Critical Behavior of the Correlation Function of Fluids Composed of Polar Diatomic Molecules

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(Received February 17, 1986)

A critical behavior of fluids composed of polar diatomic molecules is studied by the use of the Ornstein-Zernike (OZ) theory of critical phenomena extended to the interaction site model. Firstly, the asymptotic forms of the atom-atom direct correlation functions $c_{\alpha\gamma}(r)$ for the polar fluids at large separation are obtained, which are valid off the critical point. Then, the OZ hypothesis that the asymptotic forms of $c_{\alpha\gamma}(r)$ do not change near and at the critical point is examined, and the critical behavior of the total correlation function is investigated. It is found to be completely analogous to the case of simple fluids. The relation between the OZ hypothesis and some integral equation theories is also discussed.

Properties of polar fluids are extensively explored on the basis of the interaction site model.[1–6] Recently, a phase diagram of the polar hard dumbbell fluid was obtained by the use of the interaction site approximation (ISA) of RISM-1, and the existence of the critical point was shown in the phase diagram.[7] It is interesting to investigate the behavior of the atom-atom pair correlation function near and at the critical point. In the case of simple fluids, it has been found that the Ornstein-Zernike (OZ) theory of critical scattering gives qualitatively correct results. An extension of the OZ theory to the primitive model of ionic fluids was performed, and the theory showed that the critical behavior of the pair correlation function of the ionic solutions is similar to that of simple fluids.[8]

In this paper, we attempt to extend the OZ theory to the interaction site model and to analyze the critical behavior of the atom-atom pair correlation function of polar fluids by using the OZ theory. In the next section, the asymptotic forms of the atom-atom direct correlation function at large separation are obtained, which is valid off the critical point. In the last section, the critical behavior of the atom-atom pair correlation function is investigated under the assumption that the atom-atom direct correlation function near and at the critical point is similar in its form to the obtained asymptotic formula.

The Asymptotic Forms of the Atom-Atom Direct Correlation Functions.

The system considered is a fluid composed of polar diatomic molecules whose bond length is l. The charges $+q$ and $-q$ are sited on the centers of atoms of the molecule. The total potential energy of the fluid is assumed to be the sum of all intermolecular interactions. The intermolecular interaction between the i-th and j-th molecules is given by

$$U(i,j) = \sum_{\alpha}\sum_{\gamma} u_{\alpha\gamma}(|\boldsymbol{r}_i^{\alpha}-\boldsymbol{r}_j^{\gamma}|), \tag{1}$$

where $u_{\alpha\gamma}(|\boldsymbol{r}_i^{\alpha}-\boldsymbol{r}_j^{\gamma}|)$ is the interaction potential between the α-th atom of the i-th molecule and the γ-th atom of the j-th molecule. $\boldsymbol{r}_i^{\alpha}$ denotes the position of the α-th atom of the i-th molecule. The atom-atom interactions are given as

$$u_{\alpha\gamma}(r) = u^{\mathrm{sr}}(r) + \frac{q_{\alpha}q_{\gamma}}{4\pi\varepsilon_0 r}, \tag{2}$$

where ε_0 is the dielectric constant of the vacuum. $u^{\mathrm{sr}}(r)$ is the short-range part of the potential including the repulsive and the dispersion forces. For simplicity, we assume that the short-range part of the potential is independent of α and γ.

The site-site Ornstein-Zernike (SSOZ) equation in Fourier transform space is given as

$$\tilde{\boldsymbol{h}} = \tilde{\boldsymbol{\omega}}\tilde{\boldsymbol{c}}\tilde{\boldsymbol{\omega}} + \rho\tilde{\boldsymbol{\omega}}\tilde{\boldsymbol{c}}\tilde{\boldsymbol{h}}, \tag{3}$$

where ρ is the number density of molecules and $\tilde{\boldsymbol{h}}$, $\tilde{\boldsymbol{c}}$, and $\tilde{w}$ are matrices of Fourier transforms of the atom-atom total correlation function $h_{\alpha\gamma}(r)$, the atom-atom direct correlation function $c_{\alpha\gamma}(r)$, and the intramolecular pair correlation function $w_{\alpha\gamma}(r)$, respectively. The Fourier transform of $w_{\alpha\gamma}(r)$ is

$$\tilde{\omega}_{\alpha\gamma}(k) = \delta_{\alpha\gamma} + (1-\delta_{\alpha\gamma})\frac{\sin kl}{kl}, \tag{4}$$

