\mathbb{K}^3_{KK} = \frac{in^3\langle v\rangle\mathfrak{S}(20)}{5}\mathrm{Tr}_{12}\mathbf{J}_{K1}:\mathcal{V}_{12}\int_0^\infty dt[e^{-i\mathcal{L}_{12}t}$$

$$-e^{-i\mathcal{L}_{12}s_0}](\mathbf{J}_{K1}+\mathbf{J}_{2K})\varphi_1\varphi_2$$

$$= \frac{iNn^2}{5\pi^{3/2}}\langle v\rangle\mathfrak{S}(20)\int\int d\mathbf{r}\, d\boldsymbol{\gamma}[\boldsymbol{\gamma}]^{(2)}:\mathcal{V}$$

$$\times\int_0^\infty dt\{[\boldsymbol{\gamma}(-t)]^{(2)}-[\boldsymbol{\gamma}_0]^{(2)}\}e^{-\gamma^2-\beta u}. \quad (38)$$

It is to be noted that this term is proportional to $\mathbb{K}^L_{KV}(\mathrm{time})$ in the limit that $s_0\to\infty$, see Eq. (22).

C. Expansion of $\mathbb{V}_{VK}$

The low density behavior of the first term of Eq. (85) of I is given by

$$\frac{Nn\Lambda_r^3}{2}\mathrm{Tr}_{\mathrm{rel}}\mathbf{J}_{V12}:e^{-\beta H_{\mathrm{rel}}}\mathcal{L}_{12}\frac{i}{z-\mathcal{L}_{12}}\mathcal{V}_{12}\sqrt{2}[\boldsymbol{\gamma}]^{(2)}+O(Nn\sqrt{n})$$

$$= O(Nn\sqrt{n}), \quad (39)$$

where the higher density correction arises from higher density terms in $\rho_{12}^{(2)}$, Eqs. (37)–(38) of I. In the leading term of Eq. (39), the operator combination $(z-\mathcal{L}_{12})^{-1}\mathcal{V}_{12}$ is the Møller superoperator since it is operating on a function of the momentum. The intertwining relation, $\mathcal{L}\Omega=\Omega\mathcal{K}$, then implies that this term vanishes.

The second term in Eq. (85) of I involves three particles and is also $O(Nn\sqrt{n})$. That leaves the lowest order in density contribution to $\mathbb{V}_{VK}$ to be

$$\mathbb{V}_{VK} = \mathbb{V}_{VV}\frac{i}{10N}\mathrm{Tr}_{12}\mathbf{J}_{V12}:\frac{i}{z-\mathcal{L}_{12}}\rho_{12}^{(2)}\mathcal{V}_{12}(\mathbf{J}_{K1}+\mathbf{J}_{K2})$$

$$= -\mathbb{V}_{VV}\frac{\sqrt{2}n\Lambda_r^3}{10A_V}\mathrm{Tr}_{\mathrm{rel}}[\mathbf{rF}]^{(2)}:e^{-\gamma^2-\beta u}(\Omega-1)[\boldsymbol{\gamma}]^{(2)}$$

$$= \mathbb{V}_{VV}\frac{4\sqrt{2}\pi nkT\sigma^3}{15A_V}N_\eta = O(N\sqrt{n}). \quad (40)$$

The detailed connection with N_η, which represents the collisional transfer contribution to the momentum flux, defined in Ref. 7, is made in Appendix D.

D. First order density corrections to the shear viscosity

Substituting the various matrix elements into Eq. (3), it is seen that the time integral contributions of $\mathbb{K}^L_{KV}(\mathrm{time})$ and $\Delta\mathbb{K}^3_{KK}$ cancel each other so that, to first order in density, the viscosity becomes

$$\eta = \frac{kT}{\langle v\rangle\mathfrak{S}(20)}\left[1+nB(T)-\frac{4n\sigma^3}{15\pi^{1/2}}F_\eta-\frac{n\sigma^2 R(T)}{10\pi\mathfrak{S}(20)}\right.$$

$$\left.-\frac{4n\pi^{1/2}\sigma^3}{15}N_\eta-n\mathbb{K}^3_{KK}(B)\right]. \quad (41)$$

Within the approximations made, except for the presence of the termolecular collision contribution, the time correlation function formula for the viscosity up to the first order in density correction is in agreement with the expressions previously derived using the Boltzmann equation.

