Density Fluctuations in an Electrolyte from Generalized Debye-Hückel Theory

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Near-critical thermodynamics in the hard-sphere (1,1) electrolyte is well described, at a classical level, by Debye-Hückel (DH) theory with (+,−) ion pairing and dipolar-pair-ionic-fluid coupling. But DH-based theories do not address density fluctuations. Here density correlations are obtained by functional differentiation of DH theory generalized to non-uniform densities of various species. The correlation length $\xi$ diverges universally at low density $\rho_0$ as $(T_\rho)^{-1/4}$ (correcting GMSA theory). When $\rho = \rho_0$, one has $\xi \approx \xi_0^*/t^{1/2}$ as $t \equiv (T-T_\rho)\rightarrow 0$+ where the amplitudes $\xi_0^*$ compare informatively with experimental data.

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There is a major puzzle in the theory of fluid criticality in model ionic systems because experiments reveal that certain electrolyte solutions exhibit classical (i.e., van der Waals as against the usual Ising-type) critical exponents over as much as 1 to 3 decades when $|t| \equiv (T-T_\rho)/T_\rho \rightarrow 0$. Probably there is always a scale $t_\times$ below which the behavior crosses over from classical to Ising; but attempts to explain how $t_\times$ might vary from $\sim 1$ to $\sim 10^{-1}$ have so far been unconvincing. Initial efforts have addressed the simplest case: the Restricted Primitive Model, consisting of $N = N^+ + N^- \equiv V\rho$ hard-sphere ions of diameter $a$, carrying charges $\pm q$ in a medium of dielectric constant $D$. The hope has been to decide the universality class (and crossover scale $t_\times$ if appropriate) of the RPM.

To that end Fisher and Levin have shown that the original Debye-Hückel (DH) theory provides a remarkably good, albeit classical account of the critical thermodynamics as judged by current simulations. However, for a satisfactory description, pure DH theory must be extended (i), following Bjerrum, by recognizing bound, neutral but dipolar (+,−) ion pairs in equilibrium with the free ions, (ii) by including the dipolar-ionic (DI) solvation free energy, and (iii) by allowing for hard-core (HC) repulsions. In terms of $T_c \equiv k_BT_Da/\epsilon^2$, these DHBJDIHC theories yield critical points in the range $T_\rho \simeq 0.052$ to 0.057 as compared with 0.052–0.056 from recent simulations.

Now, following Ebeling and Grigo, one can also pursue theories based on the mean spherical approximation (MSA); but, for reasons currently obscure, such theories, even when improved in various ways yield estimates for $T_\rho$ too high by 35-50% . Note also that the hypernetted chain (HNC) and other integral equations have no solutions in the critical region! Further study of the DH-based theories is thus well justified.

To understand properly the nature of a critical point one must go beyond thermodynamics to study the order-parameter fluctuations. But, even for ionic fluids, the order parameter is just the overall density. Now DH-based theories illuminate the Debye-screening of the bare Coulombic potential, as seen in the exponential decay of the charge-charge correlations, but, unfortunately, they say little about the overall density-density correlation function, $G_{\rho\rho}(r) \equiv \langle \rho(r)\rho(0) \rangle - \rho^2 \equiv \langle \delta_1 (r) + \rho [g_2 (r) - 1] \rangle$. Our aim here is to rectify this deficiency.

Note, especially, that the Fourier transform of $G_{\rho\rho}(r)$ yields the k-dependent susceptibility

$$\chi(k) = \hat{G}_{\rho\rho}(k)/\rho = \chi(0)[1 + \xi^2 k^2 + \ldots]$$

which diverges at $k = 0$ at criticality. Indeed, $\chi(k)$ determines the critical opalescence and turbidity and specifies the (second-moment) correlation length $\xi(T,\rho)$ which diverges as $\xi^2 \sim \Lambda^2$ when $t \rightarrow 0^+$ at $\rho = \rho_0$; furthermore, $\chi(k)$ approaches the reduced compressibility $\chi(0) = \rho k_BT/K$ (or its solution analog) when $k \rightarrow 0$.

As stressed by Fisher and Levin [3(a),7], it is valuable to know the critical amplitude $\xi^2$ even within a classical approximation since, via the Ginzburg criterion, that offers a possible route for estimating a crossover range, $\pm t_\times$, outside which close-to-classical critical behavior might be realized.

