THE POTENTIAL OF THE AVERAGE FORCE BETWEEN TWO IONS IN AN IDEAL DIPOLAR GAS

By F. Grądzki

Department of Physics, Warsaw University, Białystok Branch*

(*Received January 18, 1980*)

The potential of mean force is obtained for two charged hard spheres immersed in an ideal dipolar gas. The ions and solvent particles have the same hard sphere diameters and the ions have equal charges of opposite signs. It is found that the longest-range part of the potential of the mean force obtained from molecular theory is the same as the interaction energy obtained from macroscopic electrostatics when the polar fluid is treated as a dielectric continuum.

1. *Introduction*

The properties of ionic solutions and partially ionized plasma are average values from the configurations of the neutral (solvent) molecules and the ions. The most important quantity is the average potential acting between two ions held at fixed positions while all the other particles are free to move under the influence of thermal agitation. If the average force of attraction between two ions α and β is written as $\partial\psi_{\alpha\beta}(r_{12})/\partial r_{12}$, this then defines the potential of mean force between the ions. Such a potential is arbitrary to the extent of an additive constant. The system is defined by three pair potentials, $\varphi_{\rm II}$, $\varphi_{\rm ID}$, and $\varphi_{\rm DD}$ which are the ion-ion, ion-solvent, and solvent-solvent interactions, respectively. These are:

$$\varphi_{\rm II}(ij) = \varphi_{\rm HS}(ij)+\frac{q_iq_j}{r_{ij}}, \tag{1}$$

$$\varphi_{\rm ID}(ik) = \varphi_{\rm HS}(ik)+\left(\frac{q_i\mu}{r_{ik}^2}\right)(\hat{r}_{ik}\cdot\hat{\mu}_k), \tag{2}$$

$$\varphi_{\rm DD}(kl) = \varphi_{\rm HS}(kl)-\left(\frac{\mu^2}{r_{kl}^3}\right)[3(\hat{\mu}_k\cdot\hat{r}_{kl})(\hat{\mu}_l\cdot\hat{r}_{kl})-(\hat{\mu}_k\cdot\hat{\mu}_l)], \tag{3}$$

---

* Address: Zakład Fizyki, Filia UW Białystok, Lipowa 41, 15-424 Białystok, Poland.

where $\hat{\mu}_k$ and $\hat{\mu}_l$ are unit vectors associated with the dipoles $\boldsymbol{\mu}_k$ and $\boldsymbol{\mu}_l$. $\hat{r}_{kl}$ is directed along the intermolecular vector $\boldsymbol{r}_{kl}$, and $\hat{r}_{ik}$ is in the direction of $\boldsymbol{r}_{ik}$, a vector directed from the ion to the solvent particle.

In this paper the potential of the average force is defined by [1]

$$\exp\left[-\beta\psi_{\alpha\beta}(r_{12})\right] = \frac{\int dr^{N_D} d\Omega^{N_D} \exp\left(-\beta\phi_N\right)}{\int dr^{N_D} d\Omega^{N_D} \exp\left(-\beta\phi_D\right)}, \tag{4}$$

where $\beta = 1/kT$ and the potential energy ϕ_N is given by

$$\phi_N = \varphi_{II}(12) + \sum_{i=1}^{2}\sum_{k=1}^{N_D} \varphi_{ID}(ik) + \phi_D, \tag{5}$$

$$\phi_D = \sum_{k<l}^{N_D} \varphi_{DD}(kl). \tag{6}$$

Here we will consider the potential of the mean force for two charged hard spheres immersed in an ideal dipolar gas made of permanent dipoles.

