Reply to "Comment on 'Algebraic perturbation theory for polar fluids: A model for the dielectric constant' "

V. I. Kalikmanov
Department of Applied Physics, Computational Physics Section, University of Delft, Lorentzweg 1, 2628 CJ Delft, The Netherlands
(Received 14 June 2000)

In their Comment [Phys. Rev. E **62**, 8842 (2000)] Szalai *et al.* use the "Fourier-transform-convolution method" to correct the two three-body integrals entering our algebraic perturbation theory for polar fluids [Phys. Rev. E **59**, 5085 (1999)]. We present an alternative analytical calculation of these integrals that is more transparent than that of Szalai *et al.* Compared with the original expression for the dielectric constant [Phys. Rev. E **59**, 5085 (1999)] the corrected one demonstrates a better agreement with the simulation data for low and moderate values of the coupling constant.

PACS number(s): 61.20.Gy, 77.22.Ch, 75.50.Mm

The Comment by Szalai *et al.* [1] corrects calculations of the two three-body integrals in Eq. (20) of Ref. [2] using the "Fourier-transform-convolution method" of Høye and Stell [3]. In this paper, I want to show that the same results can be obtained in a more transparent way.

The $b_2^{(2)}$ in Eq. (20) of Ref. [2] can be expressed as $b_2^{(2)} = b_D + b_\Delta$ with

$$b_D = \frac{1}{6}\rho(\beta s^2)^2\left(\frac{4\pi}{3}\right)^2\gamma_D, \tag{1}$$

$$\gamma_D = \int d\mathbf{r}_{12}(1-3\cos^2\Theta_{12})a_D,$$

$$a_D = \int d\mathbf{r}_3 \frac{1+3\cos\alpha_1\cos\alpha_2\cos\alpha_3}{(r_{13}r_{23})^3} g_d(123), \tag{2}$$

and

$$b_\Delta = \frac{1}{3}\rho(\beta s^2)^2\left(\frac{4\pi}{3}\right)^2\gamma_\Delta, \tag{3}$$

$$\gamma_\Delta = \int d\mathbf{r}_{12} a_\Delta, \quad a_\Delta = \int d\mathbf{r}_3 \frac{3\cos^2\alpha_3 - 1}{(r_{13}r_{23})^3} g_d(123). \tag{4}$$

$g_d(123)$ is the three-body correlation function of hard spheres and α_1, α_2, α_3 are the angles of the triangle formed by the three particles.

The detailed derivation of γ_D and γ_Δ, presented in the Appendix, is more transparent than the "Fourier-transform-convolution method" used in [1]. It yields

$$\gamma_D = -\frac{32\pi^2}{9}, \quad \gamma_\Delta = \frac{17\pi^2}{9} \tag{5}$$

in agreement with the results of [1]. Thus, in the low-density limit

$$b_2^{(2)} = \frac{1}{3}\left(\frac{4\pi}{3}\right)^2\rho(\beta s^2)^2\left(\frac{1}{9}\pi^2\right), \tag{6}$$

implying that the coefficient 5/3 in the free energy expansion (25) of Ref. [2] should be replaced by 1/9:

$$\beta\mathcal{F} = \beta\mathcal{F}_0 - N\frac{\alpha^2}{6} - \frac{\alpha^2}{54}\rho^2 V d^3\left(4\pi\lambda + \frac{1}{9}\pi^2\rho d^3\lambda^2\right), \tag{7}$$

imposing the corresponding correction of the third-order term in Eq. (26) of Ref. [2] for the dielectric constant:

$$\epsilon - 1 = 3y\left[1 + y + \frac{1}{16}y^2\right]. \tag{8}$$

Compared with the original expression the corrected one demonstrates a better agreement with the simulation data for both low and moderate values of the coupling constant $\lambda < 2.5$ as follows from Fig. 1 of Ref. [1].

