Investigation of transfer coefficients for many-component dense systems of neutral and charged hard spheres

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Investigation of transfer processes in dense weakly or fully ionized many-component gases is topical in view of construction and improvement of new gaseous lasers, plasmo-chemical reactors for ozone synthesis, and air cleaning of both nitrogen and carbon oxides and chlorine compounds.

A study and calculation of transfer coefficients taking into account the interparticle interaction nature is one of the major problems in this investigation. Recent papers by Murphy [1-4] are devoted to these calculations for some special low-density mixtures basing on the Boltzmann kinetic equation for point particles and using accurate interparticle potentials of interaction. Nevertheless, there are some problems in calculation of transfer coefficients for high-density mixtures. They are caused mainly by the fact that the Boltzmann kinetic equation is suitable for rarefied gases and plasmas only.

In present work a calculation of transfer coefficients for many-component dense gases for charged and non-charged hard spheres is carried out using the Enskog-Landau kinetic equation which takes into account realistic particle sizes.

The Enskog-Landau kinetic equation was obtained in [5,6] for a one-component system of charged hard spheres in the electron compensation field starting from the Bogolubov hierarchy with modified boundary conditions in the pair collision approximation. In paper [7] this equation was generalized for the case of many-component system and usually reads:

$$\frac{\partial}{\partial t} + \mathbf{v}_a \cdot \frac{\partial}{\partial \mathbf{r}_a} f_a(x_a; t) = \sum_{b=1}^{M} \left[ I_E^{(0)}(f_a, f_b) + I_E^{(1)}(f_a, f_b) + I_{MF}(f_a, f_b) + I_L(f_a, f_b) \right],$$

where $f_a(x_a; t)$ is the one-particle distribution function of $a$-component ($x \equiv \{ \mathbf{r}, \mathbf{p} \}$), $M$ is a number of components.

The collision integral in the right-hand part of (1) consists of several terms. Such a structure is produced due to the additivity of the interaction potential which is modelled for the mixture of charged hard spheres as a sum of the short-range part (hard spheres) and the long-range one (Coulomb particles). $I_E^{(0)}$ and $I_E^{(1)}$ are the zeroth and first expansion terms of the Enskog collision integral with respect to the spatial inhomogeneity [5]. $I_{MF}$ is the collision integral of the kinetic mean field theory KMFT [8,9]. It is the first order on the long-range interaction. The last term $I_L$ is the generalized Landau collision integral and it is the second order on the long-range interaction.

The kinetic equation (1) can be solved with operating the standard Chapman-Enskog
method [10]. The unknown distribution function in the first approximation can be taken as

\[ f^{(1)}_a(r, v_a, t) = f^{(0)}_a(r, v_a, t)[1 + \phi_a], \]  

(2)

where \( f^{(0)}_a \) is the zeroth approximation. Usually, it is chosen as the local-equilibrium Maxwell distribution function. \( \phi_a \) is a correction which is expressed through the Sonine-Laguerre polynomials [10].

Having the solution to the kinetic equation (1), one can calculate the stress tensor and the heat flow vector in a system. These quantities are expressed via such transport coefficients as bulk \( \kappa \) and shear \( \eta \) viscosities and thermal conductivity \( \lambda \), respectively:

\[ \kappa = 4 \sum_{a, b=1}^{M} \sigma_{ab}^4 g_{ab}^2 n_a n_b \sqrt{2\pi \mu_{ab} k_B T} = \sum_{a, b=1}^{M} \kappa_{ab}, \]  

(3)

\[ \eta = \frac{3}{5} \kappa + \left( \frac{1}{2} \sum_{a=1}^{M} n_a B_a(0) + \frac{4\pi}{15} \sum_{a, b=1}^{M} \sigma_{ab}^3 g_{ab}^2 n_a n_b \frac{\mu_{ab}}{m_b} B_b(0) \right) k_B T, \]  

(4)

\[ \lambda = \sum_{a, b=1}^{M} \frac{3 k_B \kappa_{ab}}{m_a + m_b} - \sqrt{2k_B T} \left( \sum_{a=1}^{M} \frac{n_a}{\sqrt{m_a}} [A_a(1) - A_a(0)] + \right. \]  

\[ \left. \frac{2\pi}{3} \sum_{a, b=1}^{M} \sigma_{ab}^3 g_{ab}^2 \frac{n_a n_b}{m_a + m_b} \left[ \frac{3\mu_{ab}}{\sqrt{m_b}} A_b(1) - \sqrt{m_b} A_b(0) \right] \right), \]  