In this Letter we show how DH theory can be generalized so as to yield, in a natural way, density fluctuations diverging at criticality. The method extends straightforwardly to the full DHBJDIHC theories as we illustrate below. In particular, we calculate the correlation length $\xi(T,\rho)$ explicitly within the simplest generalized (GDH) theory, and numerically, at improved levels of approximation. At low densities a novel, universal divergence of $\xi(T,\rho)$ is predicted for all $T$. In the critical region the results are, as expected, classical with $\nu = \frac{1}{2}$, but the amplitudes $\xi_0^*$ prove informative and are compared with experimental data in classical and Ising domains.

Explicitly we proceed, following [3], by approximating the total Helmholtz free energy $F(T,\rho)$ by a sum of terms representing ideal gas, ionic fluid, dipole-ion, and hard-core contributions; but we now aim for a functional $\beta F[(\rho_1)] = \int d^d r F$ where $\rho_1(r) = \rho_+(r) + \rho_-(r)$ and $\rho_\pm(r)$ are slowly varying local free-ion and dipolar pair densities, while $\beta = 1/k_BT$. Since we wish to probe...
only the density fluctuations, we follow DH theory and maintain electroneutrality, \( \rho_+ (\mathbf{r}) = -\rho_- (\mathbf{r}) \), on long length scales. Of central concern are the (reduced) direct correlation functions which follow by functional differentiation (with \( i, j = 1, 2 \)) as

\[
C_{ij} (\mathbf{r} - \mathbf{r'}) \equiv \delta^2 \beta F / \delta \rho_i (\mathbf{r}) \delta \rho_j (\mathbf{r'}) \Big|_{\rho_+(\mathbf{r'}) = \bar{\rho}_+},
\]

(2)

where the \( \bar{\rho}_\lambda (\lambda = +, -, 2) \) are the overall equilibrium densities. Note that various terms in \( F \) contribute linearly to the \( C_{ij} \) and, in particular, \( C_{ij}^{\text{ideal}} (\mathbf{k}) = \delta_{ij} / \bar{\rho}_+ \). However, since the total local density is \( \rho (\mathbf{r}) = \rho_1 (\mathbf{r}) + 2 \rho_2 (\mathbf{r}) \) \( [3] \), one finds, with the aid of the Ornstein-Zernike (OZ) matrix relation for \( \tilde{C}_{ij} (\mathbf{k}) \) \( [2] \), the result

\[
\frac{1}{\rho (\mathbf{k})} = \frac{1}{G_{\rho \rho} (\mathbf{k})} = \frac{\bar{C}_{11} (\mathbf{k}) C_{22} (\mathbf{k}) - |\bar{C}_{12} (\mathbf{k})|^2}{4 \bar{C}_{11} (\mathbf{k}) - 4 \bar{C}_{12} (\mathbf{k}) + C_{22} (\mathbf{k})},
\]

(3)

from which \( \xi \) follows by expansion in \( \mathbf{k} \). More expeditiously one may impose infinitesimal density variations

\[
\rho_j (\mathbf{R}) = \bar{\rho}_j [1 + \Delta_j \cos \mathbf{k} \cdot \mathbf{r}],
\]

(4)

and expand the reduced free-energy density \( \beta F / V \) in powers of the \( \Delta_j \); the quadratic term is then

\[
\frac{1}{4} \sum_{j,i} \bar{\rho}_j \bar{\rho}_i \bar{C}_{ij} (\mathbf{k}) \Delta_i \Delta_j,
\]

from which the \( \tilde{C}_{ij} \) follow.

Evidently, the crucial issue is to extend DH theory to nonuniform but slowly varying mean densities of the various species. Note first that the free-ion contribution becomes \( [4] \), via the Debye charging process \( [3] \),

\[
F^{\text{DH}} = \int d^d \mathbf{r}_1 \rho_1 (\mathbf{r}_1) \int_0^q dq_1 \psi_1 (\mathbf{r}_1, q_1),
\]

