

## Diverging correlation lengths in electrolytes: Exact results at low densities

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The restricted primitive model of an electrolyte (equisized hard spheres carrying charges  $\pm q_0$ ) is studied using Meeron's expressions [J. Chem. Phys. **28**, 630 (1958)] for the multicomponent radial distribution functions  $g_{\sigma\tau}(\mathbf{r}; T, \rho)$ , that are correct through terms of relative order  $\rho$ , the overall density. The *exact* second and fourth moment *density-density* correlation lengths  $\xi_{N,1}(T, \rho)$  and  $\xi_{N,2}(T, \rho)$ , respectively, are thereby derived for low densities: in contrast to the Debye length  $\xi_D = (k_B T / 4\pi q_0^2 \rho)^{1/2}$ , these diverge when  $\rho \rightarrow 0$  as  $(T\rho)^{-1/4}$  and  $(T/\rho^3)^{1/8}$ , respectively, with *universal* amplitudes. The asymptotic expressions agree precisely with those obtained by Lee and Fisher [Phys. Rev. Lett. **76**, 2906 (1996)] from a generalization of Debye-Hückel (GDH) theory to *nonuniform* ion densities. Other aspects of this GDH theory are checked and found to be exact at low densities. Specifically, with the further aid of the hypernetted-chain resummation, the corresponding *charge-charge* correlation lengths  $\xi_{Z,1}$  and  $\xi_{Z,2}$  and the Lebowitz length,  $\xi_L$  (which restricts charge fluctuations in large domains), are calculated up to nonuniversal terms of orders  $\rho \ln \rho$  and  $\rho$ . In accord with the Stillinger-Lovett condition, one finds  $\xi_{Z,1} = \xi_D$  although the ratios  $\xi_{Z,2}/\xi_D$  and  $\xi_L/\xi_D$  deviate from unity at nonzero  $\rho$ .

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### I. INTRODUCTION AND SUMMARY

#### A. The various correlation lengths

Considerable progress has been made in this century toward understanding the thermodynamic properties of electrolyte solutions (e.g., NaCl in water). A central problem, which remains a challenge to theory, has been applying precise methods of statistical mechanics to the simplest model of ionic solutions, namely, the restricted primitive model (RPM), consisting of  $N = N_+ + N_- \equiv V\rho$  hard spheres of diameter  $a$  with  $N_+$  carrying elementary charges  $+q_0$  and  $N_- (=N_+)$  charges  $-q_0$ , in a medium of dielectric constant  $D$ . Our aim here is to respond to this challenge by deriving explicit exact results for various *density-density* and *charge-charge correlation lengths* at low densities in order to compare them with recent approximate theories potentially valid at higher densities.

The pioneering work in 1923 of Debye and Hückel (DH) [1], who constructed and then linearized an appropriate Poisson-Boltzmann equation, shed light on the importance of ion screening characterized—in the leading approximation—by the Debye screening length  $\xi_D$ , given by

$$\xi_D^{-2} \equiv \kappa_D^2 = 4\pi\beta \sum_{\sigma} (z_{\sigma} q_0)^2 \rho_{\sigma} / D, \quad (1.1)$$

where  $\beta = 1/k_B T$ , while  $\rho_{\sigma}$  and  $z_{\sigma}$  are the number density and valence of species  $\sigma$ , respectively. For the RPM one has  $z_{\sigma} = +1, -1$  for ion species  $\sigma = +, -$ , so that  $\kappa_D^2 = 4\pi\beta q_0^2 \rho / D$  with  $\rho = \rho_+ + \rho_-$ . The DH theory, which is, in effect, a special type of mean field theory, provides a reasonably good account of the thermodynamics of electrolytes at moderate density  $\rho$ , and was shown to be exact when  $\rho \rightarrow 0$  (the DH limiting laws) by Kirkwood and Poirier [2]. However, systematic improvements of DH theory have proven elusive.

In 1950, Mayer [3] developed a systematic theory of the statistical thermodynamics of ionic solutions based on cluster expansion techniques which, in principle, allows one to calculate successive corrections to the DH limiting laws. Mayer's calculation of the osmotic pressure exerted by the ions is formally equivalent to a virial expansion of the pressure of a gas. One of the central insights of the Mayer theory is that by summing the "ring graphs" to all orders in the density  $\rho$ , one recovers Debye screening which is an inherently many-body effect. This also solves the technical problem of divergent integrals over the bare Coulomb interaction which enters in the dimensionless form

$$\beta\varphi_{\sigma\tau}(r) = z_{\sigma} z_{\tau} b / r, \quad (1.2)$$

where Bjerrum's length is

$$b = \beta q_0^2 / D \equiv a / T^*, \quad (1.3)$$

while  $T^* = k_B T D a / q_0^2$  is the reduced temperature. In considering only ring diagrams, Mayer found that his results for the osmotic pressure and ionic activity coefficient confirmed the DH limiting laws. By including graphs of more complex topological types, Haga [4] calculated the osmotic pressure and logarithm of the ionic activity up to and including correction terms of relative order  $\rho^{5/2}$  and  $\rho^{3/2}$ , respectively. Although, in principle, one may calculate thermodynamic properties of the RPM to arbitrary orders in  $\rho$  using Mayer's theory, the number and difficulty of the integrals which appear make going much beyond the second virial level [i.e.,  $O(\rho^2)$  in the free energy] analytically intractable.