where $\delta_{\alpha\gamma}$ is the Kronecker delta. Here, we introduce the total correlation function of the center of atoms $h_{\mathrm{s}}(r)$ and the total correlation function of charges $h_{\mathrm{d}}(r)$, which are defined as

$$h_{\mathrm{s}}(r) = \{h_{++}(r) + h_{+-}(r)\}/2, \tag{5}$$

and

$$h_{\mathrm{d}}(r) = \{h_{++}(r) - h_{+-}(r)\}/2. \tag{6}$$

$c_{\mathrm{s}}(r)$ and $c_{\mathrm{d}}(r)$ are also defined in a similar manner. Then, the matrix equation Eq. 3 separates into two scaler equations as follows,

$$\tilde{h}_{\mathrm{s}}(k) = (1+\tilde{w})^2\tilde{c}_{\mathrm{s}}(k) + 2\rho(1+\tilde{\omega})\tilde{c}_{\mathrm{s}}(k)\tilde{h}_{\mathrm{s}}(k), \tag{7}$$

and

$$\tilde{h}_{\mathrm{d}}(k) = (1-\tilde{\omega})^2\tilde{c}_{\mathrm{d}}(k) + 2\rho(1-\tilde{\omega})\tilde{c}_{\mathrm{d}}(k)\tilde{h}_{\mathrm{d}}(k), \tag{8}$$

where $\tilde{w}=\sin kl/kl$. From Eqs. 7 and 8, we have

$$\tilde{c}_{\mathrm{s}}(k) = \frac{\tilde{h}_{\mathrm{s}}(k)}{(1+\tilde{\omega})^2+2\rho(1+\tilde{\omega})\tilde{h}_{\mathrm{s}}(k)}, \tag{9}$$

and

$$\tilde{c}_{\mathrm{d}}(k) = \frac{\tilde{h}_{\mathrm{d}}(k)}{(1-\tilde{\omega})^2+2\rho(1-\tilde{w})\tilde{h}_{\mathrm{d}}(k)}. \tag{10}$$

For polar fluids, an asymptotic form of $h_{\alpha\gamma}(r)$ at large r off the critical point is[4,5]

$$h_{\alpha\gamma}(r) \simeq \frac{E}{r^6} + \frac{F}{r^7} + O(r^{-8}), \tag{11}$$

where E and F are constants independent of the indices α and γ. From Eq. 11, the small k expansion of the Fourier transform of $h_{\alpha\gamma}(r)$ is expressed as

$$\tilde{h}_{\alpha\gamma}(k) = \tilde{h}_{\alpha\gamma}^{\mathrm{reg}} + \tilde{h}_{\alpha\gamma}^{\mathrm{sing}}. \tag{12}$$

The regular term $\tilde{h}_{\alpha\gamma}^{\mathrm{reg}}$ and the singular term $\tilde{h}_{\alpha\gamma}^{\mathrm{sing}}$ are given by

$$\tilde{h}_{\alpha\gamma}^{\mathrm{reg}} = \tilde{h}(0) + k^2h_{\alpha\gamma}^{(2)} + k^4h_{\alpha\gamma}^{(4)} + O(k^6), \tag{13}$$

and

$$\tilde{h}_{\alpha\gamma}^{\mathrm{sing}} = E'k^3 + F'k^4\ln k + O(k^5), \tag{14}$$

where E', and F' are constants independent of indices α and γ. In Eq. 13, we use the fact that $\tilde{h}_{\alpha\gamma}(0)$ is independent of indices α and γ. By inserting Eqs. 12—14 into Eqs. 5 and 6, we have

$$\tilde{h}_{\mathrm{s}}(k) = \tilde{h}_{\mathrm{s}}^{\mathrm{reg}} + \tilde{h}_{\mathrm{s}}^{\mathrm{sing}}, \tag{15a}$$

$$\tilde{h}_{\mathrm{s}}^{\mathrm{reg}} = \tilde{h}(0) + k^2h_{\mathrm{s}}^{(2)} + k^4h_{\mathrm{s}}^{(4)} + O(k^6), \tag{15b}$$

$$\tilde{h}_{\mathrm{s}}^{\mathrm{sing}} = E'k^3 + F'k^4\ln k + O(k^5), \tag{15c}$$