2. *A single pair of ions in an ideal dipolar gas*

Suppose that two ions α and β, immersed in a solvent, are at a distance r_{12} from one another. For an ideal dipolar gas $\phi_D = 0$ and the integration in Eq. (4) over the $d\Omega^{N_D}$ and dr^{N_D} may be made (see Appendix A for details) and leads to

$$\exp\left[-\beta\psi_{\alpha\beta}(r_{12})\right] = \frac{\exp\left[-\beta\varphi_{II}(12)\right]\left[Q_{ID}(r_{12})\right]^{N_D}}{(4\pi V)^{N_D}}, \tag{7}$$

where V is the volume of the sample. The first term in $Q_{ID}(r_{12})$ is equal to

$$\frac{(4\pi)^2}{r_{12}}\frac{1}{2!}\int r_{13}dr_{13}\int r_{23}dr_{23}\exp\left\{-\beta\left[\varphi_{HS}(13)+\varphi_{HS}(23)\right]\right\} = 4\pi(V-\mathscr{V}_e), \tag{8}$$

where

$$\mathscr{V}_e(r_{12}) = \begin{cases} 4\pi\sigma^3/3 + \pi\sigma^2 r_{12} - \pi r_{12}^3/12 \\ 2\cdot 4\pi\sigma^3/3 \end{cases} \tag{9}$$

is the excluded volume for a dipole when two ions α and β are at a distance r_{12} from one another. So we can write the $Q_{ID}(r_{12})$ in the form of

$$Q_{ID}(r_{12}) = 4\pi\left[V - f(r_{12})\right], \tag{10}$$

$$f(r_{12}) = \sum_{l=0}^{\infty} f_l(r_{12}), \tag{11}$$

where $f_0(r_{12}) = \mathscr{V}_e(r_{12})$, $f_1, f_2, \ldots$ are the terms with $l = 1, 2, \ldots$ in Q_{ID} divided by -4π. Then,

$$\exp\left[-\beta\psi_{\alpha\beta}(r_{12})\right] = \exp\left[-\beta\varphi_{II}(12)\right]\left[1 - \frac{f(r_{12})}{V}\right]^{N_D}. \tag{12}$$

As $N_D \to \infty$, $V \to \infty$ and $N_D/V = \varrho_D = \text{const}$ we obtain

$$\exp[-\beta\psi_{\alpha\beta}(r_{12})] = \exp[-\beta\varphi_{II}(r_{12})]\exp[-\varrho_D f(r_{12})], \tag{13}$$

or

$$\beta\psi_{\alpha\beta}(r_{12}) = \beta\varphi_{II}(r_{12}) + \varrho_D f(r_{12}). \tag{14}$$

The contributions of $f_1(r_{12})$ and $f_2(r_{12})$ are equal

$$f_1(r_{12}) = -\frac{4\pi}{r_{12}}\frac{2}{4!}(\beta\mu)^2[(q_\alpha^2+q_\beta^2)I_{40}+q_\alpha q_\beta(2I_{31}-r_{12}^2 I_{33})], \tag{15}$$

$$f_2(r_{12}) = -\frac{4\pi}{r_{12}}\frac{3}{6!}(\beta\mu)^4[(q_\alpha^4+q_\beta^4)I_{80}+q_\alpha^2 q_\beta^2(2I_{62}+4I_{44}-4r_{12}^2 I_{64}+r_{12}^4 I_{66}) + 2(q_\alpha^3 q_\beta + q_\alpha q_\beta^3)(I_{71}+I_{53}-r_{12}^2 I_{73})], \tag{16}$$

where

$$I_{mn} = \int r_{13}dr_{13}\int r_{23}dr_{23}\exp\{-\beta[\varphi_{HS}(13)+\varphi_{HS}(23)]\}r_{13}^{-m}r_{23}^{-n}. \tag{17}$$

As $r_{12} \to \infty$ the $I_{40}/r_{12} \to 2/\sigma$ and the $I_{30}/r_{12} \to 2/5\sigma^5$. So these terms and $\mathscr{V}_e$ contribute to the constant in $\psi_{\alpha\beta}$ as $r_{12} \to \infty$. If we want $\beta\psi_{\alpha\beta}(r_{12}) \to 0$ as $r_{12} \to \infty$ we must subtract the constant. After subtraction of the constant term, one may show that as $r_{12} \to \infty$, the most dominant term will be proportional to r_{12}^{-1}. That term in this model interaction exists only for $f_1(r_{12})$, that is, for $r_{12} \geqslant 2\sigma$

$$2I_{31} - r_{12}^2 I_{33} = 4, \tag{18}$$

and the term with $q_\alpha q_\beta$ is proportional to r_{12}^{-1}. But for $\sigma \leqslant r_{12} \leqslant 2\sigma$

$$2I_{31} - r_{12}^2 I_{33} = \frac{r_{12}}{\sigma}\left(4 - \frac{r_{12}}{\sigma}\right). \tag{19}$$