In 1958, Meeron [5], using a slightly modified approach to Mayer's theory [6], was able to extend the treatment of thermodynamic properties to provide a calculation of the potentials of average force,  $w_{\sigma\tau}(r; T, \rho)$ , between two species  $\sigma$  and  $\tau$  separated by a distance  $r$ , and of the radial distribution functions,  $g_{\sigma\tau}(r; T, \rho)$ . Meeron collected terms of  $O(\rho^{1/2})$ ,

$O(\rho \ln \rho)$  and  $O(\rho)$ , and gave explicit expressions for  $w_{\sigma\tau}(r)$  and  $g_{\sigma\tau}(r)$  exact through terms of  $O(\rho)$ . Using the multicomponent virial expression relating the osmotic pressure  $p(T, \rho)$  to the  $g_{\sigma\tau}(r)$  and the (Coulombic) interactions, Meeron calculated  $p(T, \rho)$  and checked agreement with the known exact result [4] up to and including terms of  $O(\rho^2)$  (i.e., the second virial level). The expression for  $g_{\sigma\tau}(r)$ , however, is rather complicated, involving elaborate integrals [see Eq. (1.14) below], and, indeed, Meeron did not extract any other observable properties from  $g_{\sigma\tau}(r)$ .

Recent experiments on the criticality of electrolyte solutions have renewed interest in understanding the behavior of ionic systems. A powerful tool in the study of critical phenomena and the structure of liquids is the scattering of electromagnetic radiation or of neutrons which enables one to observe the density-density structure factor

$$S_{NN}(k; T, \rho) = 1 + \rho \hat{h}_N(k; T, \rho). \quad (1.4)$$

Here the appropriate number-density-number-density correlation function for the RPM is given by the sum

$$h_N(r) = \frac{1}{2}[h_{++}(r) + h_{+-}(r)] = \frac{1}{4} \sum_{\sigma, \tau} h_{\sigma\tau}(r), \quad (1.5)$$

in which, with  $\sigma, \tau = +, -$ , we employ the standard notation

$$h_{\sigma\tau}(r) = g_{\sigma\tau}(r) - 1, \quad (1.6)$$

while we define the Fourier transform generally via

$$\hat{v}(\mathbf{k}) = \int d\mathbf{r} e^{i\mathbf{k} \cdot \mathbf{r}} v(\mathbf{r}). \quad (1.7)$$

From small-angle-scattering experiments (i.e.,  $k \rightarrow 0$ ), one measures the *second moment* and (possibly) the *fourth moment density-density correlation lengths*  $\xi_{N,1}(T, \rho)$  and  $\xi_{N,2}(T, \rho)$ , defined by

$$S_{NN}(k; T, \rho) = S_{NN}(0) [1 - \xi_{N,1}^2(T, \rho) k^2 + \xi_{N,2}^4(T, \rho) k^4 + O(k^6)], \quad (1.8)$$

where, for the RPM,  $S_{NN}(0) = \rho k_B T K_T$  is the reduced compressibility. Of course, this assumes that a power series expansion of  $S_{NN}(k)$  in  $k^2$  is possible, at least to the orders shown: our analysis bears that out.

As mentioned, a principal aim of this paper is to derive *exact* expressions for  $\xi_{N,1}(T, \rho)$  and  $\xi_{N,2}(T, \rho)$ , valid when  $\rho \rightarrow 0$  by using Meeron's result for  $g_{\sigma\tau}(r)$ . In addition, we examine the dominant poles of  $S_{NN}(k)$  which yield the *true density correlation length*  $\xi_{N,\infty}(T, \rho)$  that determines the Ornstein-Zernike-like exponential decay of  $h_N(r)$  [7]. We also calculate the corresponding second and fourth moment charge-charge correlation lengths  $\xi_{Z,1}(T, \rho)$  and  $\xi_{Z,2}(T, \rho)$  from the charge-charge structure factor

$$S_{ZZ}(k; T, \rho) = 1 + \rho \hat{h}_Z(k; T, \rho) = \xi_{Z,1}^2 k^2 - \xi_{Z,2}^4 k^4 + O(k^6), \quad (1.9)$$

where the charge-charge correlation function for the RPM is given by the difference

$$h_Z(r) = \frac{1}{2}[g_{++}(r) - g_{+-}(r)] = \frac{1}{4} \sum_{\sigma, \tau} z_{\sigma} z_{\tau} h_{\sigma, \tau}(r). \quad (1.10)$$

The vanishing of  $S_{ZZ}(k)$  when  $k \rightarrow 0$  reflects electroneutrality, while  $\xi_{Z,1}^2$  is predicted by the well known second moment or Stillinger-Lovett condition [8]. Note that the dominant poles of  $S_{ZZ}(k)$  yield the true screening length,  $\xi_{Z,\infty} \equiv \kappa_{\infty}^{-1}(T, \rho)$ , which determines the exponential decay of the *charge* correlations [7].

Finally, we calculate the *first* moment charge-charge correlation length using the appropriate generalization of Eq. (1.9) for the odd moments, namely,

$$\xi_L(T, \rho) \equiv \xi_{Z,1/2} \equiv -\frac{1}{2} \int |\mathbf{r}| \rho h_Z(r) d\mathbf{r}. \quad (1.11)$$

This was shown by Martin and Yalcin [9] to relate to the charge fluctuations  $\langle Q_{\Lambda}^2 \rangle$  in a large subdomain  $\Lambda$ , which, as a consequence of screening and charge neutrality, grow like the *area*  $|\partial\Lambda|$  rather than the volume  $|\Lambda|$  [9]. Lebowitz [10] interpreted this by supposing the ions form neutral clusters of a characteristic linear dimension which we call [11] the ‘‘Lebowitz length’’  $\xi_L(T, \rho)$ . Then net charge fluctuations in  $\Lambda$  arise only when a neutral cluster is ‘‘cut’’ by the boundary  $\partial\Lambda$ . Provided the clusters have no long-range correlations, one may thus expect

$$\langle Q_{\Lambda}^2 \rangle / |\partial\Lambda| \approx \frac{1}{2} \rho q_0^2 \xi_L(T, \rho), \quad (1.12)$$

where the normalization has been chosen [11] so that Lebowitz's conjecture [10] that  $\xi_L$  should be identified with the Debye length  $\xi_D$  proves valid for the RPM when  $\rho \rightarrow 0$ .

