Averaging over orientations at the dipole-dipole and dipole-quadrupole interactions

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The method averaging over angles of arbitrary functions of the angles of mutual orientation with the use of angular form-factor is developed for the dipole-dipole and dipole-quadrupole interactions. The functions are averaged by use of a single integration over the form-factor with certain weights, for which explicit analytical equations are derived and the method of numerical calculation is formulated. For the dipole-dipole interactions, the weighting factor is expressed in terms of elementary functions; for the dipole-quadrupole interactions, it is written in terms of the first-kind elliptic integrals, and two approximations are proposed for it.

Introduction

In many problems of gas kinetics, theory of scattering of particles, and theory of multiple scattering of light, there is a need in averaging the calculated results on the sought or intermediate parameters (for example, scattering cross sections) over mutual orientation of particles participating in the pair interactions. Important particular cases are interactions between two dipoles and between a dipole and a quadrupole. Since two polar and one axial angle describe the mutual orientation of the latter, the averaging over orientations is, in fact, a triple integration of some preset function over angles. This procedure, in the presence of some other parameters, significantly increases the dimensionality of the problem and the time needed for making numerical calculations.

At the same time, there is a possibility of reducing the triple integration to a single one, in which the integration parameter is the angular form-factor (indicator function) of the interaction between particles (δ). In this case, the preset function of angles is averaged with the weight $w(\delta)$, being the density of probability that the angular form-factor takes a fixed value δ. The direct method of numerically calculating $w(\delta)$ for any interaction consists in dividing the integration intervals for every variable into a great number of equal sub-intervals, calculation of δ for all the elementary volumes of the space of integration variables, and then estimating the number of cases that the angular form-factor takes the value in the given narrow interval about δ with δ varying in the entire range of its values. At the same time, the exact analytical calculation of $w(\delta)$ is possible for relatively simple form-factors.

The aim of this paper is to find exact analytical equations for the weighting factor $w(\delta)$ for the dipole-dipole and dipole-quadrupole interactions and thus to implement the economical method of averaging the sought function by means of single integration over the angular form-factor of the interaction.

1. Dipole-dipole interaction

The potential of the dipole-dipole interaction[1] can be presented in the form

$$V_{dd}(r) = -\frac{2d_1d_2}{r^3}\,\delta(\theta_1,\theta_2,\varphi),$$
$$\delta(\theta_1,\theta_2,\varphi) = \cos\theta_1\cos\theta_2 - \frac{1}{2}\sin\theta_1\sin\theta_2\cos\varphi, \qquad (1)$$
$$\varphi = \varphi_1 - \varphi_2,$$

where $\delta(\theta_1, \theta_2, \varphi)$ is the angular form-factor whose values vary from -1 to 1; θ_1 and θ_2 are the polar angles that determine the orientation of the vectors of dipole moments d_1 and d_2 about the axis z passing through the centers of molecules (atoms); φ is the difference between the axial angles connected with the dipole moments; r is the distance between the centers of molecules.

To be averaged over angles is some preset function (for example, transport scattering cross section) dependent on angles via the angular form-factor, $P[\delta(\theta_1, \theta_2, \varphi)]$, so that its average value is determined by the quadrature

$$\overline{P} = \frac{1}{8\pi}\int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta_1\, d\theta_1 \int_0^{\pi} P[\delta(\theta_1,\theta_2,\varphi)]\ \sin\theta_2\, d\theta_2\,. \qquad (2)$$

Replacing the variables in Eqs. (1) and (2) as

$$x = \cos\theta_1\,,\quad y = \cos\theta_2\,,\qquad z = \cos\varphi \qquad (3)$$

and taking into account the symmetry of $\cos\varphi$ with respect to the replacement $\varphi \to \varphi + \pi$, we obtain from Eq. (2) the equation for $w(\delta)$:

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$$\int_{-1}^{1} w(\delta)\, P(\delta)\, \mathrm{d}\delta = \frac{1}{4\pi} \int_{-1}^{1} \frac{\mathrm{d}z}{\sqrt{1-z^2}} \int_{-1}^{1} \mathrm{d}x \int_{-1}^{1} \mathrm{d}y\, P[\delta(x, y, z)]. \quad (4)$$