We have no terms proportional to r_{12}^{-1}. The integral I_{40} is equal to

$$I_{40} = \begin{cases} \dfrac{r_{12}}{\sigma}\dfrac{(r_{12}+2\sigma)(r_{12}+3\sigma)}{4\sigma(r_{12}+\sigma)} + \frac{1}{2}\ln\dfrac{r_{12}+\sigma}{\sigma} & \text{for} \quad \sigma \leqslant r_{12} \leqslant 2\sigma \\ \dfrac{r_{12}}{\sigma}\left(2 - \dfrac{\sigma^2}{r_{12}^2-\sigma^2}\right) + \frac{1}{2}\ln\dfrac{r_{12}+\sigma}{r_{12}-\sigma} & \text{for} \quad r_{12} \geqslant 2\sigma \end{cases} \tag{20}$$

and gives the contribution to the "cavity term". This is because the ion β shields ion α for dipoles and the ion α shields ion β for dipoles.

3. *Discussion*

The results reported concern ions having the same hard sphere diameter, σ, as the solvent particles. The system can then be characterized by a reduced density $\varrho_D^* = N_D\sigma^3/V$, a reduced solvent dipole moment μ^* defined by $\mu^{*2} = \beta\mu^2/\sigma^3$, and a reduced ionic charge

q^* defined by $q^{*2} = \beta q^2/\sigma$, where μ and q are the corresponding dipole moments and charges. The numerical calculations were done for small ϱ_D^*, $\mu^* = 1.0$, and $q^{*2} = 188.0$. For this, μ^*, q^{*2} and $\varrho_D^* = 0.8$ were carried out using Monte Carlo calculations [2] to obtain the interionic potential of mean force. The potential observed of the average force is quite unlike that of the primitive model for small separations. This paper concerns investigation on the nature of the solvent-averaged electrostatic pair interaction in an ideal dipolar solvent for short and long separations between ions.

In $f(r_{12})$ only $f_1(r_{12})$ contains the term with r_{12}^{-1} (for $r_{12} \geqslant 2\sigma$) and this corresponds to $(1-\varepsilon^{-1})$, where ε is given by the Debye formula

$$\frac{\varepsilon-1}{\varepsilon+2} = \frac{4\pi}{9}\,\varrho_D^*\mu^{*2}. \tag{21}$$

In Fig. 1 are compared the $\Delta\beta\psi_{\alpha\beta}(r_{12}) \equiv \beta\psi_{\alpha\beta}(r_{12}) - \beta\psi_{\alpha\beta}^{\mathrm{PM}}(r_{12})$ obtained from Eq. (14) for $\varrho_D^* = 0.01$ up to term $f_1(r_{12})$ and the same quantity obtained by Patey and Valleau