Noting that  $\rho h_Z(r)$  in Eq. (1.11) is essentially the inverse Fourier transform of  $S_{ZZ}(k)$ , one can show [9(c)] that the Lebowitz length is also given by

$$\xi_L(T, \rho) = \frac{2}{\pi} \int_0^{\infty} \frac{dk}{k^2} S_{ZZ}(k), \quad (1.13)$$

where the convergence of the integral at the lower limit is ensured by  $S_{ZZ}(k) \sim k^{\epsilon}$  with  $\epsilon > 1$  as embodied in Eq. (1.9).

## B. Relevance to ionic criticality

By way of motivation, let us review briefly how knowledge of the exact low-density expressions for these correlation lengths may contribute to our understanding of the *anomalous criticality* observed in some electrolyte solutions. An unresolved problem is understanding the possible cross-over behavior from classical (or van der Waals) to Ising-type criticality when the reduced temperature deviation from criticality,  $t = |T - T_c|/T_c$ , approaches zero. Certain systems dis-

play pure Ising criticality [12], others exhibit crossover at scales  $t_\times \sim 10^{-1.5}-10^{-2.5}$  [13,14] and, in some cases, reveal no hint of Ising character [15]. For example, the system triethylhexylammonium triethylhexylboride ( $\text{N}_{2226}\text{B}_{2226}$ ) in diphenyl ether [15] has displayed classical critical exponents down to  $t \sim 10^{-4}$ , and is also one that appears to best approximate the RPM. Thus, an important theoretical challenge of deciding the universality class (and crossover scale  $t_\times$  if appropriate) of the RPM remains [16,17].

To understand the behavior of any system near a critical point, one must study the order parameter fluctuations. The primary order parameter for ionic fluids is simply the overall number density of ions,  $\rho$ . The original DH theory [1] and its extensions [17] shed light on the charge-charge correlations, but say essentially nothing about the overall density-density correlations. Recently, however, Lee and Fisher [14] generalized DH theory to *nonuniform* ion densities thereby deriving a free-energy functional of  $\rho(r)$ . This GDH theory then yields (approximate) density correlations via functional differentiation. In particular, Lee and Fisher calculated the second moment density correlation length  $\xi_{N,1}(T, \rho)$  for the RPM which they found exhibited a novel, universal divergence for all  $T$  when  $\rho \rightarrow 0$ . In the critical region, the prediction was  $\xi_{N,1}(\rho_c, T) \approx \xi_0^+ / t^{1/2}$  for  $t \rightarrow 0+$ , as expected for a mean field theory. Using this latter result, Fisher and Lee [18] were able to implement the Ginzburg criterion for classical critical behavior. Indeed, the Ginzburg temperature  $t_G$  ( $\sim t_\times$ ) was explicitly evaluated but was found to be similar in magnitude to that derived for simple fluids using a comparable approach. Their analysis thus suggested that the RPM exhibits little if any classical behavior. If that is correct, the explanation of the experiments must be sought in new directions.

Other approaches to deriving a Landau-Ginzburg free-energy functional for the RPM [19,20] from which  $\xi_0^+$  and  $t_G$  can be extracted [17] have also been reported. Leote de Carvalho and Evans [19] used a generalized mean-spherical approximation (GMSA) which repairs the simple MSA (for which the critical density fluctuations remain bounded!) by adding to the direct correlation function a term with parameters which are adjusted to satisfy various sum rules; then  $\xi_{N,1}$  diverges at criticality, and  $\xi_0^+$  can be estimated. Weiss and Schröer [20] followed a procedure similar to that originally proposed by van der Waals in the theory of surface tension: however, they replaced the original square-gradient term by one derived from the pair distribution function predicted by DH theory. Both these theories exhibit serious defects. In particular, as suggested by Fisher and Lee [14,18] and confirmed by the exact calculations reported here, the density correlation length  $\xi_{N,1}(\rho, T)$  predicted by the GMSA [19] and by the Weiss-Schröer approach [20] prove to be significantly in error at low densities: the former has a completely incorrect dependence on  $T$  and  $\rho$  ( $\rightarrow 0$ ); the latter yields the correct form (see below), as does the GDH approach [14], but the numerical amplitude is in error by a factor of about 5.7. Now the critical density of the RPM appears to be rather small ( $\rho_c^* \equiv \rho_c a^3 \approx 0.03-0.08$ : see Ref. [16(b)]); furthermore, the Ginzburg temperature  $t_G$  ( $\sim t_\times$ ) varies as  $(a/\xi_0^+)^6$ . Consequently, an error by a factor of 5.7

in estimating the amplitude of  $\xi_{N,1}$  at low densities suggests that the Weiss-Schröer estimate of  $t_G$  [20] may well be in error by a few orders of magnitude. Conversely, the GDH theory [14] also yields the *exact* low-density amplitude for  $\xi_{N,1}$ , and so seems likely to be more reliable in the critical region [18,20(c)].

### C. Meeron's expression and its analysis

We calculate the correlation lengths  $\xi_{N,1}$  and  $\xi_{N,2}$  from Meeron's expressions for  $g_{\sigma\tau}(r)$ ; thus in Sec. II, we briefly review Meeron's derivation, which yields

$$g_{\sigma\tau}(|\mathbf{r}|; T, \rho) = g_{\sigma\tau}^D(r; T, \rho) [1 + \eta_{\sigma\tau}(r; T, \rho) + \mathcal{E}_{\sigma\tau}(r; T, \{\rho_\sigma\})], \quad (1.14)$$

where the leading factor, which may be regarded simply as the DH approximation for the correlation functions, is

$$g_{\sigma\tau}^D(\mathbf{r}; T, \rho) = \exp[-\beta u_{\sigma\tau}^\dagger(\mathbf{r}) + w_{\sigma\tau}^D(\mathbf{r})], \quad (1.15)$$

in which the hard-core potentials for the RPM (but, more generally, the short-range potentials) are just

$$u_{\sigma\tau}^\dagger(\mathbf{r}) = u^\dagger(\mathbf{r}) = \infty, \quad r < a \\ = 0, \quad r \geq a, \quad (1.16)$$

while the ionic coupling enters through

$$w_{\sigma\tau}^D(\mathbf{r}; T, \rho) = -z_\sigma z_\tau b e^{-\kappa_D r / r}, \quad (1.17)$$

which is just the Debye-Hückel screened Coulomb interaction: recall Eqs. (1.1)–(1.3).