IV. THERMAL CONDUCTIVITY

The heat flux vector $\mathbf{J}$, with its kinetic and potential contributions, is

$$\mathbf{J} = \sum_j\left(\frac{p_j^2}{2m}-h\right)\frac{\mathbf{p}_j}{m}+\frac{1}{2}\sum_{j\neq l}[\mathbf{r}_{jl}\mathbf{F}_{jl}+u(r_{jl})\mathbf{U}]\cdot\frac{\mathbf{p}_j}{m}, \quad (42)$$

where $\mathbf{U}=\mathbf{E}^{(1)}$ is the unit tensor of rank two. $\mathbf{U}$ is rotationally invariant and also acts as the identity for the three-dimensional irreducible representation of the three-dimensional rotation group. The scale factor B in Eq. (3) is $1/(kT^2)$. For a monatomic gas, the enthalpy per molecule is, to first order in density,

$$h = \frac{5}{2}kT+nkT\left[B(T)-T\frac{dB}{dT}\right]\equiv\frac{5}{2}kT+h_V. \quad (43)$$

It is necessary to define the kinetic and potential flux functions so that they are orthogonal, and also normalized, Eqs. (5). This is the motivation for breaking up the enthalpy per molecule into a kinetic, $5kT/2$, and a potential, h_V, contribution, as defined in Eq. (43). With this separation, the normalized flux components are defined as

$$\mathbf{J}_K = \frac{2}{\sqrt{5}}\sum_j\left(W_j^2-\frac{5}{2}\right)\mathbf{W}_j \quad (44)$$

and

$$\mathbf{J}_V \equiv \frac{1}{2A_V}\sum_{j\neq l}\left[\mathbf{r}_{jl}\mathbf{F}_{jl}+\left(u_{jl}-\frac{2h_V}{N}\right)\mathbf{U}\right]\cdot\frac{\mathbf{p}_j}{m}. \quad (45)$$

In order to make the relations more compact u'_{jl} is defined as $u'_{jl}\equiv u_{jl}-2h_V/N$. It follows from the normalization conditions, Eqs. (5), that $A_K=kT\sqrt{5kT/2m}$ and $A_V=\sqrt{nkT\Gamma_\lambda/m}$. The latter arises from the computation, restricted to low density, of A_V according to

$$3NA_V^2 = \frac{1}{4}\int\int d\mathbf{r}^N d\mathbf{p}^N \left[\sum_{j\neq l}(\mathbf{r}_{jl}\mathbf{F}_{jl}+u'_{jl}\mathbf{U})\cdot\frac{\mathbf{p}_j}{m}\right]$$

$$\cdot\left[\sum_{j'\neq l'}(\mathbf{r}_{j'l'}\mathbf{F}_{j'l'}+u'_{j'l'}\mathbf{U})\cdot\frac{\mathbf{p}_{j'}}{m}\right]\rho^{(N)}$$

$$=\frac{NnkT}{4m}\int d\mathbf{r}\left[3u^2-2ru\frac{du}{dr}+\left(r\frac{du}{dr}\right)^2\right]e^{-\beta u}$$

$$=3NnkT\Gamma_\lambda \tag{46}$$

where Γ_λ is defined by

$$\Gamma_\lambda\equiv\frac{1}{12}\int d\mathbf{r}\left[3u^2-2ru\frac{du}{dr}+\left(r\frac{du}{dr}\right)^2\right]e^{-\beta u}. \tag{47}$$

In terms of dimensionless momenta, $\mathbf{J}_V$ can be written as

$$\mathbf{J}_V=\frac{1}{\sqrt{n\Gamma_\lambda}}\sum_{j\leqslant l}(\mathbf{r}_{jl}\mathbf{F}_{jl}+u'_{jl}\mathbf{U})\cdot\mathcal{G}_{jl}. \tag{48}$$

The integrals with $2h_V/N$ give terms that are $O(1/N)$, so they have been neglected in Eq. (46).

The computation of the various matrix elements in Eq. (3) for the thermal conductivity are now examined. These evaluations are subject to the same assumptions as used for the evaluation of the viscosity. The combination of kinetic flux functions,

$$\mathbf{J}_{K1}+\mathbf{J}_{K2}=\sqrt{\tfrac{2}{5}}(\mathcal{G}^2+\gamma^2-5)\mathcal{G}+2\sqrt{\tfrac{2}{5}}(\boldsymbol{\gamma}\cdot\mathcal{G})\boldsymbol{\gamma}, \tag{49}$$

appears often in these calculations, so is given for reference.