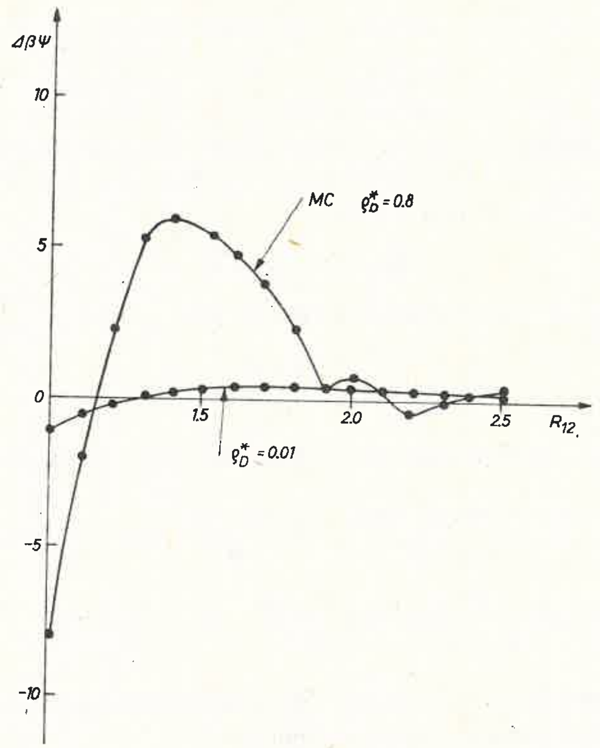

Fig. 1. $\Delta\beta\psi_{\alpha\beta}(r_{12}) \equiv \beta\psi_{\alpha\beta}(r_{12}) - \beta\psi_{\alpha\beta}^{\mathrm{PM}}(r_{12})$ obtained from Eq. (14) for $\varrho_D^* = 0.01$ up to the term $f_1(r_{12})$ and obtained by the Monte Carlo method [2] for $\varrho_D^* = 0.8$

[2] for $\varrho_D^* = 0.8$. The qualitative behaviour is similar because we have a negative value of $\Delta\beta\psi_{\alpha\beta}$ for small values of r_{12} and a positive value of $\Delta\beta\psi_{\alpha\beta}$ for larger values of r_{12}. We may not obtain $\Delta\beta\psi_{\alpha\beta}$ for $\varrho_D^* = 0.8$ because our model is very crude. For $r_{12} > 2\sigma$

the departure from the primitive model is influenced by the "cavity term" in $f_1(r_{12})$, which for large values of r_{12} and small densities is consistent with Jepsen and Friedman [3] and Stell [4] and is proportional to r_{12}^{-4}.

For large r_{12} the term with $q_\alpha^2 q_\beta^2$ is of the order of r_{12}^{-4}, the term $(q_\alpha^3 q_\beta + q_\alpha q_\beta^3)$ is of the order of r_{12}^{-5}, and they are consistent with the results obtained previously by Stecki [5].

Bellemans and Stecki [6] outlined a general formalism appropriate to the problem of the free energy of charging the set of ions. For a system containing two ions α and β the free energy of charging $W_{ch}(\mathbf{r}_\alpha, \mathbf{r}_\beta, q_\alpha, q_\beta)$ is equal to the potential of average force between the two ions α and β, which is given by Eq. (14). One may decompose $W_{ch}(\mathbf{r}_\alpha, \mathbf{r}_\beta, q_\alpha, q_\beta)$ into three terms [6]

$$W_{ch}(\mathbf{r}_\alpha, \mathbf{r}_\beta, q_\alpha, q_\beta) = w_1^{(\alpha)} + w_1^{(\beta)} + w_2^{(\alpha\beta)}(\mathbf{r}_\alpha, \mathbf{r}_\beta), \tag{22}$$

where $w_1^{(\alpha)}$ and $w_1^{(\beta)}$ is the solvation free energy of ion α and ion β, respectively, and $w_2^{(\alpha\beta)}$ is the potential of the average force between ions α and β so that $w_2^{(\alpha\beta)}(r_{12}) \to 0$ as $r_{12} \to \infty$.

Nienhuis and Deutch [7] also considered the potential of the mean force and found that the longest-range part of the potential of the mean force obtained from a molecular theory is the same as the interaction energy obtained from macroscopic electrostatics when the polar fluid is treated as a dielectric continuum.

In this paper the potential of the average force between two ions in an ideal dipolar gas is considered in a canonical ensemble. One may treat the same problem in a grand canonical ensemble. Then the potential of average force will be a function of distance r_{12}, temperature T and fugacity z. Expressing the fugacity z by density ϱ one may obtain the same result as in Eq. (14).

The author thanks Professor J. Stecki for suggesting the problem and for many helpful discussions and also Doc. dr hab. J. S. Brzosko for his interest in this work.

APPENDIX A

The integral to be calculated is

$$Q = \int \exp(-\beta\phi_N) d\mathbf{r}^{N_D} d\Omega^{N_D}, \tag{A1}$$

where

$$\phi_N = \varphi_{II}(12) + \sum_{i=1}^{2} \sum_{k=1}^{N_D} \varphi_{ID}(ik). \tag{A2}$$

Then Q can be written in the form

$$Q = \exp[-\beta\varphi_{II}(12)] \{\int \exp[-\beta \sum_{i=1}^{2} \varphi_{ID}(i3)] d\mathbf{r}_3 d\Omega_3\}^{N_D}. \tag{A3}$$