(5)

where \( \psi_1 (\mathbf{r}_1; q_1) \) is the mean electrostatic potential at the site \( \mathbf{r}_1 \) of a fixed ion due to all the other ions when each carries charges \( \pm q \). If \( \phi (\mathbf{r}, \mathbf{r}_1) \) is the mean electrostatic potential at a general point \( \mathbf{r} \) when the ion 1 is fixed at \( \mathbf{r}_1 \), one has \( [2] \)

\[
\psi_1 (\mathbf{r}; q_1) = \lim_{\mathbf{r}_1 \to \mathbf{r}_1} \phi (\mathbf{r}; \mathbf{r}_1) - q_1 / D |\mathbf{r} - \mathbf{r}_1|.
\]

DH derived their celebrated equation for \( \phi \) by approximating the probability density for a particle species \( \lambda (= +, -, 2) \) with charge \( q_\lambda \) by \( \bar{\rho}_\lambda \exp [\beta q_\lambda \phi (\mathbf{r})] \approx \bar{\rho}_\lambda [1 - \beta q_\lambda \phi (\mathbf{r})] \) \( [3] \). (Note \( q_\lambda = 0 \).) In the same spirit we now propose to replace the constant partial (species) density \( \bar{\rho}_\lambda \) by \( \rho_\lambda (\mathbf{r}) \) the (slowly varying) non-uniform density \( [3] \). Our generalized (GZ) equation then reads

\[
[\nabla^2 - \tilde{\kappa}^2 (\mathbf{r}) \Theta_1 (\mathbf{r})] \phi (\mathbf{r}; \mathbf{r}_1) = -4\pi q_1 \delta (\mathbf{r} - \mathbf{r}_1) / D,
\]

(6)

where, utilizing \( \theta (y) \), the Heaviside step function, \( \Theta_1 (\mathbf{r}) \equiv \theta (|\mathbf{r} - \mathbf{r}_1| - \alpha) \) embodies the crucial hard-core boundary condition \( [3] \), while the spatially varying coefficient

\[
\tilde{\kappa}^2 (\rho_\lambda) = 4\pi \beta \sum_\lambda g_\lambda^2 \bar{\rho}_\lambda (\mathbf{r}) / D = 4\pi \beta q^2 \bar{\rho}_1 (\mathbf{r}) / D,
\]

(7)

reduces to the standard expression for \( \kappa^2 \), the inverse Debye length squared, when \( \rho_\lambda (\mathbf{r}) = \bar{\rho}_\lambda \) is constant \( [3] \).

To solve \( [2] \), we adopt \( [4] \) and expand \( \phi \) in powers of \( \Delta_1 \). The coefficient \( \phi_\alpha (\mathbf{r}, \mathbf{r}_1) \) of \( \Delta_1^\alpha \) can be computed recursively, setting \( \tilde{k} = \kappa \) and \( \mathbf{r}_1 = 0 \), with the aid of the Green’s function

\[
G(\mathbf{r}; \mathbf{r'}) = \frac{\kappa}{4\pi} \sum_{\ell = 0}^\infty G_\ell (\mathbf{k} \mathbf{r}, \mathbf{k} \mathbf{r'}) P_\ell \left( \frac{\mathbf{r} - \mathbf{r'}}{\mathbf{r} \cdot \mathbf{r'}} \right),
\]

(8)

where, employing modified spherical Bessel functions,

\[
G_\ell (s, s') = \frac{s \ell}{s'} \frac{\ell!}{\ell^2 + 1} \frac{s'}{k_{\ell+1}(x)} \left[ k_{\ell+1}(x) \mathbf{r} \cdot \mathbf{r'} - i_{\ell+1}(x) s' k_{\ell+1}(x) \right],
\]

(9)

for \( s, s' > x \), and \( P_\ell (\mu) \) denotes a Legendre polynomial.

Substituting in \( [2] \) and expanding \( C_{\rho \rho} \equiv 1 / G_{\rho \rho} \) to \( O (k^2) \) yields \( \xi^2 \). This requires only the \( \ell = 0 \) and 1 terms in \( [8] \). Consequently, within pure DH theory, the simplest level of approximation, we find the correlation length is given explicitly by (recalling \( x \equiv \kappa a \))

\[
\frac{\xi^2}{a^2} = \frac{\chi^{\text{DH}} (0)}{24 T^* x^2} \left[ \ln \left( \frac{1 + x}{1 + \sqrt{1 + x}} \right)^{10} - \frac{x - 5x^2 - 8x^3}{2(1 + x)^2} \right],
\]

(11)

where \( 1 / \chi^{\text{DH}} (0) = 1 - x / 4 T^* (1 + x)^2 \) \( [3] \).