APPENDIX

In this appendix we present an alternative calculation of the three-body integrals γ_D and γ_Δ given by Eqs. (2) and (4). Since both of them are dimensionless we scale all distances with the hard-sphere diameter d. Placing the origin of the coordinate system in the center of particle 1 we replace $d\mathbf{r}_3$ by $d\mathbf{r}_{13}$:

$$\gamma_D = \int d\mathbf{r}_{12}(1-3\cos^2\Theta_{12})a_D, \tag{A1}$$

$$a_D = \int d\mathbf{r}_{13} \frac{1+3\cos\alpha_1\cos\alpha_2\cos\alpha_3}{(r_{13}r_{23})^3}\prod_{i<j}\Theta(r_{ij}-1), \tag{A2}$$

$$\gamma_\Delta = \int d\mathbf{r}_{12} a_\Delta, \tag{A3}$$

$$a_\Delta = \int d\mathbf{r}_{13} \frac{3\cos^2\alpha_3 - 1}{(r_{13}r_{23})^3}\prod_{i<j}\Theta(r_{ij}-1), \tag{A4}$$

where $\Theta(x)$ is the Heaviside step function. It is important to note that if a dependence on particle separation is short range, it is possible to replace integration over a cylinder

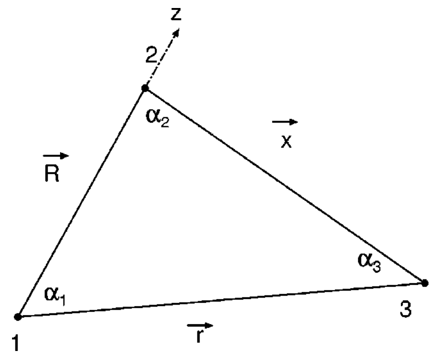

FIG. 1. Three-particle configuration.

(which is an assumed form of the container) by integration over a sphere. To simplify notations we set

$$\mathbf{r}_{12}=\mathbf{R},\quad \mathbf{r}_{13}=\mathbf{r},\quad \mathbf{r}_{23}=\mathbf{x},\quad \cos\alpha_1=\mu$$

and choose the z axis along $\mathbf{r}_{12}$ (see Fig. 1). Then $d\mathbf{r}_{13}=d\mathbf{r}=-2\pi r^2 dr d\mu$ and the elements of the 123-triangle are expressed in terms of R, r, and μ:

$$x=\sqrt{R^2+r^2-2rR\mu},\tag{A5}$$

$$\cos\alpha_2=\frac{R-r\mu}{x},\tag{A6}$$

$$\cos\alpha_3=\frac{r-R\mu}{x}.\tag{A7}$$

We start with the function a_D, which, after substitution of Eqs. (A5)–(A7), reads

$$a_D=2\pi\int dr\frac{1}{r}\int_{-1}d\mu f_D(r,R,\mu)\Theta(R-1)\times\Theta(r-1)\Theta\big(x(r,R,\mu)-1\big)$$

with

$$f_D=\frac{1}{x^5}[(r^2+R^2)(1-3\mu^2)+\mu rR(1+3\mu^2)].$$

The condition $x>1$ can be presented using Eq. (A5) as

$$\mu<h\equiv\frac{r^2+R^2-1}{2rR}.\tag{A8}$$

Since both r and R are larger than unity, h is always positive. Recall that by definition the values of μ are limited by $-1<\mu<1$. Two cases are possible: (1) $h>1$ implying that integration over μ is from -1 to 1, and (2) $h<1$ implying that integration over μ is from -1 to h.

Performing the standard algebraic integration it is easy to verify that $\int_{-1}^{1}d\mu f_D=0$ implying that the first case gives zero contribution to γ_D. Thus, $h<1$, or equivalently; $|r-R|<1$. For a fixed R it determines the domains of variation of r:

$$R-1<r<R+1,\quad \text{if}\ \ R>2,$$

$$1<r<R+1,\quad \text{if}\ \ 1<R<2.$$

So,

$$\gamma_D=\int_{1<R<2}d\mathbf{R}a_D(R)(1-3\cos^2\theta_R)+\int_{R>2}d\mathbf{R}a_D(R)(1-3\cos^2\theta_R).\tag{A9}$$

Integration in the first term is over a finite domain, and therefore can be performed in spherical coordinates yielding zero. Thus, the only nontrivial contribution comes from the second term in which

$$a_D(R)=2\pi\int_{R-1}^{R+1}dr\frac{1}{r}\int_{-1}^{h}d\mu f_D(r,R,\mu)=\frac{8\pi}{3}\frac{1}{R^3},\quad R>2.\tag{A10}$$