and

$$\tilde{h}_{\mathrm{d}}(k) = \tilde{h}_{\mathrm{d}}^{\mathrm{reg}} + \tilde{h}_{\mathrm{d}}^{\mathrm{sing}}, \tag{16a}$$

$$\tilde{h}_{\mathrm{d}}^{\mathrm{reg}} = k^2h_{\mathrm{d}}^{(2)} + k^4h_{\mathrm{d}}^{(4)} + O(k^6), \tag{16b}$$

$$\tilde{h}_{\mathrm{d}}^{\mathrm{sing}} = O(k^5). \tag{16c}$$

By inserting Eqs. 15 and 16 into Eqs. 9 and 10, and by expanding the right hand side of Eqs. 9 and 10, we can obtain a small k expansion of $\tilde{c}_{\mathrm{s}}(k)$ and $\tilde{c}_{\mathrm{d}}(k)$. The results are as follows,

$$\tilde{c}_{\mathrm{s}}(k) = \tilde{c}_{\mathrm{s}}^{\mathrm{reg}} + \tilde{c}_{\mathrm{s}}^{\mathrm{sing}}, \tag{17a}$$

$$\tilde{c}_{\mathrm{s}}^{\mathrm{reg}} = c_{\mathrm{s}}^{(0)} + k^2c_{\mathrm{s}}^{(2)} + k^4c_{\mathrm{s}}^{(4)} + O(k^6), \tag{17b}$$

$$\tilde{c}_{\mathrm{s}}^{\mathrm{sing}} = C'k^3 + D'k^4\ln k + O(k^5), \tag{17c}$$

and

$$\tilde{c}_{\mathrm{d}}(k) = \frac{A}{k^2} + c_{\mathrm{d}}^{(0)} + O(k), \tag{18}$$

where $c_{\mathrm{s}}^{(0)}=\tilde{h}(0)/4(1+\rho\tilde{h}(0))$, $C'=E'/4(1+\rho\tilde{h}(0))$, $D'=F'/4(1+\rho\tilde{h}(0))$ and

$$A = \frac{36h_{\mathrm{d}}^{(2)}}{l^2(l^2+12\rho h_{\mathrm{d}}^{(2)})}. \tag{19}$$

Thus, the asymptotic forms of $c_{\mathrm{s}}(r)$ and $c_{\mathrm{d}}(r)$ off the critical point are given as

$$c_{\mathrm{s}}(r) \simeq \frac{C}{r^6} + \frac{D}{r^7} + O(r^{-8}), \tag{20}$$

and

$$c_{\mathrm{d}}(r) \simeq \frac{A}{4\pi r} + O(r^{-4}). \tag{21}$$

$h_{\mathrm{d}}^{(2)}$ is expressed in terms of the dielectric constant ε as[4—6]

$$4q^2h_{\mathrm{d}}^{(2)} = \frac{\mu^2}{9\rho}\left(\frac{\varepsilon-\varepsilon_0}{y\varepsilon}-3\right), \tag{22}$$

where $\mu=ql$ is the magnitude of the dipole moment of molecules, $y=\rho\mu^2/9\varepsilon_0k_{\mathrm{B}}T$, k_{B} the Boltzmann constant and T the absolute temperature. Thus, we have

$$A = -\frac{3y\varepsilon-\varepsilon+\varepsilon_0}{3y(\varepsilon-\varepsilon_0)}\cdot\frac{q^2}{\varepsilon_0k_{\mathrm{B}}T}. \tag{23}$$

Equations 20 and 21 are the result of this section. The first term of Eq. 21 with Eq. 23 was already given in a different way.[9] Equation 20 and the second term of the right hand side of Eq. 21 are new results.

The Critical Behavior of Correlation Functions.

Here, we set up the hypothesis of the OZ theory for the system considered in this paper by assuming that the asymptotic forms of the atom-atom direct correlation function does not change near and at the critical point. Thus, the asymptotic forms near and at the critical point are given as

$$c_{\mathrm{s}}(r) \simeq O(r^{-6}), \tag{24a}$$

and

$$c_{\mathrm{d}}(r) \simeq \frac{A}{4\pi r} + O(r^{-4}). \tag{24b}$$

We define a new function $c_{\mathrm{e}}(r)$ by

$$c_{\mathrm{e}}(r) \equiv c_{\mathrm{d}}(r) - \frac{A}{4\pi r}. \tag{25}$$

From Eq. 24b, $c_e(r) \simeq O(r^{-4})$ as $r \rightarrow \infty$. Then, the Fourier transforms of $c_s(r)$ and $c_e(r)$ can be expressed as