Now corrections to this result enter only in \( O (x^2) = O (\rho) \), i.e., beyond the leading low-density behavior which, in fact, exhibits the novel divergence

\[
\xi (T, \rho) = \frac{1}{4} (b / 36 \pi \rho)^{1/4} [1 + (1/2) b + O (\rho^*)],
\]

(12)

when \( \rho \to 0 \), where \( b = q^2 / D k_b T \) is Bjerrum’s length. This expression for the density-density correlation length is independent of the hard-core diameter \( a \) and is thus universal! We believe it represents the exact limiting behavior not previously noted. At low densities Debye’s screening length \( \xi_D = 1 / \kappa \) controls the decay of the charge correlations \( [4(b), 17] \). It also diverges universally when \( \rho \to 0 \); but since we find \( \kappa \approx \sqrt{b \xi_D / 48} \), the density correlations then decay on a shorter scale than the charge correlations.

Our conclusion \( [12] \) can be checked further by using the HNC relation \( c_{ij} \approx -\beta \mu_{ij} + \frac{1}{2} \delta_{ij} [4(b), 17, 18] \), which is probably generally valid in the low density limit \( [17] \) when \( h_{ij} \equiv g_{ij} - 1 \) decays exponentially fast, as expected here. This leads to \( [16, 19] \)

\[
1 / \chi (k) \approx 1 - \frac{1}{2} \kappa^2 b \tan^{-1} (k / 2\kappa / k) \quad (\rho \to 0),
\]

(13)

which, on expansion to order \( k^2 \), yields the DH limiting law for \( \chi (0) \) and reproduces \( [12] \) ! However, the true correlation length, \( \xi_{\infty} (T, \rho) \), that determines the OZ-like
exponential decay of $G_{pp}(r)$ is determined by the dominant zeros of $\{1\}$. These give the different expression

$$\xi_{\infty} \approx \frac{1}{2} \xi_{D} \{1 + 2 \exp[-4/(\pi \rho b^3)^{1/2}] + \ldots\} \quad \text{(14)}$$

[16,19] which diverges as $(T/\rho)^{1/2}$. Thus $G_{pp}(r)$ has a small but longer-range tail decaying slightly more slowly than $e^{-2x^2/r^2}$, the squared charge-charge correlation.

By contrast to (12) and (13), (one finds (11) that the GMSA or generalized mean-spherical approximation gives $1/\chi(k)$ predicts $1/\chi(k) = 1 - \frac{1}{2} k b / [2 + k^2 a/k]$ when $\rho \to 0$. This gives $\chi(0)$ correctly to order $(\rho^0/2^2)$ but leads to

$$\xi_{\text{GMSA}} \approx \xi_{\infty\text{GMSA}} \approx \left(\frac{1}{2} \alpha_2 \xi_{D}\right)^{1/2} = \frac{1}{2} (a^2/\pi \rho b)^{1/4}. \quad \text{(15)}$$

Thus $\xi_{\text{GMSA}}$ also diverges as $\rho^{-1/4}$, but the power of $T$ differs and the result is non-universal, depending on $a$. This reveals an unsuspected defect of the GMSA [24], which was especially devised to satisfy a variety of correlation-function sum rules [23]. (The original MSA gives only a hard-sphere result for $G_{pp}(r)$: see, e.g., [13].)

In the critical region the pure DH result (12) diverges with exponent $2 \nu = 1$ at $T_\nu^c = \frac{k_B}{\sigma_a}$, $x_c = 1$, $\rho_c = 1/64 \pi$. The correlation length amplitude is found to be

$$\langle \xi^+_{i} / a \rangle_{DH} = \left[1 + \frac{20}{3} \ln 2 - 6 \ln \frac{\gamma}{2} \right]^{1/2} \approx 0.7329. \quad \text{(16)}$$

This is surprisingly close to the GMSA value 0.75 [24, 25], although $T_\nu^c$ and $\rho_c$ differ significantly [24].