Now we consider the integral

$$Q_{ID} = \int \exp[-\beta \sum_{i=1}^{2} \varphi_{ID}(i3)] d\mathbf{r}_3 d\Omega_3. \tag{A4}$$

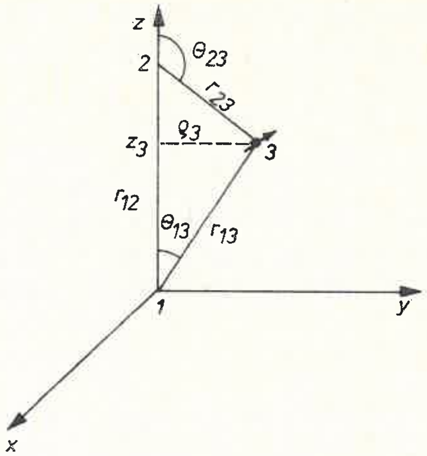

Fig. 2. The coordinate system to calculate Q_{ID}

To calculate Q_{ID} we introduce the coordinate system as in Fig. 2. Then the Q_{ID} is equal to

$$Q_{\mathrm{ID}} = \int \exp\{-\beta[\varphi_{\mathrm{HS}}(13)+\varphi_{\mathrm{HS}}(23)]\} \exp\left\{-\beta\mu\left[\hat{\mu}_3\cdot\left(\frac{q_1}{r_{13}^2}\hat{r}_{13} + \frac{q_2}{r_{23}^2}\hat{r}_{23}\right)\right]\right\} dr_3 d\Omega_3 = \int \exp\{-\beta[\varphi_{\mathrm{HS}}(13)+\varphi_{\mathrm{HS}}(23)]\} dr_3$$
$$\times \exp\left\{-\beta\mu\left[\left(\frac{q_1}{r_{13}^2}\cos\theta_{13}+\frac{q_2}{r_{23}}\cos\theta_{23}\right)\cos\theta_3+\left(\frac{q_1}{r_{13}^2}\sin\theta_{13} + \frac{q_2}{r_{23}^2}\sin\theta_{23}\right)\sin\theta_3\cos(\phi_3-\phi_{13})\right]\right\}\sin\theta_3 d\theta_3 d\phi_3. \quad \text{(A5)}$$

Because

$$\int_0^{2\pi} e^{\pm\gamma\cos(\phi_3-\phi_{13})} d\phi_3 = 2\pi \mathrm{I}_0(\gamma) = 2\pi \sum_{k=0}^{\infty}\left[\frac{1}{k!}\left(\frac{\gamma}{2}\right)^k\right]^2, \quad \text{(A6)}$$

thus we obtain

$$Q_{\mathrm{ID}} = 2\pi \int dr_3 \exp\{-\beta[\varphi_{\mathrm{HS}}(13)+\varphi_{\mathrm{HS}}(23)]\}\sin\theta_3 d\theta_3$$
$$\times\exp\left\{-\beta\mu\left[\left(\frac{q_1}{r_{13}^2}\cos\theta_{13}+\frac{q_2}{r_{23}^2}\cos\theta_{23}\right)\cos\theta_3\right]\right\}$$
$$\times\sum_{k=0}^{\infty}\frac{1}{(k!)^2}\left(\frac{\beta\mu}{2}\right)^{2k}\sin^{2k}\theta_3\left(\frac{q_1}{r_{13}^2}\sin\theta_{13}+\frac{q_1}{r_{23}^2}\sin\theta_{23}\right)^{2k}. \quad \text{(A7)}$$

Since

$$\int_0^\pi \sin\theta_3 d\theta_3 \sin^{2k}\theta_3 e^{-\delta\cos\theta_3} = \sum_{m=0}^{\infty} (-\delta)^{2m} 2^{2k+2} \frac{k!}{m!} \frac{(k+m+1)!}{(2k+2m+2)!} \tag{A8}$$

with

$$\delta = \beta\mu\left(\frac{q_1}{r_{13}^2}\cos\theta_{13} + \frac{q_2}{r_{23}^2}\cos\theta_{23}\right), \tag{A9}$$