Now, to express  $\eta_{\sigma\tau}(\mathbf{r})$  in Eq. (1.14), Meeron [5,21] formulated integral kernels  $\eta_{\sigma\tau, \nu \dots}^{(n)}(\mathbf{r}; \mathbf{r}_1, \dots, \mathbf{r}_n)$  in diagrammatic terms. With the notation

$$h_{\sigma\tau}^D(\mathbf{r}) = g_{\sigma\tau}^D(\mathbf{r}) - 1, \quad (1.18)$$

the first- and second-order kernels may be written

$$\eta_{\sigma\tau, \nu}^{(1)}(\mathbf{r}, \mathbf{r}') = h_{\sigma\nu}^D(\mathbf{r} - \mathbf{r}') h_{\nu\tau}^D(\mathbf{r}') - w_{\sigma\nu}^D(\mathbf{r} - \mathbf{r}') w_{\nu\tau}^D(\mathbf{r}'), \quad (1.19)$$

$$\eta_{\sigma\tau, \nu\mu}^{(2)}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') = w_{\sigma\nu}^D(\mathbf{r}') f_{\nu\mu}^\dagger(\mathbf{r}'' - \mathbf{r}') w_{\mu\tau}^D(\mathbf{r} - \mathbf{r}'') \\ + \frac{1}{2} w_{\sigma\nu}^D(\mathbf{r}') [1 + f_{\nu\mu}^\dagger(\mathbf{r}'' - \mathbf{r}')] \\ \times [w_{\nu\mu}^D(\mathbf{r}'' - \mathbf{r}')]^2 w_{\mu\tau}^D(\mathbf{r} - \mathbf{r}'), \quad (1.20)$$

where the short-range Mayer  $f$  bond (for the hard-core potential) is

$$f_{\sigma\tau}^\dagger(\mathbf{r}) = f^\dagger(\mathbf{r}) = e^{-\beta u^\dagger(\mathbf{r})} - 1. \quad (1.21)$$

Then in Eq. (1.14) we have

$$\eta_{\sigma\tau}(\mathbf{r}; T, \rho) = \sum_{\nu} \rho_{\nu} \int d\mathbf{r}' \eta_{\sigma\tau, \nu}^{(1)}(\mathbf{r}; \mathbf{r}') + \sum_{\nu, \mu} \rho_{\nu} \rho_{\mu} \int d\mathbf{r}' \int d\mathbf{r}'' \eta_{\sigma\tau, \nu\mu}^{(2)}(\mathbf{r}; \mathbf{r}', \mathbf{r}''). \quad (1.22)$$

Finally,  $\mathcal{E}_{\sigma\tau}(r; T, \{\rho_{\sigma}\})$  is a ‘‘remainder’’ function formally of order  $\rho^3$ , whose specific character when  $\rho$  becomes small is discussed in Sec. II: see also below Eq. (1.24).

In Sec. III, we derive  $S_{NN}(k)$  for the RPM by taking the Fourier transform of Eq. (1.14) and using Eqs. (1.4)–(1.7). By employing the convolution theorem, we first write  $\hat{h}_{\sigma\tau}(k)$ , explicitly in terms of  $\hat{h}_{\sigma\tau}^D(k)$ ,  $\hat{w}_{\sigma\tau}^D(k)$ , and  $\hat{f}^{\dagger}(k)$ . Then, by expanding the exponential defining  $h_{\sigma\tau}^D(\mathbf{r})$  in powers of  $w_{\sigma\tau}^D(\mathbf{r})$  and taking the Fourier transform of each term, we show that  $\hat{h}_{\sigma\tau}^D(k)$  may be written in terms of  $\hat{f}^{\dagger}(k)$  plus an infinite series of exponential integrals (or incomplete gamma functions) [22]. Finally, to find  $\hat{h}_N(k)$ , we calculate the sums over the species  $\sigma$ ,  $\tau$ ,  $\nu$ , and  $\mu$ . Using the result for  $\hat{h}_N(k)$  obtained in Eq. (3.30), we find that  $S_{NN}(k)$  takes the simple form

$$S_{NN}(k) = [1 - \rho \hat{h}_N^D(k)]^{-1} + \tilde{\mathcal{E}}_N(k \xi_D; T, \rho), \quad (1.23)$$

where the density-density DH correlation function is defined via Eqs. (1.18) and (1.15) as

$$h_N^D(r) = \frac{1}{2} [h_{++}^D(r) + h_{+-}^D(r)], \quad (1.24)$$

while  $\tilde{\mathcal{E}}_N(s; T, \rho)$  is a remainder function derived from  $\mathcal{E}_{\sigma\tau}(r; T, \rho)$  with some additional terms, which, in orders  $s^0$ ,  $s^2$ , and  $s^4$ , behaves as  $\rho^{3/2}(\ln \rho)^j$  when  $\rho \rightarrow 0$ , where  $j$  is a small integer; but recall, also, that  $\xi_D \sim \rho^{-1/2}$  as  $\rho \rightarrow 0$ .