$$\tilde{c}_s(k) = c_s^{(0)} + k^2 c_s^{(2)} + O(k^3), \tag{26}$$

and

$$\tilde{c}_e(k) = c_e^{(0)} + O(k), \tag{27}$$

where $c_s^{(0)}$, $c_s^{(2)}$ and $c_e^{(0)}$ are expressed as follows:

$$c_s^{(0)} = \int c_s(r)\mathrm{d}\boldsymbol{r},$$

$$c_s^{(2)} = -\frac{1}{6}\int r^2 c_s(r)\mathrm{d}\boldsymbol{r},$$

and

$$c_e^{(0)} = \int c_e(r)\mathrm{d}\boldsymbol{r}.$$

The compressibility equation is

$$\rho k_B T \kappa_T = 1 + \rho \tilde{h}(0), \tag{28}$$

where κ_T is the isothermal compressibility of the fluid. This equation shows that in the approach to the critical point $\tilde{h}(0)$ tends to infinity. Thus, from Eq. 9, we have

$$c_s^{(0)} = \tilde{c}_s(0) \rightarrow 1/(4\rho_c), \tag{29}$$

where ρ_c is the number density at the critical point. This result confirms that $c_s^{(0)}$ is analytic at the critical point. However, the analyticity of $c_s^{(2)}$ and $c_e^{(0)}$ is not verified in general. Thus, the present OZ hypothesis for this system is expressed mathematically as follows: $c_s^{(2)}$ and $c_e^{(0)}$ are analytic near and at the critical point.

From Eqs. 7 and 8, we have

$$\tilde{h}_s(k) = \frac{(1+\tilde{\omega})^2 \tilde{c}_s(k)}{1-2\rho(1+\tilde{\omega})\tilde{c}_s(k)}, \tag{30}$$

and

$$\tilde{h}_d(k) = \frac{(1-\tilde{\omega})^2 \tilde{c}_d(k)}{1-2\rho(1-\tilde{\omega})\tilde{c}_d(k)}. \tag{31}$$

By inserting Eqs. 26 and 27 together with Eq. 23 into Eqs. 30 and 31, we have

$$\tilde{h}_s(k) = \frac{4c_s^{(0)} + (4c_s^{(2)} - 2l^2 c_s^{(0)}/3)k^2 + \cdots}{(1-4\rho c_s^{(0)}) + (\rho l^2 c_s^{(0)}/3 - 4\rho c_s^{(2)})k^2 + \cdots}, \tag{32}$$

and

$$\tilde{h}_d(k) = \frac{(Al^4/36)k^2 + \cdots}{3y\varepsilon/(\varepsilon-\varepsilon_0) - (\rho l^2/3)(c_e^{(0)} - l^2 A/20)k^2 \cdots}. \tag{33}$$

By taking Eq. 30 into consideration, the compressibility equation Eq. 28 can be expressed as

$$1 - 4\rho c_s^{(0)} = (\rho k_B T \kappa_T)^{-1} = \kappa_T^0/\kappa_T, \tag{34}$$

where $\kappa_T^0 = (\rho k_B T)^{-1}$ is the isothermal compressibility of the ideal gas. Equation 34 shows that $(1-4\rho c_s^{(0)}) \neq 0$ off the critical point. Thus, the asymptotic forms of $h_s(r)$ and $h_d(r)$ off the critical point obtained from the Eqs. 32 and 33 return to Eq. 11. However, since $(1-4\rho c_s^{(0)}) \rightarrow 0$ with the approach to the critical point, we obtain from Eq. 32.

$$h_s(r) \simeq \frac{c_s^{(0)}}{\pi(\rho l^2 c_s^{(0)}/3 - 4\rho c_s^{(0)})} \cdot \frac{1}{r} \cdot \exp(-\alpha r), \tag{35}$$

and

$$\alpha = \sqrt{\frac{1-4\rho c_s^{(0)}}{\rho l^2 c_s^{(0)}/3 - 4\rho c_s^{(2)}}} \rightarrow 0. \tag{36}$$

