

EXACT ASYMPTOTIC FORM OF THE SITE-SITE DIRECT  
CORRELATION FUNCTION FOR RIGID POLAR MOLECULES

Peter T. Cummings and G. Stell

Departments of Mechanical Engineering and Chemistry  
State University of New York  
Stony Brook, New York 11794

Abstract

It is found that the site-site direct correlation functions for rigid-diatomic molecules bearing two point charges  $q_a$  and  $q_b$  have the form  $c_{\alpha\gamma} = -\beta q_a q_b A r^{-1}$ ,  $r \rightarrow \infty$ ,  $\beta = (kT)^{-1}$ . The parameter  $A$  is expressed in terms of the dielectric constant.

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Under quite general conditions, for a wide variety of intermolecular pair potentials  $u(12)$  the molecular direct correlation function  $c(12)$  can be expected to have the large- $r$  form given by

$$c(12) = -\beta u(12) , \quad r_{12} \rightarrow \infty \quad (1)$$

where  $r_{12}$  is the distance between the molecular centers.' In this note we wish to point out that an analogous statement is not true in the case of the site-site or "atom-atom" direct correlation function  $c_{\alpha\gamma}(r)$  of rigid molecules. In particular, if the site-site potential  $u_{\alpha\gamma}(r)$  is assumed to be of Coulombic form for large  $r$ , 'so that

$$u_{\alpha\gamma}(r) = q_{\alpha}q_{\gamma}r^{-1} , \quad r \rightarrow \infty \quad (2)$$

where  $r$  is the distance between a pair of sites associated with charges  $q_{\alpha}$  and  $q_{\gamma}$ , respectively, each on a different molecule, then we do not find

$$c_{\alpha\gamma}(r) = -\beta q_{\alpha}q_{\gamma}r^{-1} , \quad r \rightarrow \infty . \quad (3)$$

Instead we find, for diatomic dipolar molecules bearing two point charges of equal magnitude and opposite sign, the result (valid off critical points),

$$c_{\alpha\gamma}(r) = -\beta q_{\alpha}q_{\gamma}Ar^{-1} , \quad r \rightarrow \infty \quad (4a)$$

where

$$A = \frac{1 + \epsilon(3\gamma-1)}{3\gamma(\epsilon-1)} , \quad \gamma = \frac{4\pi}{9} \rho\beta\mu^2 . \quad (4b)$$

Here  $\rho$  is the number density,  $\mu$  is the molecular dipole moment strength, and  $\beta$  is  $(kT)^{-1}$ , with  $k$  Boltzmann's constant and  $T$  absolute temperature. The  $\epsilon$  is the dielectric constant of the molecular fluid at density  $\rho$  and temperature  $T$ .

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If (3) is assumed, as it is in the approximation suggested by Andersen and Chandler<sup>2</sup> for their Interaction Site Model (ISM) as well as in a further large class of approximations discussed by Sullivan and Gray,<sup>3</sup> then  $A$  is approximated in (4a) by 1, which yields, immediately from (4b), the "ideal gas" result

$$\epsilon = 1 + 3y . \quad (5)$$

This result is already known to be the approximation that follows from (2) in the ISM; it was recently demonstrated and discussed in detail by Sullivan and Gray.<sup>3</sup>

Perhaps the most remarkable feature of (4a) is that (3) is not even approached for small  $y$ . Instead, because  $\epsilon \rightarrow 1 + 3y + 3y^2$  as  $y \rightarrow 0$ ,<sup>4</sup>

$$A \rightarrow 2/3 \quad \text{as} \quad y \rightarrow 0 \quad (6)$$

so that

$$c_{\alpha\gamma}(r) = -\frac{2}{3} \beta q_{\alpha} q_{\gamma} r^{-1}, \quad r \rightarrow \infty, \quad y \rightarrow 0. \quad (7)$$

When (4a) is assumed, Eq. (4b) is easily verified by a minor modification of the analysis given by Sullivan and Gray.<sup>3</sup> We need only note that in Section 3 of their paper the elimination of the low-k divergence in the Fourier transform of  $c_{\alpha\gamma}(r)$ , given by their Eq. (3.8), is still valid for the form for  $c_{\alpha\gamma}(r)$  given in (4a) above. Hence their analysis can be followed through to their Eq. (3.14). The analogous result for  $c_{\alpha\gamma}(r)$  given by (4a) is

$$\sum_{\alpha\gamma} q_{\alpha} h_{\alpha\gamma}^{(2)} q_{\gamma} = -4\pi\beta A M^2 / (1 + 4\pi\beta A \rho M) \quad (8)$$

where, as in Sullivan and Gray,<sup>3</sup>  $h_{\alpha\gamma}^{(2)}$  is the coefficient of the  $0(k^2)$  term in the expansion of the Fourier transform of  $ll_{\alpha\gamma}(r)$ , the site-site total correlation function, and  $M = \mu^2/3$ . Equation (8) may be rewritten as

$$\sum_{\alpha\gamma} q_{\alpha} h_{\alpha\gamma}^{(2)} q_{\gamma} = -\gamma \mu^2 A / [\rho(1 + 3yA)] . \quad (9)$$

Noting the Høye-Stell<sup>5</sup> expression for the dielectric constant in terms of the  $ll_{\alpha\gamma}$ , given by

$$\frac{\mu^2}{9\rho} \left[ \frac{\epsilon-1}{y\epsilon} - 3 \right] = \sum_{\alpha\gamma} q_{\alpha} h_{\alpha\gamma}^{(2)} q_{\gamma} \quad (10)$$

the result (4b) follows immediately. Details of our analysis, which will be given in a subsequent publication,<sup>6</sup> include the (nontrivial) demonstration that in the somewhat more general expression than (4a),

$$c_{\alpha\gamma}(r) = -\beta q_{\alpha} q_{\gamma} A_{\alpha\gamma} r^{-1}, \quad r \rightarrow \infty \quad (11)$$

the  $A_{\alpha\gamma}$  are independent of  $a$  and  $\gamma$ , yielding (4a). [From the remarks of this paragraph, (11) itself is immediate, once it is assumed that there are no terms<sup>7</sup> in the large- $r$  form of  $c_{\alpha\gamma}(r)$  that dominate the  $r^{-1}$  term, since if it did not hold, (10) would yield a manifestly incorrect expression for  $\epsilon$ .] An application of the results given in this note to a specific molecular model will appear shortly.<sup>8</sup>

#### Acknowledgments

Acknowledgment is made to the National Science Foundation, and to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Grateful acknowledgment of several valuable discussions with C. Gray and D. Sullivan, as well as the latter's critical suggestions on an earlier draft of this manuscript, is also made.

#### References

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5. Høye, J. S. and Stell, G., 1976, J. Chem, Phys. 65, 18.
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- 7, For the case of molecules **with** certain symmetries such terms indeed exist, as we shall demonstrate in [6], and for such molecules one has no guarantee **that** (3) even yields the correct power of  $r$ . For diatomic **molecules** under discussion here, there are no terms in the intermolecular or intramolecular potentials that can be expected to give rise to terms that dominate that shown in (11).
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