A. Expansion of $\mathbb{K}_{KV}^L$

From the one-moment approximation of Eq. (51) of I and the density dependence of the flux vectors given in Eqs. (44) and (45), it is seen that to the lowest order in density,

$$\mathbb{K}_{KV}^L=\frac{1}{6}\mathrm{Tr}_{12}(\mathbf{J}_{K1}+\mathbf{J}_{K2})\cdot\mathcal{V}_{12}\frac{i}{z-\mathcal{L}_{12}}\mathbf{J}_{V12}\rho_{12}^{(2)}$$

$$=-\frac{inN}{6A_V\pi^{3/2}}\sqrt{\frac{2kT}{5m}}\int\int d\mathbf{r}\,d\boldsymbol{\gamma}\left[\left(\gamma^2-\frac{5}{2}\right)\mathbf{U}\right.$$

$$+2\boldsymbol{\gamma\gamma}\right]:\left(\mathbf{F}\cdot\frac{\partial}{\partial\mathbf{p}}\right)\int_0^\infty dt[\mathbf{r}(-t)\mathbf{F}(-t)$$

$$+u(-t)\mathbf{U}]e^{-\gamma^2-\beta u}. \tag{50}$$

Here the integration over the center of mass has been carried out and the resolvent interpreted as a time integral, as in Eq. (20). Two integrations by parts, one with respect to the momentum and the second with respect to the time [on the $\mathbf{r}(-t)\mathbf{F}(-t)$ term], results in a separation into a term still involving a time integral,

$$\mathbb{K}_{KV}^L(\text{time})=\frac{inNkT}{3mA_V\pi^{3/2}}\sqrt{\frac{2}{5}}\int\int d\mathbf{r}\,d\boldsymbol{\gamma}[\boldsymbol{\gamma}\cdot\mathbf{FU}$$

$$+2\boldsymbol{\gamma}\mathbf{F}]:\int_0^{s_0}dt\left[\boldsymbol{\gamma}_0\boldsymbol{\gamma}_0-\boldsymbol{\gamma}(-t)\boldsymbol{\gamma}(-t)\right.$$

$$+\frac{u(-t)}{2kT}\mathbf{U}\right]e^{-\gamma^2-\beta u}, \tag{51}$$

and a part associated with collision nonlocality,

$$\mathbb{K}_{KV}^L(\text{nonlocal})=\frac{inN}{6mA_V\pi^{3/2}}\sqrt{\frac{2}{5}}\int\int d\mathbf{r}\,d\boldsymbol{\gamma}[\boldsymbol{\gamma}\cdot\mathbf{FU}+\boldsymbol{\gamma}\mathbf{F}$$

$$+\mathbf{F}\boldsymbol{\gamma}]:[\mathbf{rp}-\mathbf{r}'\mathbf{p}_0]e^{-\gamma^2-\beta u}$$

$$=i\frac{NnkT}{A_V}\sqrt{\frac{2kT}{5m}}\left[\frac{5}{2}B(T)-\frac{20\sigma^3}{6\pi^{1/2}}F_\lambda\right], \tag{52}$$

where $B(T)$ is the second virial coefficient and F_λ is a temperature dependent factor defined by Snider and McCourt,[7] see Appendix C.

B. Evaluation of $\mathbb{K}_{KK}$

With approximations similar to those used in deriving Eq. (28), up to terms quadratic in density, $\mathbb{K}_{KK}$ is written as

$$\mathbb{K}_{KK}=\mathbb{K}_{KK}^2+\mathbb{K}_{KK}^3(B)+\Delta\mathbb{K}_{KK}^3. \tag{53}$$

The $\mathbb{K}_{KK}^2$ term includes the binary cross section appropriate for the thermal conductivity along with a correction from the static presence of a third particle on this cross section

$$\mathbb{K}_{KK}^2\approx\frac{n^2\Lambda^6}{3}\mathrm{Tr}_{12}\mathbf{J}_{K1}\cdot Y_{[0]}\mathcal{V}_{12}e^{-\beta H_{12}^{(2)}}\frac{i}{z-\mathcal{L}_{12}}\mathcal{L}_{12}(\mathbf{J}_{K1}+\mathbf{J}_{K2})$$

$$=\frac{2Nn\langle v\rangle\mathfrak{S}(20)}{3}\left[1+\frac{n\sigma^2R(T)}{10\pi\mathfrak{S}(20)}\right]. \tag{54}$$