For a fixed value of the angular form-factor $\delta = \text{const}$, from the second equation of the system (1) using new variables

$$xy - \frac{1}{2} z \sqrt{1-x^2}\sqrt{1-y^2} = \delta , \quad (5)$$

we derive

$$z = 2\frac{xy - \delta}{\sqrt{1-x^2}\sqrt{1-y^2}}, \quad \frac{\partial z}{\partial \delta} = -\frac{2}{\sqrt{1-x^2}\sqrt{1-y^2}}. \quad (6)$$

Then, from Eq. (4) taking into account that $\mathrm{d}z = (\partial z/\partial\delta)\mathrm{d}\delta$ we have the explicit equation for the weighting factor in the form of a double integral

$$w(\delta) = \frac{1}{\pi} \int_{\xi}^{1} \mathrm{d}x \int_{y_1(x)}^{y_2(x)} \frac{\mathrm{d}y}{\sqrt{1 - x^2 - y^2 - 3x^2y^2 + 8xy\delta - 4\delta^2}}. \quad (7)$$

In Eq. (7) the symmetry of the integrand with respect to the simultaneous alternation of the signs of x and δ is taken into account. This allows our consideration to be restricted to only positive values of x. The limits of integration over y in Eq. (7) are determined from the condition of positive definiteness of the radicand in the denominator of Eq. (7) and equal to

$$y_{1,2}(x) = \frac{4\delta x \mp \sqrt{1-x^2}\sqrt{1+3x^2-4\delta^2}}{1+3x^2}. \quad (8)$$

The lower limit of integration over x in Eq. (7) is dependent on δ and determined from the condition of positive definiteness of the second radicand in the numerator of Eq. (8):

$$\xi = \begin{cases} 0, & |\delta| \le 1/2; \\ \sqrt{(4\delta^2-1)/3}, & |\delta| > 1/2. \end{cases} \quad (9)$$

Upon calculation of the integral (7), we obtain the final equation for the weighting function $w(\delta)$ in terms of the elementary functions:

$$w(\delta) = \begin{cases} \operatorname{arcsinh}\sqrt{3}/\sqrt{3} = 0.7603459963, & |\delta| \le 1/2, \\ (\operatorname{arcsinh}\sqrt{3} - \operatorname{arcsinh}\sqrt{4\delta^2-1})/\sqrt{3}, & 1/2 < |\delta| \le 1, \end{cases} \quad (10)$$

$$\operatorname{arcsinh} x = \int_0^x \frac{\mathrm{d}t}{\sqrt{1+t^2}},$$

where arcsinh x is the inverse hyperbolic sine.

Figure 1 shows the plot of $w(\delta)$ (curve *1*).

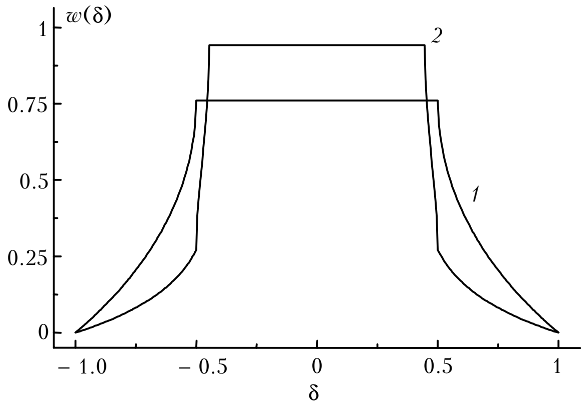

Fig. 1. Weighting factor $w(\delta)$ as a function of angular form-factor δ: dipole-dipole (curve *1*) and dipole-quadrupole (*2*) interactions.

2. Dipole-quadrupole interaction

The potential of the dipole-quadrupole interactions is[1,2]:

$$V_{dQ}(r) = -\frac{3dQ}{2r^4}\delta(\theta_1, \theta_2, \varphi);$$

$$2\delta(\theta_1, \theta_2, \varphi) = \cos\theta_1 - 3\cos\theta_1\cos^2\theta_2 + 2\sin\theta_1\sin\theta_2\cos\theta_2\cos\varphi. \quad (11)$$

Here d and Q are the dipole and quadrupole moments, and subscripts 1 and 2 of polar angles correspond to the dipole and quadrupole moments. Similarly to the case of dipole-dipole interaction, $|\delta| \le 1$.