we have

$$Q_{\mathrm{ID}} = 8\pi \sum_{k=0}^{\infty}\sum_{m=0}^{\infty} \frac{(k+m+1)!}{k!m!(2k+2m+2)!}(\beta\mu)^{2k+2m}$$

$$\times \int dr_3 \left(\frac{q_1}{r_{13}^2}\cos\theta_{13} + \frac{q_2}{r_{23}^2}\cos\theta_{23}\right)^{2m}\left(\frac{q_1}{r_{13}^2}\sin\theta_{13}\right.$$

$$\left. + \frac{q_2}{r_{23}^2}\sin\theta_{23}\right)^{2k} \exp\{-\beta[\varphi_{\mathrm{HS}}(13)+\varphi_{\mathrm{HS}}(23)]\}. \tag{A10}$$

If we introduce the cylindrical coordinate system then Q_{ID} is given by

$$Q_{\mathrm{ID}} = 8\pi \sum_{k=0}^{\infty}\sum_{m=0}^{\infty} \frac{(k+m+1)!}{k!m!(2k+2m+2)!}(\beta\mu)^{2k+2m}\int d\phi_3 \int dz_3 \int \varrho_3 d\varrho_3.$$

$$\times \left\{\frac{q_1 z_3}{(\varrho_3^2+z_3^2)^{3/2}} + \frac{q_2(z_3-r_{12})}{[\varrho_3^2+(z_3-r_{12})^2]^{3/2}}\right\}^{2m}\left\{\frac{q_1\varrho_3}{(\varrho_3^2+z_3^2)^{3/2}}\right.$$

$$\left. + \frac{q_2\varrho_3}{[\varrho_3^2+(z_3-r_{12})^2]^{3/2}}\right\}^{2k} \exp\{-\beta[\varphi_{\mathrm{HS}}(13)+\varphi_{\mathrm{HS}}(23)]\}. \tag{A11}$$

The variables z_3 and ϱ_3 can be written in bipolar coordinates

$$z_3 = \frac{r_{12}^2+r_{13}^2-r_{23}^2}{2r_{12}},$$

$$\varrho_3 = (r_{13}^2-z_3^2) = \left[r_{13}^2 - \left(\frac{r_{12}^2+r_{13}^2-r_{23}^2}{2r_{12}}\right)^2\right]^{1/2}, \tag{A12}$$

and then,

$$Q_{\mathrm{ID}} = \frac{8\pi}{r_{12}} \sum_{k=0}^{\infty}\sum_{m=0}^{\infty} \frac{(k+m+1)!}{k!m!(2k+2m+2)!}(\beta\mu)^{2k+2m}\int d\phi_{13}\int r_{13}dr_{13}$$

$$\times \int r_{23} dr_{23} \left(\frac{q_1}{r_{13}^3} \frac{r_{12}^2 + r_{13}^2 - r_{23}^2}{2r_{12}} + \frac{q_2}{r_{23}^3} \frac{r_{13}^2 - r_{12}^2 - r_{23}^2}{2r_{12}} \right)^{2m}$$

$$\times \left\{ \left(\frac{q_1}{r_{13}^3} + \frac{q_2}{r_{23}^3} \right)^2 \left[r_{13}^2 - \left(\frac{r_{12}^2 + r_{13}^2 - r_{23}^2}{2r_{12}} \right)^2 \right] \right\}^k \exp\{-\beta[\varphi_{\mathrm{HS}}(13) + \varphi_{\mathrm{HS}}(23)]\}. \tag{A13}$$

Integrating over $d\phi_{13}$ and substituting $l = k+m$ we obtain

$$Q_{\mathrm{ID}} = \frac{16\pi^2}{r_{12}} \sum_{k=0}^{\infty} \sum_{l=k}^{\infty} \frac{(l+1)!}{k!(l-k)!(2l+2)!} (\beta\mu)^{2l} \int r_{13} dr_{13} \int r_{23} dr_{23}$$

$$\times \left(\frac{q_1}{r_{13}^3} \frac{r_{12}^2 + r_{13}^2 - r_{23}^2}{2r_{12}} + \frac{q_2}{r_{23}^3} \frac{r_{13}^2 - r_{12}^2 - r_{23}^2}{2r_{12}} \right)^{2(l-k)} \left\{ \left(\frac{q_1}{r_{13}^3} + \frac{q_2}{r_{23}^3} \right)^2 \right.$$

$$\left. \times \left[r_{13}^2 - \left(\frac{r_{12}^2 + r_{13}^2 - r_{23}^2}{2r_{12}} \right)^2 \right] \right\}^k \exp\{-\beta[\varphi_{\mathrm{HS}}(13) + \varphi_{\mathrm{HS}}(23)]\}. \tag{A14}$$