The inclusion of three-body collisions in $\mathbb{K}_{KK}$ involves the same type of calculations as in Sec. III B 2. $\mathbb{K}_{KK}^3(B)$ is the term which accounts for the contributions of 3-particle collisions to the first order density correction with the collision operator in Bogoliubov form. Finally, the correction term $\Delta\mathbb{K}_{KK}^3$, with the limit of $s_0\to-\infty$ implied, is

$$\Delta\mathbb{K}_{KK}^3=\frac{in^3}{3}\frac{2\langle v\rangle\mathfrak{S}(20)}{3}\mathrm{Tr}_{12}\mathbf{J}_{K1}\cdot\mathcal{V}_{12}$$

$$\times\int_0^\infty dt[e^{-i\mathcal{L}_{12}t}-e^{-i\mathcal{L}_{12}s_0}](\mathbf{J}_{K1}+\mathbf{J}_{2K})\varphi_1\varphi_2$$

$$=-\sqrt{\frac{2}{5}}\frac{2n^3\langle v\rangle\mathfrak{S}(20)}{9\pi^{3/2}\sqrt{mkT}}\int\int d\mathbf{r}\,d\boldsymbol{\gamma}[\boldsymbol{\gamma}\cdot\mathbf{FU}+\boldsymbol{\gamma}\mathbf{F}$$

$$+\mathbf{F}\boldsymbol{\gamma}]:\int_0^\infty dt\left[\frac{-u(-t)}{2kT}\mathbf{U}+\boldsymbol{\gamma}(-t)\boldsymbol{\gamma}(-t)\right.$$

$$-\boldsymbol{\gamma}_0\boldsymbol{\gamma}_0\right]e^{-\gamma^2-\beta u}. \tag{55}$$

Clearly this is proportional to $\mathbb{K}_{KV}^L(\text{time})$.

C. Evaluation of $\mathbb{V}_{VK}$

As in the viscosity case, the lowest order term in $\mathbb{V}_{VK}$ comes entirely from the third term in Eq. (85) of I. After simplification, this term is

$$\mathbb{V}_{VK} \approx -\mathbb{V}_{VV} \frac{1}{6N} \mathrm{Tr}_{12} \mathbf{J}_{V12} \cdot \frac{1}{z - \mathcal{L}_{12}} \rho_{12}^{(2)} \mathcal{V}_{12}(\mathbf{J}_{K1} + \mathbf{J}_{K2})$$

$$= -\mathbb{V}_{VV} \frac{nkT}{6\sqrt{5\Gamma_\lambda}} \left(-4\pi^{1/2}\sigma^3 N_\lambda - 7T\frac{dB}{dT} - 5T^2\frac{d^2B}{dT^2} \right),$$
(56)

where the collisional transfer contribution to the thermal conductivity, N_λ is defined in Eq. (D3).

D. First order density correction to the thermal conductivity

Within the lowest order in density and within the one-moment approximation for the $\mathbb{K}$ terms, Eq. (3) for the thermal conductivity becomes

$$\lambda = \frac{3k^2T}{4m\langle v\rangle\mathfrak{S}(20)} \left[5 + 5nB(T) - \frac{20n\sigma^3}{3\pi^{1/2}}F_\lambda \right.$$

$$- \frac{n\sigma^2 R(T)}{10\pi\mathfrak{S}(20)} - \frac{4n\pi^{1/2}\sigma^3}{3}N_\lambda - \frac{7}{3}nT\frac{dB}{dT}$$

$$\left. - \frac{5}{3}nT^2\frac{d^2B}{dT^2} + 5n\mathbb{K}_{KK}^3(B) \right].$$
(57)

The $\Delta\mathbb{K}_{KK}^3$ and $\mathbb{K}_{KV}^L(\text{time})$ contributions have cancelled each other.

V. DISCUSSION

This paper and Paper I have examined the density expansion of the coefficients of viscosity and thermal conductivity, based on the time correlation formulation. Detailed comparison of the resulting expressions with those derived[6–8] from a generalization of the Boltzmann equation have been made. The comparison shows that there is complete agreement between the approaches, provided similar restrictions are placed on the evaluation of the formulas. It is the latter set of equations, together with an estimate of bound state contributions,[9] which are the basis for the standard estimation[3,20] of gas transport coefficients at moderate densities.

The only other direct density expansion of the time correlation function formula for a transport coefficient is the work by Oppenheim and his co-workers.[21,22] Their method of approach followed the original method of Zwanzig,[23] which involved the direct binary collision expansion of the time correlation function and the resummation of the resulting divergent series. It can be demonstrated[24] that for a repulsive potential, the Kawasaki and Oppenheim expressions for the first order density corrections to the viscosity and thermal conductivity reduce to the Snider and McCourt[7] results along with a 3-particle collision contribution. The present work avoids this by projecting onto the space of the flux operators, and with the aid of the rotational invariance of

the resulting thermal averages, leads to an expression of a transport coefficient, Eq. (16) of Paper I, in terms of a combination of memory kernels. The need for a combination of terms is due to the differing properties of the kinetic and potential contributions to the appropriate (momentum or energy) flux. The identification and separation of true 3-particle collisions (whose contributions have not been evaluated) from successive isolated binary collisions, is based on the work of Kawasaki and Oppenheim.[21,25]