However, although the pure DH theory based on (12)-(14) is sufficient at low density, one must, as mentioned in the introduction [24], include ion-pairing to study the critical region. Bjerrum’s ansatz for the association constant is appealing but Ebeling’s result is superior [24] and used here. (Near criticality the numerical changes are minor.) In simple “DHBjl” theory the ion pairs are supposed ideal [24] and one finds $\hat{C}_{22} = 1/\hat{\rho}_2$, $\hat{C}_{12} = 0$, and $\hat{C}_{11}(k)$ is unaltered. But that is too naive and proves unphysical: it is essential to include the dipole-ionic fluid (DI) interactions [24].

We calculate the new non-uniform DI effects by using the GDH equation, (14), but with a dipolar source term, i.e., $+ \rho_a B_1$ and $- \rho_a B_2$ at $r_1 = \pm \frac{1}{2} a_1$, where $a_1$ specifies the orientation and typical charge separation, $a_1(T) \equiv |a_1| = 3 [\text{B}]$. The associated bispherical exclusion zone is approximated by a sphere of radius $a_2$ [24]. Thus the Green’s function [24] still applies, but with $x \to x_2 = \kappa a_2$. At low $T$, $a_2 = a$ (“contact”) and $a_2 = 1.16198a$ (angular average) are reasonable [24] and the sensitivity to these values is readily tested.

Angular integration over the dipole orientations is complicated, yielding the solution $\phi_{\text{dip}}(r; r_1)$ as a multiple sum with Clebsch-Gordan coefficients, $\mathcal{C}_{\ell_1, \ell_2}(m_1, m_2 | \ell, m)$. To obtain $\phi_{\text{dip}}(r; q)$ in the pair analogy of (14), the self-potential of the source dipole is subtracted. To order $k^2$ one needs only $\ell = 0, 1, 2$, which give explicit expressions [24] with low-density expansions

$$\hat{C}^{DI}_{11}(k) = \frac{\chi_1^2 \rho_1}{20 T^* \rho_1} \left\{1 - \frac{4}{27} x_2 + \frac{25}{27} x_2^2 + O(x_2^3) \right\}$$

$$- \frac{k^2}{\pi^2} \left[1 + \frac{1}{7} x_2^2 + O(x_2^3) \right] + O(k^4) \right\}, \quad \text{(17)}$$

Finally, hard-core exclusion may be approximated by local, free-volume terms $\mathcal{F}_{\text{HC}} = - \sum_i \rho_i \ln \left[1 - \sum_j B_{ij} \rho_j \right]$ with (i) $B_1 = \frac{1}{2} B_2 = 4 a^3 / 3 \sqrt{3}$ to yield bcc close-packing or (ii) $B_1 = \frac{1}{2} B_2 = 2 \pi a^3 / 3$ for the exact ion-ion second virial coefficient [24] or (iii), perhaps preferably, by the local Carnahan-Starling mixture form [24]

$$6 \pi \left[\left(\zeta_n - \frac{\zeta_3}{\zeta_5}\right) \ln(1 - \zeta_n) - \frac{3 \zeta_1 \zeta_2}{1 - \zeta_5} - \frac{\zeta_3^2}{\zeta_5 (1 - \zeta_3)^2}\right]. \quad \text{(19)}$$

where $\zeta_n = \frac{1}{2} \pi \sum_i \rho_i \sigma_i$ with $\sigma_i$ the hard-core diameter of species $i$; we take $\sigma_1^2 = \frac{1}{2} \sigma_2^2 = a^3$. For densities near critical, only the second virial coefficients prove significant. Being local, the approximations (i)-(iii) give $\hat{C}^{HC}_{\text{IG}}(k)$ independent of $k$. Nonlocal effects are easily included at the second-virial-coefficient level; but that changes the critical amplitude $\xi_0^c$ by less than 1%.

![FIG. 1. Inverse square of the density-density correlation length, $\xi(T, \rho)$, on the critical isochore according to: (a) pure DH theory; (b) with Bjerrum association and dipole-pair-ionic-fluid coupling (DHBjl) with $a_1 = a$, $a_2 = 1.16198a$; (c)-(e) with hard-core terms (i)-(iii); see text.](image-url)
are less dramatic near \( T_c \) than might have been guessed. With the assignments \( a_1 = a, a_2 \approx 1.162a \) the critical amplitudes are \( \xi_0^+ / a \approx 0.7511, 0.7776, 0.8186, \) and 0.8147 for pure DHBJD theory and with HC treatments (i)-(iii), respectively. Increasing \( a_1 \) to 1.150 lowers \( \xi_0^+ \) by no more than 8.3%. Similarly, taking \( a_2 \) to be 1.150 leads to a reduction of less than 1.1%. (The corresponding changes in \( T_c, \rho_c \), etc. can be found in [3(b)].)