Because

$$\sum_{k=0}^{\infty} \sum_{l=k}^{\infty} (\ldots) = \sum_{l=0}^{\infty} \sum_{k=0}^{l} (\ldots), \tag{A15}$$

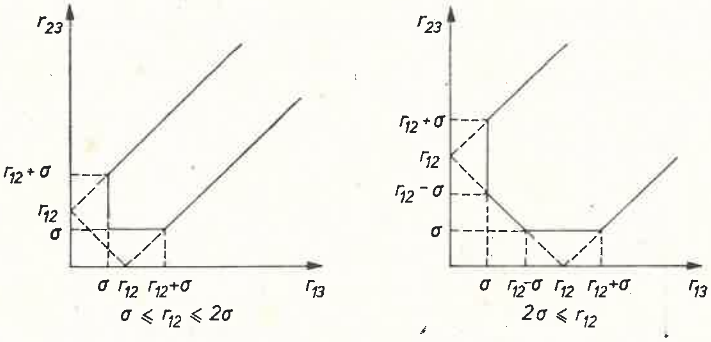

Fig. 3. The regions of integration of Eq. (A17)

the Q_{ID} can be written as

$$Q_{\mathrm{ID}} = \frac{(4\pi)^2}{r_{12}} \sum_{l=0}^{\infty} \frac{(l+1)!}{(2l+2)!} (\beta\mu)^{2l} \int r_{13} dr_{13} \int r_{23} dr_{23} \exp\{-\beta[\varphi_{\mathrm{HS}}(13)$$

$$+ \varphi_{\mathrm{HS}}(23)]\} \sum_{k=0}^{l} \left\{ \left[r_{13}^2 - \left(\frac{r_{12}^2 + r_{13}^2 - r_{23}^2}{2r_{12}} \right)^2 \right] \left(\frac{q_1}{r_{13}^3} + \frac{q_2}{r_{23}^3} \right)^2 \right\}^k$$

$$\times \left(\frac{q_1}{r_{13}^3} \frac{r_{12}^2 + r_{13}^2 - r_{23}^2}{2r_{12}} + \frac{q_2}{r_{23}^3} \frac{r_{13}^2 - r_{12}^2 - r_{23}^2}{2r_{12}} \right)^{2(l-k)}. \tag{A16}$$

Summing over k we obtain

$$Q_{\mathrm{ID}} = \frac{(4\pi)^2}{2r_{12}} \sum_{l=0}^{\infty} \frac{(\beta\mu)^{2l}}{(2l+1)!} \int r_{13} dr_{13} \int r_{23} dr_{23} \exp\{-\beta[\varphi_{\mathrm{HS}}(13)$$

$$+\varphi_{\mathrm{HS}}(23)]\} \left[\frac{q_1^2}{r_{13}^4} + \frac{q_2^2}{r_{23}^4} + \frac{q_1 q_2}{r_{13}^3 r_{23}^3}(r_{13}^2 + r_{23}^2 - r_{12}^2)\right]^l, \qquad \text{(A17)}$$

where the regions of integration are shown in Fig. 3.

REFERENCES

[1] J. Stecki, *Adv. Chem. Phys.* **6**, 413 (1962).
[2] G. N. Patey, J. P. Valleau, *J. Chem. Phys.* **63**, 2334 (1975).
[3] D. W. Jepsen, H. L. Friedman, *J. Chem. Phys.* **38**, 846 (1963).
[4] G. Stell, *J. Chem. Phys.* **59**, 3926 (1973).
[5] J. Stecki, *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **9**, 663 (1961).
[6] A. Bellemans, J. Stecki, *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **9**, 339 (1961).
[7] G. Nienhuis, J. M. Deutch, *J. Chem. Phys.* **56**, 1819 (1972).