While the emphasis here has been on the density expansion of the thermal transport coefficients, the general result of Eq. (16) of I may be of use for estimating other time correlation functions. What is still missing from a general procedure is a unified treatment of both moderately dense gas and bound state effects on the transport coefficients. The bound states were treated in a separate article,[26] but the question of how to correctly separate the bound state and weakly interacting (van der Waals) effects in a common formalism has yet to be done. Such a combined treatment, together with a proper estimate of the contribution of true 3-particle collisions, is necessary before an improvement can be made to the Rainwater and Friend[3] theory prediction of transport coefficients.

ACKNOWLEDGMENTS

APPENDIX A: BINARY COLLISIONS

The collision integrals in this article involve collision trajectories that pass through a given phase point. Within classical mechanics, and for a known spherical intermolecular potential, the trajectory of a collision is uniquely determined by the relative position $\mathbf{r}$ and relative momentum $\mathbf{p}$ of a single point on the trajectory. For a spherical potential as assumed here, the trajectory lies in the plane determined by $\mathbf{r}$ and $\mathbf{p}$. In this work, which follows the notation of Ref. 6, the coordinate system is chosen so that the z axis is in the $-\mathbf{p}$ direction. The azimuthal angle θ of the position vector determines whether the reference phase point $\mathbf{r},\mathbf{p}$ is on the incoming or outgoing part of the trajectory, with $\theta < \pi/2$ if the reference point is on the incoming part of the trajectory and $\theta > \pi/2$ if it is on the outgoing part. The angle between $\mathbf{r}$ and $\mathbf{p}$ is $\pi - \theta$. These relations are shown in Fig. 1. The angle around the z-axis describing the orientation of the plane of the trajectory does not play any role in the collision dynamics, so it will not be designated.

A general point on the trajectory is characterized by a position vector $\boldsymbol{\xi}$ and a relative momentum vector $\mathbf{p}_\xi$. The vector $\boldsymbol{\xi}$ makes an angle β_ξ with respect to the z-axis while $\mathbf{p}_\xi$ makes an angle of η_ξ with respect to the z-axis. The angular momentum $\mathbf{L}$ is a constant of the motion whose direction is normal to the plane of the trajectory. Its constant magnitude is determined by the initial reference point, so

$$L = |\boldsymbol{\xi} \times \mathbf{p}_\xi| = \xi p_\xi \sin(\eta_\xi - \beta_\xi) = rp\sin\theta. \tag{A1}$$
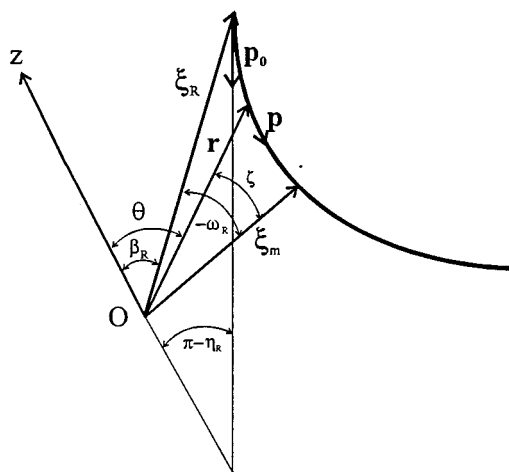
FIG. 1. Binary collision parameters. The reference point on the trajectory is characterized by the position $\mathbf{r}$ and the corresponding momentum $\mathbf{p}$. R is the cutoff distance of the potential, at which point the relative momentum is $\mathbf{p}_0$. ξ_m is the position of closest approach. Various angles in the figure are defined with reference to these vectors.

For computational purposes, the potential is considered to be cutoff at a distance R, beyond which it is zero. This distance is eventually taken to infinity. At the cutoff distance on the incoming part of the trajectory, the position vector ξ_R has an azimuthal angle β_R and the momentum $\mathbf{p}_R = \mathbf{p}_0$ is the initial constant momentum before the collision begins. The azimuthal angle of this vector is denoted by η_R. From the constancy of the angular momentum, these angles are related by

$$\eta_R = \pi + \beta_R - \arcsin[L/R(mE)^{1/2}]. \qquad (A2)$$

As the distance $R \to \infty$, η_R rapidly approaches its asymptotic value η while β_R varies as $1/R$ as it approaches its asymptotic value β.