To compare our results for \( \xi_0^+ \) with experiments on systems that might plausibly be modeled by the RPM, one needs not only data for \( \xi_0^+ \) [3] but also some estimate of the effective hard-core diameter, \( a \). That might be obtained by matching the \( \rho_c^* \) predictions to experiment. To that end, we re-express our results above as \( \xi_0^+ \rho_c^{1/3} \approx 0.2275, 0.2302, 0.2375, \) and 0.2368 (in contrast to 0.1251 for pure DH theory and 0.1828 for the GMSA [3]).

Beyond that one must recall that our theory is classical with \( \nu = \nu_{MF} = 1/2 \) whereas observations indicate the Ising value \( \nu_{Is} \approx 0.63 \) or crossover to that for \( T \lesssim T_x \). However, for 3-D lattice gases, which are described by \( \nu_{Is} \) for all \( T \lesssim 1 \), the mean-field estimates for \( \xi_0^+ \), say \( \xi_0^{MF} \), agree with numerical estimates, say \( \xi_0^{MC} \), to within 10% [25] (for various lattice structures). On the other hand, if crossover is found, the fits for \( T < T_x \) and \( T > T_x \) should roughly obey the matching formula \( \xi_0^{MC}/\xi_0^{MF} = (t_x)^{\nu_{Is} - \nu_{MF}} \). Data for Na+ND3 with \( T_x \approx (7-9) \times 10^{-3} \) have been fitted in both regions [2(a)(c)] and confirm the relation. For this system we find \( \xi_0^{MC} \rho_c^{1/3} = 0.34 \pm 0.03 \), which is some 40 to 50% above our estimates. For Pitzer’s salt [2(b)(e)] we may postulate a crossover at \( T_x \approx 1 \times 10^{-4} \): this yields \( \xi_0^{MC} \rho_c^{1/3} = 0.21 \pm 0.04 \) which encompasses our values. Tetra-n-butyl-ammonium picrate in n-tridecanol [2(d)] displays crossover and we find \( \xi_0^{MC} \rho_c^{1/3} \approx 0.22 \), close to our prediction. Finally, for the same salt in other solvents [2(f)] quite similar values of \( \xi_0^{MC} \) fit the turbidity data. Overall the agreement is encouraging when using the Ising-fitted amplitudes. It is puzzling, but perhaps significant, that in the mean-field region outside \( T_x \) the values of \( \xi_0^{MC} \rho_c^{1/3} \) are all larger (by factors of 2-3) than our classical theory predicts!

In conclusion, we have shown how to calculate density-density correlations within DH theory and its extensions [3]. At low densities the correlation length, \( \xi(T, \rho) \), diverges in unexpected but universal fashion potentially amenable to experimental check. In the critical region comparison with experiments on electrolytes proves instructive and raises further questions. More concretely, the present theory enables the observed classical-to-Ising crossover to be addressed via the Ginzburg criterion [3].

A naive extension of the functional approach outlined is not sufficient for studying the charge correlations at higher densities since, when \( k \to 0 \), the associated density perturbations, even when infinitesimal, induce a macroscopic charge imbalance. However, approaches which separate out the long-range Coulombic contributions should lead to progress.

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derive $G_{rr}(r)$ by functional differentiation with respect to ion-ion interactions. They used MSA and DH theory, with ion pairs (but not DI effects). However, the method also fails to give $\xi \to \infty$ at criticality.

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[20] Recently Ennis, et al. [19] in a Note added in proof have remarked that the GMSA does not predict $\xi_\infty$ approaching $\frac{1}{2}$ when $\rho \to 0$.

[21] See, e.g., G. Jackson, Molec. Phys. 72, 1365 (1991); but Eq. (19) itself may not be in the literature.

[22] H. B. Tarko and M. E. Fisher, Phys. Rev. B 11, 1217 (1975).

[23] H. van Beijeren and M. U. Felderhof, Molec. Phys. 38, 1179 (1979).