Thus, we find that $h_s(r)$ becomes a long-range function, that is, $h_s(r) \sim O(r^{-1})$ in the vicinity of the critical point. On the other hand, it is found from Eq. 33 that the asymptotic form of $h_d(r)$ at large r does not change at the critical point. This shows that near and at the critical point the density fluctuation diverges but the charge fluctuation remains finite. Identifing the correlation length ξ with α^{-1}, we obtain the critical exponent relation $2\nu = \gamma$. ν and γ are defined as

$$\kappa_T^0/\kappa_T \propto \varepsilon^{-\check{\gamma}}(1+\cdots),$$

and

$$\xi \propto \varepsilon^{-\nu},$$

where $\varepsilon = |(T-T_c)/T_c|$ and T_c is the critical temperature. These results are quite analogous with the case of simple fluids, which is in accordance with the prediction of Stell.[10]

Let us consider the relation of the OZ theory with integral equation theories. The ISA consists of the SSOZ equation Eq. 3 and the ISA closure given by

$$h_{\alpha\gamma}(r) = -1, \quad r < \sigma_{\alpha\gamma} \tag{37a}$$

and

$$c_{\alpha\gamma}(r) = -u_{\alpha\gamma}(r)/k_B T, \quad r > \sigma_{\alpha\gamma} \tag{37b}$$

where $\sigma_{\alpha\gamma}$ is the hard-sphere diameter of atoms. For the fluid composed of polar hard dumb-bells with the same diameter σ, Eqs. 37a and 37b can be expressed as

$$\begin{cases} h_s(r) = -1, & r < \sigma \\ c_s(r) = 0, & r > \sigma \end{cases} \tag{38}$$

and

$$\begin{cases} h_d(r) = 0, & r < \sigma \\ c_d(r) = -q^2/4\pi\varepsilon_0 k_B Tr. & r > \sigma \end{cases} \tag{39}$$

Thus, the ISA satisfies the OZ hypothesis introduced in this section. Equations 7 and 38 becomes the PY-like integral equation of RISM-1[11,12] for neutral hard dumb-bell fluids (HDF), and so the quantity $(1-4\rho c_s{}^{(0)})$ is the same as that of the solution of the PY-like integral equation for HDF. Since the critical point does not exist for HDF, no critical point can be observed in the correlation function of the polar hard dumb-bell fluids in the ISA. However, if the phase behavior is investigated through the energy equation instead of the compressibility equation, it is possible to detect the critical point. In fact, Morriss and Isbister showed the existence of the critical point through the energy equation. The circumstances are quite similar to the case of the restricted primitive model of ionic solutions.[8] Since $h_s(r) \neq h(r)^{\mathrm{HDF}}$ in the other approximations (for example, PY-like and HNC-like approximations), the critical point will be observed in the correlation function by using these approximations. The critical behavior obtained through these approximations will be different from the result in this work, because these approximations do not satisfy the OZ hypothesis presented here.

Appendix

The Critical Behavior of Nonpolar Fluids Composed of Homonuclear Diatomic Molecules.

The critical point of nonpolar fluids composed of homonuclear diatomic molecules was recently detected through the compressibility equation by using the PY-like integral equation of RISM-1.[13]

The asymptotic form of the atom–atom direct correlation function for this system off the critical point is expressed as[9]

$$c(r) \simeq -u(r)/k_B T \sim O(r^{-6}). \qquad \text{as } r \to \infty \tag{A1}$$

Hereafter, the indices α and γ are omitted, because the atom–atom functions for this system are independent of the indices. For this system, the OZ hypothesis is expressed as follows: the first two coefficients of the small k expansion of the Fourier transform of $c(r)$ are analytic near and at the critical point. Thus, we have

$$\tilde{c}(k) = c^{(0)} + k^2 c^{(2)} + \cdots, \tag{A2}$$

where

$$c^{(0)} = \int c(r)\mathrm{d}\boldsymbol{r},$$

and

$$c^{(2)} = -\frac{1}{6}\int r^2 c(r)\mathrm{d}\boldsymbol{r}.$$

Then, from the similar discussion described in the last section, we have the same equations as Eqs. 35 and 36 in the approach to the critical point.

PY-like approximation for fluids interacting through the short-range interaction satisfies the OZ hypothesis presented in this appendix, and so it is found that the asymptotic form of $h(r)$ given by the PY-like approximation is $h(r) \sim O(r^{-1})$ at the critical point. On the other hand, HNC-like approximation does not satisfy the OZ hypothesis, and thus the critical behavior is different from that given by the PY-like approximation. In fact, we have found that $h(r)$ decays as r^{-2} in the HNC-like approximation, which is the same as that for simple fluids interacting through the short-range interactions.[14]

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