Following a similar procedure, we are able to calculate  $S_{ZZ}(k)$  in terms of  $\hat{h}_Z^D(k)$ , the Fourier transform of the DH difference or charge correlation function

$$h_Z^D(r) = \frac{1}{2} [h_{++}^D(r) - h_{+-}^D(r)]. \quad (1.25)$$

However, we now find that we lose precision by a factor of order  $\rho^{1/2}$ . Explicitly, the Stillinger-Lovett (SL) zeroth and second moment sum rules, that specify  $S_{ZZ}(0) = 0$  and  $\xi_{Z,1}$ , are satisfied only up to errors of relative order  $\rho \ln \rho$  in the density. Consequently, our expression for  $\xi_{Z,2}$  will be valid only up to the same relative order. Moreover, to determine the Lebowitz length from Eq. (1.13) we need an expression for  $S_{ZZ}(k)$  which satisfies the electroneutrality condition to all orders in the density. To overcome these difficulties we appeal to the well known hypernetted chain (HNC) resummation [23] which, as we now indicate, resolves these problems and provides a higher-order precision.

#### D. HNC and Meeron resummations (HNCM)

It has been shown [24] that the zeroth and second moment SL sum rules can be derived from the Ornstein-Zernike (OZ) relation [25]

$$h_{\sigma\tau}(r) = c_{\sigma\tau}(r) + \sum_{\nu} \rho_{\nu} \int c_{\sigma\nu}(|\mathbf{r} - \mathbf{r}'|) h_{\nu\tau}(r') d\mathbf{r}', \quad (1.26)$$

by assuming that the direct correlation function takes the form

$$c_{\sigma\tau}(r) = -\frac{\beta z_{\sigma} z_{\tau} q_0^2}{Dr} + c_{\sigma\tau}^0(r), \quad (1.27)$$

where  $c_{\sigma\tau}^0(r)$  is short ranged and its Fourier transform  $\hat{c}_{\sigma\tau}^0(k)$  possesses an expansion in powers of  $k$ . Indeed, the expression for the direct correlation function derived by the HNC resummation [23] takes a similar form, namely,

$$c_{\sigma\tau}(r) = -\beta v_{\sigma\tau}(r) + h_{\sigma\tau}(r) - \ln[1 + h_{\sigma\tau}(r)] + b_{\sigma\tau}(r), \quad (1.28)$$

where the total (reduced) potential is

$$\beta v_{\sigma\tau}(r) = z_{\sigma} z_{\tau} (b/r) + \beta u^{\dagger}(r), \quad (1.29)$$

while  $b_{\sigma\tau}(r)$  is represented graphically by a sum over all bridge diagrams.

Inserting Meeron’s expansion (1.14) into Eq. (1.28) and using Eq. (1.6) yields an explicit, exact expression for the short-range parts of the direct correlation function, namely,

$$c_{\sigma\tau}^0(r) = h_{\sigma\tau}^D(r) - w_{\sigma\tau}^D(r) + \mathcal{R}_{\sigma\tau}(r), \quad (1.30)$$

where the remainder function is

$$\begin{aligned} \mathcal{R}_{\sigma\tau}(r) &= h_{\sigma\tau}^D(r) [\eta_{\sigma\tau}(r) + \mathcal{E}_{\sigma\tau}(r)] + b_{\sigma\tau}(r) \\ &\quad - \sum_{n=2}^{\infty} (-1)^n [\eta_{\sigma\tau}(r) + \mathcal{E}_{\sigma\tau}(r)]^n / n. \end{aligned} \quad (1.31)$$

In Appendix A we bound the leading contributions to  $\mathcal{R}_{\sigma\tau}(r)$ , namely,  $h_{\sigma\tau}^D(r) \eta_{\sigma\tau}(r)$ ; in Appendix B we bound the leading bridge-diagram contribution to  $b_{\sigma\tau}(r)$  [26,27] and the leading contribution to the sum in Eq. (1.31), namely,  $[\eta_{\sigma\tau}(r)]^2$ . We find that  $\mathcal{R}_{\sigma\tau}(r)$  contributes up to relative order  $\rho^{3/2}(\ln \rho)^j$  and higher, and can, therefore, be neglected in our analysis.

Equations (1.27) and (1.30) [neglecting  $\mathcal{R}_{\sigma\tau}(r)$ ] constitute the HNC Meeron (HNCM) result for the direct correlation function, which, along with the OZ relation (1.26), allow us to calculate  $S_{NN}(0)$ ,  $\xi_{Z,1}$ ,  $\xi_{Z,2}$ , and  $\xi_L$  exactly up to errors of relative order  $\rho^{3/2}(\ln \rho)^j$ , and  $\xi_{N,1}$  and  $\xi_{N,2}$  up to order  $\rho \ln \rho$ .

In Sec. III D we show that the HNCM result for  $S_{NN}(k)$  agrees precisely with that derived by the ‘‘Meeron only’’ approach recorded in Eq. (1.23). Section IV considers the charge-charge structure factor for the RPM and establishes the simple form

$$1/S_{ZZ}(k) = (\kappa_D/k)^2 + 1 - \rho[\hat{h}_Z^D(k) - \hat{w}_Z^D(k) + \hat{\mathcal{R}}_Z(k)], \quad (1.32)$$

where the charge-charge Debye correlation function  $h_Z^D(r)$  is defined in Eq. (1.25), and  $w_Z^D(r)$  and  $\mathcal{R}_Z(r)$  are defined analogously via Eqs. (1.17) and (1.31). Finally, note that Eq. (1.32) satisfies both the zeroth and second moment SL relations to all orders in the density even when  $\hat{\mathcal{R}}_Z(k)$  is neglected.