(5)

where \( \sigma_{ab} = (\sigma_a + \sigma_b)/2 \), \( \sigma_a, \sigma_b \) – hard sphere diameters, \( g_{ab}^2 \) – quasiequilibrium binary correlation function, \( n_a \) – particle number density, \( \mu_{ab} = m_a m_b / (m_a + m_b) \) – reduced mass, \( A_a(0), A_a(1) \) and \( B_a(0) \) are zeroth and first coefficients of expansion of the correction \( \phi_a \) on the Sonine-Laguerre polynomials.

In numerical calculations of transfer coefficients (3)–(5) for some binary and ternary mixtures of neutral and charged hard spheres we considered their temperature and concentration ratio dependences. The values of hard sphere diameters were fixed: \( \sigma_{He} = 2.15\text{Å}, \sigma_{Ar} = 3.405\text{Å}, \sigma_{Kr} = 3.67\text{Å}, \sigma_{Xe} = 3.924\text{Å} \). These values were borrowed from [11].

Calculating \( A_a(0), A_a(1) \) and \( B_a(0) \) we faced with the problem of divergency of the so-called \( \Omega \)-integrals at large distances. To avoid this circumstance we should change upper limit of integration and use finite screening radius \( D \) instead of infinity. This screening radius, in contrast to the Debye formula for point-like particles, explicitly takes into account realistic sizes of charged particles in accordance with [12]. Contact values of the binary correlation function in expressions (3)–(5) were borrowed from [13].

Not only the transport coefficients \( \kappa, \eta, \) and \( \lambda \) were studied. Numerical calculation for thermal diffusion \( D_T^a \) and mutual diffusion coefficients \( D^{a\beta} \) has been performed as well. For two- and three-component mixtures of neutral and charged hard spheres we studied their dependences on density, temperature, and concentration ratio of some mixture components [14]. Figs. 1 and 2 show our calculations in brief.

The obtained Enskog-Landau kinetic equation for charged hard spheres turned out to be very useful for several purposes. First of all, the collision integral of this equation does not contain a divergency at small distances. Secondly, the normal solution and all transport coefficients have analytical structure. They can be easily used to study some
Though this model is not entirely suitable as a hard spheres model, because the H\textsubscript{2}-molecule is not spherical, nonetheless obtained results give an information about the successfulness of the application of the model for nonspherical molecules. Somewhat worse agreement is between the theory and experimental data \cite{15} when temperature increases. At high temperatures the role of the attractive part of interparticle interaction potential becomes weaken in comparison with the repulsive one. However, this behaviour can be explained by ignoring in the theory the temperature and concentration dependence of hard sphere diameters for molecules of Ar and H\textsubscript{2}. At the same time it is known that \( \sigma \) depends both on \( T \) and \( n \). b), c) and d) – temperature and concentration ratio dependences of shear viscosity \( \eta \) and thermal conductivity \( \lambda \) coefficients for the mixture Ar\textsuperscript{+}-Kr\textsuperscript{+} at the fixed total density \( n = 2 \cdot 10^{26} \text{m}^{-3} \). These calculations were performed for three fixed concentration ratios of the heavy component \( \chi_{\text{Kr+}} = 0.25; 0.5; 0.75 \), \( \chi_{\text{Kr+}} = n_{\text{Kr+}}/(n_{\text{Ar+}} + n_{\text{Kr+}}) \). The coefficients \( \eta \) and \( \lambda \) have very similar temperature dependence. But concentration ratio dependence for \( \lambda \) has a different curve fit. More detailed analysis is given in \cite{14}. 

Fig. 1: a) – temperature dependence of shear viscosity \( \eta \) for mixture 40%H\textsubscript{2}, 60%Ar at pressures \( P = 300, 400, 500 \) atm., respectively. Curves are plotted in order of increasing pressure. 

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A very important step in this theory is to calculate a dynamical screening radius in a system. Partially this problem has been already solved in our recent paper [16].

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