In using the variables (3) we have from the equation, similar to Eq. (5),

$$x - 3xy^2 + 2yz\sqrt{1-x^2}\sqrt{1-y^2} = 2\delta \quad (12)$$

that

$$z = \frac{2\delta - x + 3xy^2}{2y\sqrt{1-x^2}\sqrt{1-y^2}}; \quad \frac{\partial z}{\partial\delta} = \frac{1}{y\sqrt{1-x^2}\sqrt{1-y^2}}. \quad (13)$$

Substituting Eq. (13) into the equation similar to Eq. (7), for the weighting function we have (taking into account the domains of existence) that

$$w(\delta) = \begin{cases} \dfrac{1}{\pi}\displaystyle\int_0^1 \mathrm{d}y \int_{x_1(y)}^{x_2(y)} \frac{\mathrm{d}x}{\sqrt{G}}, & |\delta| \le 1/\sqrt{5}, \\ \dfrac{1}{\pi}\displaystyle\int_0^{y_1} \mathrm{d}y \int_{x_1(y)}^{x_2(y)} \frac{\mathrm{d}x}{\sqrt{G}} + \frac{1}{\pi}\int_{y_2}^{1} \mathrm{d}y \int_{x_1(y)}^{x_2(y)} \frac{\mathrm{d}x}{\sqrt{G}}, & 1/\sqrt{5} < |\delta| \le 1/2, \\ \dfrac{1}{\pi}\displaystyle\int_{y_2}^{1} \mathrm{d}y \int_{x_1(y)}^{x_2(y)} \frac{\mathrm{d}x}{\sqrt{G}}, & 1/2 < |\delta| \le 1; \end{cases} \quad (14)$$

$$G = -4\,(y^4 - y^2 + \delta^2) + 4x\delta(1 - 3y^2) - x^2(5y^4 - 2y^2 + 1) = [x_2(y) - x]\,[x - x_1(y)]\,(1 - 2y^2 + 5y^4),$$

$$x_{1,2} = 2\,\frac{\delta(1-3y^2) \mp y\sqrt{1-y^2}\,\sqrt{(1-y^2)^2 + 4(y^4 - \delta^2)}}{(1-y^2)^2 + 4y^4},$$

$$y_{1,2} = \sqrt{1 \mp 2\sqrt{5\delta^2 - 1}}\,/\,\sqrt{5}.$$

Integration over x in Eq. (14) yields

$$\int_{x_1}^{x_2} \frac{\mathrm{d}x}{\sqrt{(x_2 - x)(x - x_1)}} = \pi, \tag{15}$$

whereupon Eq. (14) becomes simpler:

$$w(\delta) = \begin{cases} w_1(\delta) = \displaystyle\int_0^1 \frac{\mathrm{d}y}{\sqrt{h(y)}}, & |\delta| \le 1/\sqrt{5}, \\ w_2(\delta) = \displaystyle\int_0^{y_1} \frac{\mathrm{d}y}{\sqrt{h(y)}} + \int_{y_2}^1 \frac{\mathrm{d}y}{\sqrt{h(y)}}, & 1/\sqrt{5} < |\delta| \le 1/2, \\ w_3(\delta) = \displaystyle\int_{y_2}^1 \frac{\mathrm{d}y}{\sqrt{h(y)}}, & 1/2 < |\delta| \le 1, \end{cases}$$

$$h(y) = 1 - 2y^2 + 5y^4. \tag{16}$$

Integrals in Eq. (16) have no singularities, and they can be easily calculated numerically. Besides, they can be expressed in terms of the first-kind elliptic integrals $F(\varphi, k)$ (Ref. 3):

$$w_1(\delta) = F(\varphi_0, k)/\sqrt{1-2i} = 0.94145838065,$$

$$w_2(\delta) = [F(\varphi_0, k) + F(\varphi_1, k) - F(\varphi_2, k)]/\sqrt{1-2i}, \tag{17}$$

$$w_3(\delta) = [F(\varphi_0, k) - F(\varphi_2, k)]/\sqrt{1-2i};$$

$$\varphi_0 = i\,\mathrm{arcsinh}\left(i\sqrt{1-2i}\right),$$

$$\varphi_{1,2} = i\,\mathrm{arcsinh}\left(i\sqrt{1-2i}\,\sqrt{1 \mp 2\sqrt{5\delta^2 - 1}}\,/\sqrt{5}\right),$$

$$k = (-3 + 4i)/5;$$

$$F(\varphi, k) = \int_0^{\varphi} \frac{\mathrm{d}\alpha}{\sqrt{1 - k^2 \sin^2\alpha}}.$$