It is, perhaps, worth recalling that the HNC *approximation* [23–25] is an integral equation for the  $h_{\sigma\tau}(r)$  or, equivalently, for the  $c_{\sigma\tau}(r)$ , obtained by combining Eq. (1.26) with Eq. (1.28) and neglecting the bridge functions  $b_{\sigma\tau}(r)$ . What we here call the HNCM procedure has some resemblance to a first iteration of the HNC approximation in which, initially,  $h_{\sigma\tau}(r)$  is neglected in Eq. (1.28), and Eq. (1.26) is used to obtain a first nontrivial approximation for  $h_{\sigma\tau}$  which, in turn, is then used in Eq. (1.28). However, because of the density ordering that we (and Meeron) employ, the suggested correspondence is not precise. Furthermore, in extending our results to encompass *nonsymmetric, multicomponent* primitive models [11], even though only to the *same* orders in density as obtained here, it proves essential to retain a leading bridge diagram contribution [and also to allow for a (2,1,2) chain not included by Meeron in his truncation].

### E. Overview of results

Using our results for  $\hat{h}_{\sigma\tau}(k)$  and  $S_{NN}(k)$  we derive, in Sec. III,  $\xi_{N,1}$  and  $\xi_{N,2}$  by expanding in powers of  $k$ . Thus we obtain the exact expressions

$$\begin{aligned} \xi_{N,1}(T, \rho) &= \left( \frac{b}{48\kappa_D} \right)^{1/2} \left[ 1 + \frac{1}{8} \kappa_D b + O(\rho \ln^j \rho) \right] \\ &\approx \frac{1}{4} \left( \frac{b}{36\pi\rho} \right)^{1/4}, \end{aligned} \quad (1.33)$$

$$\begin{aligned} \xi_{N,2}(T, \rho) &= \left( \frac{b}{320\kappa_D^3} \right)^{1/4} \left[ 1 + \frac{7}{72} \kappa_D b + O(\rho \ln^j \rho) \right] \\ &\approx \frac{b^{-1/8}}{4(10)^{1/4}(\pi\rho)^{3/8}}, \end{aligned} \quad (1.34)$$

for the second and fourth moment correlation lengths, respectively. (Recall, that, here and below,  $j$  is a small integer.) Evidently, both correlation lengths diverge when  $\rho \rightarrow 0$ , but with different laws, namely, as  $1/(T\rho)^{1/4}$  and  $(T/\rho^3)^{1/8}$ , respectively. Furthermore, both amplitudes are *universal* in that they do not depend on the short-range potential  $u_{\sigma\tau}^\dagger(\mathbf{r})$ ,

which enters, here, only through the hard-core diameter  $a$ . The divergence of  $\xi_{N,1}(\rho)$  and  $\xi_{N,2}(\rho)$  when  $\rho \rightarrow 0$  is reminiscent of the divergence of density fluctuations at a critical point [16(a)]. Note that these divergences are much weaker than that of the charge-charge correlation length which (see below) is asymptotically determined by  $\xi_D \sim (T/\rho)^{1/2}$ .

Result (1.33) for  $\xi_{N,1}(T, \rho)$  precisely confirms the prediction of GDH theory *up* to the correction term shown: see Eq. (10) of Ref. [14(a)]. The leading correction term in GDH theory is proportional to  $(\kappa_D a)^2 \sim \rho a^2/T$ , which is clearly nonuniversal; the exact correction term in Eq. (1.33) is, no doubt, also nonuniversal but we have not calculated it from Meeron’s analysis. On the other hand, it transpires that the GDH analysis also yields the form (1.34) of  $\xi_{N,2}(T, \rho)$  as  $\rho \rightarrow 0$  [14(b)]. Indeed, following Lee and Fisher [14], we note that the leading terms of the HNC approximation for the direct correlation function (see, e.g., Ref. [25]), namely,

$$c_{ij}(\mathbf{r}) \approx -\beta u_{ij}(\mathbf{r}) + \frac{1}{2} h_{ij}^2(\mathbf{r}) + \dots, \quad (1.35)$$

with  $u_{ij}(\mathbf{r}) = u_{ij}^\dagger(\mathbf{r}) + \varphi_{ij}(\mathbf{r})$ , lead to

$$S_{NN}(k) \approx [1 - \frac{1}{4} \kappa_D b s(k/2\kappa_D)]^{-1}, \quad s(y) = (\tan^{-1} y)/y, \quad (1.36)$$

if one uses the DH form [Eq. (1.15)] as an approximation for long distances and low densities. On expansion in powers of  $k$  and use of Eq. (1.8), this leads *precisely* to Eqs. (1.33) and (1.34) [excluding only the  $O(\rho \ln \rho)$  terms]. This further suggests the general asymptotic behavior

$$\xi_{N,n}^{2n}(T, \rho) \approx b/8(2n+1)(2\kappa_D)^{2n-1} \quad (1.37)$$

for  $\rho \rightarrow 0$ , which we believe is correct since the analysis described in connection with Eqs. (3.38) and (3.39) below indicates that the error terms in Eq. (1.36) will contribute only to higher order in  $\rho$ .

As a further check, we have verified that our result (1.23) for  $S_{NN}$  leads via the sum rules [25] to the reduced isothermal compressibility correct up to the second-virial level, namely,

$$\begin{aligned} S_{NN}(0) &= 1 + \frac{1}{4} \kappa_D b + \frac{1}{16} (\kappa_D b)^2 \\ &+ 4\pi\rho a^3 \sum_{m=0}^{\infty} \frac{(T^*)^{-2m}}{(2m)!(2m-3)} + O(\rho^{3/2}(\ln \rho)^j), \end{aligned} \quad (1.38)$$

which agrees with the reduced compressibility calculated from the known low density expansion of the free energy for the RPM [4,28]. It is remarkable that the leading nonuniversal form of the second-virial corrections follows just from the DH forms (1.15)–(1.17). For completeness we quote the expansion for  $1/S_{NN}(0)$  which *includes* the  $O(\rho^{3/2} \ln \rho)$  term omitted in Eq. (1.38): this follows from Haga’s analysis [4] as