The vector ξ_m denotes the point of closest approach of the two particles. The angle between ξ_m and the cutoff point at R on the incoming trajectory is denoted by $-\omega_R$ and the angle between ξ_m and the reference position $\mathbf{r}$ is denoted by ζ. These relations are illustrated in Fig. 1 for $\mathbf{r}$ on the incoming part of the trajectory. From this figure, it is obvious that the following relations hold among these angles:

$$\beta_R - \theta = \omega_R \pm \zeta, \qquad (A3)$$

with the upper sign, here $(+)$, appropriate if the reference point is on the incoming part of the trajectory, and the lower sign, here $(-)$, on the outgoing portion of the trajectory. The calculation of these quantities requires an integration along a trajectory.

The time that it takes to go along the trajectory from ξ_R on the incoming part of the trajectory to $\mathbf{r}$ is denoted by s_0. During this time the momentum changes from $\mathbf{p}_0$ to $\mathbf{p}$. In the text, the time s_0 appears as the independent parameter of a point on the initial part of the trajectory whereas here R is the independent variable. Setting $\xi_R = \mathbf{r}(-s_0)$ identifies the different notations, see in particular Eq. (24).

In terms of polar variables, the magnitude of the angular momentum is

$$L = \frac{m}{2} \xi^2 \frac{d\beta_\xi}{dt} \qquad (A4)$$

and the total (kinetic plus potential) relative energy is

$$E = \frac{p_0^2}{m} = \frac{m}{4}\left(\frac{d\xi}{dt}\right)^2 + \frac{2L^2}{m\xi^2} + u(\xi). \qquad (A5)$$

Note that the reduced mass is $m/2$. The time derivatives in these two equations can be combined to describe how β_ξ varies with ξ as the trajectory is traversed. On integration between the reference point and the point $\xi = R$ on the incoming part of the trajectory, the angle difference is given by Eq. (A3) with ω_R and ζ identified as the integrals

$$\omega_R \equiv -\frac{L}{p_0}\int_{\xi_m}^{R}\frac{d\xi}{\xi^2}\left[1 - \frac{L^2}{2mE\xi^2} - \frac{u(\xi)}{E}\right]^{-1/2}$$

$$= -\frac{L}{p_0}\int_{\xi_m}^{\infty}\frac{d\xi}{\xi^2}\left\{\left[1 - \frac{L^2}{2mE\xi^2} - \frac{u(\xi)}{E}\right]^{-1/2}\right.$$

$$\left. -\left[1 - \frac{L^2}{2mE\xi^2}\right]^{-1/2}\right\} - \arcsin\left(\frac{L}{p_0\xi}\right) + \frac{L}{p_0 R} + O\left(\frac{1}{R^2}\right)$$

$$\equiv \omega + \frac{L}{p_0 R} + O\left(\frac{1}{R^2}\right) \qquad (A6)$$

and

$$\zeta = \frac{L}{p_0}\int_{\xi_m}^{r}\frac{d\xi}{\xi^2}\left[1 - \frac{L^2}{2mE\xi^2} - \frac{u(\xi)}{E}\right]^{-1/2}. \qquad (A7)$$

A term with the potential set equal to zero is subtracted and added in the equation for ω_R. The integral of the difference converges rapidly as $R \to \infty$, while the remainder is straightforwardly integrated to give the dominant behavior of ω_R as $R \to \infty$.

Integrating Eq. (A5) on its own, the time s_0 is determined by

$$\frac{2p_0}{m}s_0 = \int_{\xi_m}^{R}d\xi\left[1 - \frac{L^2}{2mE\xi^2} - \frac{u(\xi)}{E}\right]^{-1/2} \pm \frac{L}{p_0}Y, \qquad (A8)$$

where

$$\frac{L}{p_0}Y \equiv -\int_{\xi_m}^{r}d\xi\left[1 - \frac{L^2}{2mE\xi^2} - \frac{u(\xi)}{E}\right]^{-1/2}. \qquad (A9)$$