The plot of $w(\delta)$ for the interaction of dipole with quadrupole is shown in Fig. 1 (curve *2*). The equations (10), (16), and (17) for $w(\delta)$ were checked by comparing their numerical values over the entire variability range of δ with the values determined by direct numerical calculation using the method mentioned in the Introduction. As the variability range of the variables x, y, and z was divided into 400 sub-intervals, the calculation error did not exceed several tenths of percent.

The approximation of $w(\delta)$ in Eq. (16) for $1/\sqrt{5} \le |\delta| \le 1$ with the use of Eq. (17) is

$$w_{\mathrm{ap}}(\delta) = \begin{cases} f_1(\delta), & 0.447214 \le |\delta| \le 0.460410, \\ f_2(\delta), & 0.460410 \le |\delta| \le 0.486803, \\ f_3(\delta), & 0.486803 \le |\delta| \le 0.5, \\ f_4(\delta), & 0.5 \le |\delta| \le 1, \end{cases} \tag{18}$$

$$10^{-9} f_1(\delta) = 0.0572191769026292185 - 0.628380667200095199\,|\delta| + 2.760318048547410 36\,\delta^2 - 6.06262165127714869\,|\delta|^3 + 6.6577390572264905\,\delta^4 - 2.92447532902603946\,|\delta|^5,$$

$$10^{-9} f_2(\delta) = 0.00811885729601806716 - 0.119650507837565367\,|\delta| + 0.755840193510700864\,\delta^2 - 2.65304108695197449\,|\delta|^3 + 5.58829300287731012\,\delta^4 - 7.06374094050267409\,|\delta|^5 + 4.961197118953355 02\,\delta^6 - 1.49358449218467121\,|\delta|^7,$$

$$f_3(\delta) = 16072.6946208560477 - 72799.257818450842\,|\delta| + 86783.541543784536 96\,\delta^2 - 233.853195736137298/(1 - 1.76683750229503599\,|\delta|) + 51.4883116122848782/(1 - 1.87620251865767855\,|\delta|) - 8.19828229331884 0017/(1 - 1.91572960193305181\,|\delta|),$$

$$10^{-6} f_4(\delta) = 0.00108604508377038611 - 0.0158115037861306202\,|\delta| + 0.104590683732212963\,\delta^2 - 0.414388692997690455\,|\delta|^3 + 1.09193292695932097\,\delta^4 - 2.00851644379019989\,|\delta|^5 + 2.6308951188267744\,\delta^6 - 2.45356710277850886\,|\delta|^7 + 1.59634164811143053\,\delta^8 - 0.690011705239826156\,|\delta|^9 + 0.178321640536417991\,\delta^{10} - 0.0208726146576362703\,|\delta|^{11}.$$

The error of approximation (18) is $2{\cdot}10^{-6}$.

For some applications, it may be more convenient to use the following simplified approximation of $w(\delta)$ given by Eq. (16), whose maximum error is ~0.1%:

$$w_{\text{ap}}(\delta)=\begin{cases} 0.94145838065, & |\delta|\le 1/\sqrt{5}, \\ 8.69412\left(0.47453-|\delta|\right)\left(1+\left|\dfrac{|\delta|-0.47453}{0.02932}\right|^{7.90928}\right)+0.56797, & 1/\sqrt{5}<|\delta|\le 1/2, \\ 0.50303\left||\delta|-1\right|^{0.89053}\exp\left[-\left|\dfrac{|\delta|-0.5}{0.49192}\right|^{0.77553}\right], & 1/2<|\delta|\le 1. \end{cases} \quad (19)$$

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