$$\begin{aligned} \frac{1}{S_{NN}(0)} &= 1 - \frac{1}{4}\kappa_D b - 4\pi\rho a^3 \sum_{m=0}^{\infty} \frac{(T^*)^{-2m}}{(2m-3)(2m)!} - \frac{5}{4}\pi\kappa_D\rho b^4 [\ln(4\kappa_D a) + \gamma_E - \frac{7}{15}] - \frac{15}{16}\kappa_D^3 a^3 / T^* \\ &+ \frac{15}{4}\pi\kappa_D b \rho a^3 \sum_{m=2}^{\infty} \frac{(T^*)^{-2m-1}}{(m-1)(2m+1)!} + O(\rho^2(\ln \rho)^j), \end{aligned} \quad (1.39)$$

and confirms Meeron's conclusions as to the order of the residual term in Eqs. (1.23) and (1.38).

Using our results for  $\hat{c}_{\sigma\tau}(k)$  and  $S_{ZZ}(k)$  we derive, in Sec. IV,  $\xi_{Z,1}$  and  $\xi_{Z,2}$  by expanding in powers of  $k$ , and also  $\xi_L$  by evaluating the integral (1.13). Thus we obtain the exact expressions

$$1/\xi_{Z,1}(T, \rho) = \kappa_D, \quad (1.40)$$

$$\begin{aligned} 1/\xi_{Z,2}(T, \rho) &= \kappa_D \left\{ 1 + \frac{1}{8}x^2 + \frac{1}{24}(\kappa_D b)^2 \right. \\ &\times [\ln x + e_2 - Y(T^*)] + O(\rho^{3/2} \ln^j \rho) \left. \right\}, \end{aligned} \quad (1.41)$$

$$\begin{aligned} \xi_L(T, \rho) &= \kappa_D^{-1} \left\{ 1 + \frac{1}{4}x^2 + \frac{1}{12}(\kappa_D b)^2 \right. \\ &\times [\ln x + e_L - Y(T^*)] + O(\rho^{3/2} \ln^j \rho) \left. \right\}, \end{aligned} \quad (1.42)$$

where  $x = \kappa_D a$  and, employing Euler's constant  $\gamma_E \approx 0.57721 \dots$ , the coefficients are

$$e_2 = \gamma_E + \ln 3 \approx 1.67583, \quad (1.43)$$

$$e_L = \gamma_E + \ln 4 \approx 1.96351. \quad (1.44)$$

Note that the leading *nonuniversal* corrections can be calculated (although we have been unable to do this for the density correlation lengths): explicitly one finds

$$Y(T^*) = 6 \sum_{n=3}^{\infty} (T^*)^{4-2n} / (2n-4)(2n-1)! \quad (1.45)$$

Not surprisingly Eqs. (1.41) and (1.42) do *not* confirm the GDH approximation [29] beyond leading order since this cannot generate the leading  $\kappa_D^2 \ln x \sim \rho \ln \rho$  term. We discuss the GDH results for  $S_{ZZ}(k)$ ,  $\xi_{Z,1}$ ,  $\xi_{Z,2}$ , and  $\xi_L$  further in Sec. IV.

Finally, in Sec. V, we compare our results in more detail with those derived from the correlation-function calculations of Kjellander and Mitchell (KM) [27], who evaluated the leading order bridge-diagram corrections to the HNC predictions at long distances. The main focus of the careful KM analysis was, in fact, on the nature of the long-range *decay* of the correlation functions at low densities. In particular, they

determined the true correlation length  $\xi_{Z,\infty} \equiv 1/\kappa_\infty$  for the screening of the charge-charge correlation functions finding, generally,

$$\begin{aligned} \frac{\kappa_\infty^2}{\kappa_D^2} &\approx 1 + \frac{\kappa_D b \ln 3}{4} \left[ \frac{\sum_{\sigma} z_{\sigma}^3 c_{\sigma}}{\sum_{\sigma} z_{\sigma}^2 c_{\sigma}} \right]^2 \\ &+ \frac{(\kappa_D b)^2 \ln(\kappa_D b)}{6} \left[ \frac{\sum_{\sigma} z_{\sigma}^4 c_{\sigma}}{\sum_{\sigma} z_{\sigma}^2 c_{\sigma}} \right]^2 + \dots, \end{aligned} \quad (1.46)$$

where the  $c_{\sigma} = \rho_{\sigma}/\rho$  are the relative concentrations or, equivalently, the stoichiometric coefficients. (See KM, Eq. (150), in Ref. [27(a)].) In the case of the RPM, the first correction term here vanishes by symmetry and the second squared factor reduces to unity. KM wrote a correction term in Eq. (1.46) of order  $(\kappa_D b)^2$ , but this is an oversight to the extent that nonuniversal terms entailing  $\kappa_D a$  actually arise as, in fact, KM mention in their subsequent discussion.

The KM formulation can also be used to study the decay of the density correlation function  $h_N(r; T, \rho)$  [see Eq. (1.5)]. The corresponding true correlation length is found to satisfy

$$\xi_{N,\infty} = \frac{1}{2} \xi_{Z,\infty} [1 + 2 \exp(-8/\kappa_D b) + \dots], \quad (1.47)$$

where the argument of the exponential neglects corrections of relative order  $\rho^{1/2}$ , while the additive terms are of order  $e^{-16/\kappa_D b}$ . This result also confirms the predictions of the GDH theory in leading order except insofar as the exact result (1.46) for  $\xi_{Z,\infty}$  is replaced in Eq. (12) of Ref. [14(a)] by the leading behavior  $\xi_D = \kappa_D^{-1}$ . As remarked in Ref. [14(a)], this result means that the density-density correlation function  $h_N(r)$  decays as  $e^{-r/\xi_{N,\infty}}/r$  which is slightly *more slowly* than  $e^{-2\kappa r/r^2}$ , the square of the charge-charge correlation function decay [27]: however, the associated amplitude should vanish as  $\rho \rightarrow 0$ .