Now s_0 occurs in the text only in the combination $\mathbf{r}' = \mathbf{r}(-s_0) + 2\mathbf{p}_0 s_0/m$, Eq. (24). This vector is obtained by starting at the vector $\mathbf{r}$ and tracing backwards a time s_0 along the trajectory to reach $\mathbf{r}(-s_0)$. The intermolecular potential is then "turned off" and the relative position allowed to evolve freely forward in time for a duration of s_0. Under the same transformation, the relative momentum $\mathbf{p}$ becomes the initial momentum $\mathbf{p}_0$. These quantities are illustrated in Fig. 2, which is adapted from Ref. 27. Only certain scalar products involving $\mathbf{r}'$ occur in the text, and this only in the limit $R \to \infty$. The simplest of these is
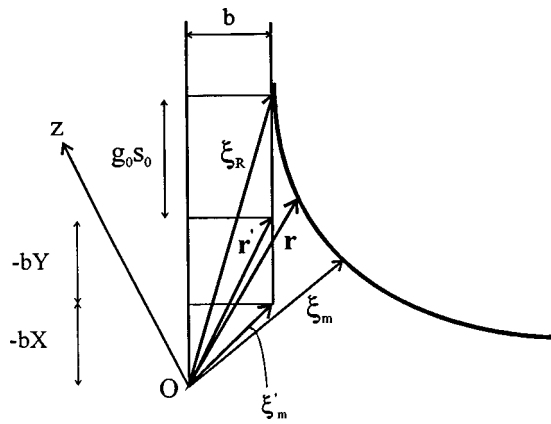
FIG. 2. Primed position variables and their related collision parameters. The impact parameter is $b=L/p_0$, and the initial relative speed of approach is $g_0=2p_0/m$. Other parameters are defined in the text.

$$\mathbf{p}\cdot\mathbf{r}' = -pR\cos\beta_R - \frac{2}{m}pp_0s_0\cos\eta_R$$

$$\approx -p\left[R-\frac{2}{m}p_0s_0\right]\cos\beta + \frac{pL}{p_0}\sin\beta$$

$$\xrightarrow[R\to\infty]{} \frac{pL}{p_0}(X\pm Y)\cos\beta + \frac{pL}{p_0}\sin\beta, \qquad (A10)$$

where

$$\frac{L}{p_0}X = \int_{\xi_m}^{\infty}d\xi\left\{\left[1-\frac{L^2}{mE\xi^2}-\frac{u(\xi)}{E}\right]^{-1/2}-1\right\}-\xi_m. \qquad (A11)$$

Two other contractions are

$$\mathbf{r}\cdot\mathbf{r}' = r\left(R-\frac{2p_0}{m}s_0\right)\cos(\beta-\theta)-\frac{rL}{p_0}\sin(\beta-\theta)$$

$$\xrightarrow[R\to\infty]{} -\frac{rL}{p_0}[(X\pm Y)\cos(\beta-\theta)+\sin(\beta-\theta)] \qquad (A12)$$

and

$$\mathbf{p}_0\cdot\mathbf{r}' \xrightarrow[R\to\infty]{} L(X\pm Y). \qquad (A13)$$

These relations are used in the other appendices to evaluate certain collision integrals.

APPENDIX B: IDENTIFICATION OF F_η

The trace in Eq. (26) is converted to a classical expression by

$$I = -\Lambda_r^3\,\mathrm{Tr}_{\mathrm{rel}}\cdots$$

$$= \frac{1}{\pi^{3/2}}\int\int d\mathbf{r}\,d\gamma\frac{1}{r}\frac{du}{dr}[\gamma\mathbf{r}]^{(2)}:[\mathbf{r}'\gamma_0]^{(2)}e^{-\gamma^2-\beta u}. \qquad (B1)$$

This is a sixfold integral over the relative position and momentum. In the following, it is reduced to the form of a standard integral from the work of Snider and McCourt.[7] This facilitates the comparison of the results of the present article with previous work.

The tensorial contraction in the integrand can be expressed in terms of the collision angles defined in Appendix A:

$$[\gamma\mathbf{r}]^{(2)}:[\mathbf{r}'\gamma_0]^{(2)} = \frac{1}{2}[(\gamma\cdot\mathbf{r}')(\mathbf{r}\cdot\gamma_0)+(\mathbf{r}\cdot\mathbf{r}')(\gamma\cdot\gamma_0)]$$

$$-\frac{1}{3}(\gamma\cdot\mathbf{r})(\gamma_0\cdot\mathbf{r}')$$

$$= -\frac{rL\gamma}{2\sqrt{mkT}}\left\{(X\pm Y)\left[\cos(2\beta-\theta)\right.\right.$$

$$\left.+\frac{1}{3}\cos\theta\right]+\sin(2\beta-\theta)\Big\}$$

$$= -\frac{1}{2}\gamma^2r^2\sin\theta\Big\{(X\pm Y)\left[\cos(2\beta-\theta)\right.$$

$$\left.+\frac{1}{3}\cos\theta\right]+\sin(2\beta-\theta)\Big\}. \qquad (B2)$$

This has been simplified by combining similar terms, using various trigonometric identities and replacing L by $rp\sin\theta$. On noting that only θ and the explicit $\pm$ changes on interchanging the outgoing and incoming parts of the trajectory ($\theta\to\pi-\theta$), these two parts can be combined to give

$$I = \frac{-8\pi^{1/2}}{3}\int\int\int_0^{\pi/2}d\theta\,dr\,d\gamma\frac{du}{dr}r^3e^{-\beta u}e^{-\gamma^2}\gamma^4$$

$$\times\sin^2\theta[Y\cos\theta+3Y\cos 2\omega\cos(\theta+2\zeta)$$

$$-3X\sin 2\omega\sin(\theta+2\zeta)+3\cos 2\omega\,\sin(\theta+2\zeta)]. \qquad (B3)$$