Substituting it into Eq. (A9) we get

$$\gamma_D=\frac{8\pi}{3}\int_{R>1}d\mathbf{R}\frac{1}{R^3}(1-3\cos^2\theta_R),$$

where the integration domain is extended to $R>1$ (the contribution of the interval $1<R<2$ is zero) yielding [cf. Eq. (21) of Ref. [2]]

$$\gamma_D=-\frac{32}{9}\pi^2.\tag{A11}$$

The function a_Δ in Eq. (A4) reads

$$a_\Delta=2\pi\int dr\frac{1}{r}\int_{-1}d\mu f_\Delta(r,R,\mu)\Theta(R-1)\Theta\times(r-1)\Theta\big(x(r,R,\mu)-1\big)$$

with

$$f_\Delta=\frac{1}{x^5}[2r^2-4rR\mu+R^2(3\mu^2-1)].$$

Again the condition $x>1$ can be expressed in the form (A8). We begin with dividing the R domain into $1<R<2$ and $R>2$.

Short-ranged part: $1<R<2$. As previously we proceed by discussing the two possibilities $h>1$ and $h<1$. The case $h>1$ corresponds to $r>R+1$. Integration over μ gives

$$\int_{-1}^{1}d\mu f_\Delta(r,R,\mu)=\frac{2}{r^3}\left(\frac{|r-R|}{r-R}+1\right),\tag{A12}$$

which for $r>R+1$ results in

$$\int_{-1}^{1}d\mu f_\Delta(r,R,\mu)=\frac{4}{r^3},\quad r>R+1.$$

Its contribution to a_Δ is

$$a_{\Delta,h>1}^{(1<R<2)}=8\pi\int_{R+1}^{\infty}dr\frac{1}{r^4}=\frac{8\pi}{3}\frac{1}{(R+1)^3}.\tag{A13}$$

The opposite case $h<1$ corresponds to $1<r<R+1$ and integration over μ gives

$$\int_{-1}^{h} d\mu f_\Delta(r,R,\mu) = \frac{1}{4r^3R}(-3+2r^2+r^4+8R-6R^2 -2r^2R^2+R^4). \tag{A14}$$

The contribution to a_Δ becomes

$$a_{\Delta,h<1}^{(1<R<2)} = 2\pi\int_1^{R+1} dr\,\frac{1}{r}\int_{-1}^{h} d\mu f_\Delta = 2\pi\frac{R}{12(1+R)^3}(36+12R-19R^2 -9R^3+3R^4+R^5). \tag{A15}$$

So,

$$a_\Delta^{(1<R<2)} = a_{\Delta,h>1}^{(1<R<2)} + a_{\Delta,h<1}^{(1<R<2)} = 2\pi\left(\frac{4}{3}-R+\frac{R^3}{12}\right)$$

and the corresponding contribution to γ_Δ reads

$$\gamma_\Delta^{(1<R<2)} = \frac{17}{9}\pi^2. \tag{A16}$$

Long-ranged part: $2<R<\infty$. We follow the same route studying first the case $h>1$, which now can be realized for r belonging to one of the two domains:

$$r>R+1 \quad \text{and/or} \quad 1<r<R-1.$$

According to Eq. (A12) integration over μ results in

$$\int_{-1}^{1} d\mu f_\Delta(r,R,\mu) = \begin{cases} \dfrac{4}{r^3} & \text{for } r>R+1 \\ 0 & \text{for } 1<r<R-1, \end{cases} \tag{A17}$$

yielding

$$a_{\Delta,h>1}^{(R>2)} = a_{\Delta,h>1}^{(1<R<2)} = \frac{8\pi}{3}\frac{1}{(R+1)^3}.$$

For $h<1$ we use Eq. (A14) to obtain

$$a_{\Delta,h<1}^{(R>2)} = 2\pi\int_{R-1}^{R+1} dr\,\frac{1}{r}\int_{-1}^{h} d\mu f_\Delta = -\frac{8\pi}{3}\frac{1}{(R+1)^3}.$$

Thus, the long-ranged quantities $a_{\Delta,h>1}^{(R>2)}$ and $a_{\Delta,h<1}^{(R>2)}$ cancel:

$$a_{\Delta,h>1}^{(R>2)} + a_{\Delta,h<1}^{(R>2)} = 0,$$

yielding the final result:

$$\gamma_\Delta = \frac{17}{9}\pi^2. \tag{A18}$$

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