The integral can be recognized as that appearing in the definition of F_η of Snider and McCourt,[6] so

$$I = \frac{-8\pi^{1/2}}{3}\left(\frac{kT\sigma^3}{2\pi}F_\eta\right)=\frac{-4kT\sigma^3}{3\pi^{1/2}}F_\eta. \qquad (B4)$$

APPENDIX C: IDENTIFICATION OF F_λ

The classical integral of Eq. (52) is denoted here by I_{KKV}. This can be simplified by explicitly identifying the dot products involved and their expression in terms of the angles defined in Appendix A, as

$$I_{KKV} = \frac{1}{\pi^{3/2}}\int\int d\mathbf{r}\,d\gamma[\gamma\cdot\mathbf{F}\mathbf{U}+\gamma\mathbf{F}+\mathbf{F}\gamma]:$$

$$\times[\mathbf{r}\mathbf{p}-\mathbf{r}'\mathbf{p}_0]e^{-\gamma^2-\beta u}$$

$$= 8\pi^{1/2}\int\int\int_0^{\pi}d\theta\,dr\,d\gamma\sin\theta r^2\gamma^2e^{-\gamma^2-\beta u}Frp\gamma$$

$$\times\{(2\cos^2\theta+1)+\sin\theta[(X\pm Y)(\cos(2\beta-\theta)$$

$$+2\cos\theta)+\sin(2\beta-\theta)]\}$$

$$= 15kT\sqrt{mkT}\left[B(T)-\frac{4\sigma^3}{3\pi^{1/2}}F_\lambda\right]. \qquad (C1)$$

The resulting integrals have been written in terms of the second virial coefficient and the integral F_λ defined in Eq. (18) of Ref. 7.

APPENDIX D: IDENTIFICATION OF N_η AND N_λ

The classical mechanical expression for the trace in Eq. (40) is denoted by

$$I = \Lambda_r^3 \, \text{Tr}_{\text{rel}} \cdots$$

$$= \frac{1}{\pi^{3/2}} \int \int d\mathbf{r} \, d\boldsymbol{\gamma} \frac{du}{dr} \frac{1}{r} \left[(\mathbf{r} \cdot \boldsymbol{\gamma}_0)^2 - \frac{r^2 \gamma_0^2}{3} \right] e^{-\gamma^2 - \beta u}. \quad (D1)$$

Using the coordinate system of Appendix A, this becomes

$$I = 8\pi^{1/2} \int \int \int_0^\pi \sin\theta \, d\theta \, dr \, d\gamma \, r^3 \frac{du}{dr} e^{-\gamma_0^2} \gamma_0^2 \gamma^2$$

$$\times \left[\cos^2(\eta_R - \theta) - \frac{1}{3} \right]. \quad (D2)$$

On taking the limit $R \to \infty$, combining together the outgoing and incoming contributions and integrating over θ and γ in the second term

$$I = 8\pi^{1/2} \int \int \int_0^{\pi/2} \sin\theta \, d\theta \, dr \, d\gamma \, r^3 \frac{du}{dr} e^{-\gamma_0^2} \gamma_0^2 \gamma^2$$

$$\times (1 + \cos 2\omega \cos 2\zeta)$$

$$- \frac{4\pi}{3} \int d\mathbf{r} \frac{du}{dr} r e^{-\beta u} \left(\frac{3}{2} + \beta u \right)$$

$$= 4\pi^{1/2} kT \sigma^3 N_\lambda + kT \left[5B(T) + 2T \frac{dB(T)}{dT} \right]. \quad (D3)$$

The first term, arising from $(\mathbf{r} \cdot \boldsymbol{\gamma}_0)^2$, can thus be recognized as being proportional to the integral N_λ defined in Eq. (31) of Ref. 7 while the second term can be expressed in terms of the second virial coefficient and its derivatives. This combination is exactly proportional to N_η, defined in Eq. (34) of Ref. 7, thus

$$I = \frac{8\sigma^3 \pi^{1/2} kT}{3} N_\eta. \quad (D4)$$

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