Although KM mainly addressed the long-distance correlation decay, their incidental low-density results, specifically for the Fourier transform  $\hat{c}_{\sigma\tau}(k; T, \rho)$  of the direct correlation function, can be used to examine the correlation lengths  $\xi_{N,1}$  and  $\xi_{N,2}$  by expanding in powers of  $k$ . These KM results lack the short-distance contributions of the bridge function, and are not claimed to be correct to a specific order in the density (in contradistinction to Meeron's results [4,21]). However, to the leading orders in the density that we have evaluated, the

formal results of KM agree precisely with our results. Once again, then, the validity of the GDH treatment [14] at low densities is confirmed.

## II. RADIAL DISTRIBUTION FUNCTIONS

### A. Short-range diagrammatics

The diagrammatic analysis of the radial distribution functions,  $g_{\sigma\tau}(r)$ , presented by Meeron [5] is fairly complex, and a helpful overview (Ref. [21]) is not readily accessible. For our purposes, it is also useful to understand the origin of the basic results quoted in Eqs. (1.14)–(1.22). Accordingly, here we present a brief review and, in particular, discuss the character of the error function  $\mathcal{E}_{\sigma\tau}(r; T, \{\rho_\sigma\})$  in Eq. (1.14).

Meeron's starting point, following Mayer [3], is a general multicomponent system with short-range interaction potentials  $u_{\sigma\tau}(\mathbf{r})$  and corresponding Mayer  $f$  functions

$$f_{\sigma\tau}(\mathbf{r}) = e^{-\beta u_{\sigma\tau}(\mathbf{r})} - 1. \quad (2.1)$$

One then has the density expansion

$$g_{\sigma\tau}(|\mathbf{r}|) = e^{-\beta u_{\sigma\tau}(\mathbf{r})} \left[ 1 + \sum_{\nu} \rho_{\nu} g_{\sigma\tau}^{(\nu)}(\mathbf{r}) + \sum_{\nu, \mu} \rho_{\nu} \rho_{\mu} g_{\sigma\tau}^{(\nu\mu)}(\mathbf{r}) + \dots \right], \quad (2.2)$$

in which the first-order coefficients are given by the cluster integrals

$$g_{\sigma\tau}^{(\nu)}(\mathbf{r}) = \int d\mathbf{r}' f_{\sigma\nu}(\mathbf{r}-\mathbf{r}') f_{\nu\tau}(\mathbf{r}'), \quad (2.3)$$

corresponding simply to a chain diagram of two  $f$  bonds with one field point,  $(\mathbf{r}'; \nu)$ , and two root points,  $(0; \sigma)$  and  $(\mathbf{r}; \tau)$ : see, e.g., Eq. (5.3.4) of Hansen and McDonald (HMc) [25] where the single-component case was described. The higher order coefficients  $g_{\sigma\tau}^{(\nu\mu)}, \dots$ , have corresponding diagrammatic representations as sums of cluster integrals: in second order there are five diagrams with two field points, the diagram of longest range being a simple chain of three  $f$  bonds: [HMc, Eq. (5.3.5)]. In general, each field point is associated with a factor  $\rho_{\mu}$  and must be connected to each root point via disjoint chains of  $f$  bonds.

For the RPM the pair potential is

$$u_{\sigma\tau}(\mathbf{r}) = u_{\sigma\tau}^{\dagger}(\mathbf{r}) + \varphi_{\sigma\tau}(r). \quad (2.4)$$

This is of long range and leads to divergent integrals in all the coefficients  $g_{\sigma\tau}^{(\nu)}(\mathbf{r}), \dots$ . To avert this problem Meeron, following Mayer, multiplied  $\varphi_{\sigma\tau}(r)$  by a convergence factor

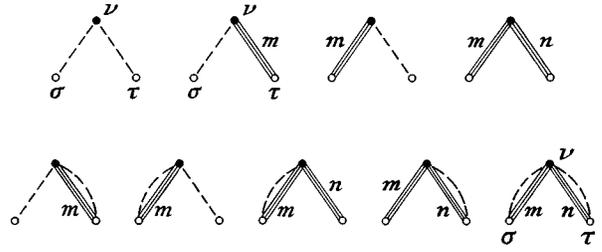


FIG. 1. The first-order coefficient for  $g_{\sigma\tau}(r)$  expanded diagrammatically in terms of  $f^{\dagger}$  bonds (dashed lines) and  $q^m$  bonds (triple lines) where  $m=1,2,\dots$  and  $q_{\sigma\tau}(r) \equiv -\beta\varphi_{\sigma\tau}(r)e^{-\alpha r}$ . After resummation and the exclusion of diagrams with simple  $q$ -bond chains (see text), each individual  $q$  bond becomes a screened  $w_D$  bond.

$e^{-\alpha r}$ , rearranged the density expansion by summing chains of appropriate bonds, and, finally, took  $\alpha \rightarrow 0$ . Specifically, invoking Eq. (1.21), Meeron wrote

$$f_{\sigma\tau} = f_{\sigma\tau}^{\dagger} + (1 + f_{\sigma\tau}^{\dagger}) \sum_{n=1}^{\infty} q_{\sigma\tau}^n / n!, \quad (2.5)$$

$$q_{\sigma\tau}(r) = -\beta\varphi_{\sigma\tau}(r)e^{-\alpha r}. \quad (2.6)$$

Then each diagram of  $f$  bonds in the  $g_{\sigma\tau}$  expansion generates an infinite sum of diagrams of the same form but with each bond now being either an  $f^{\dagger}$  bond or a  $q^m$  bond (that carries a factor  $q_{\sigma\tau}^m$  with  $m=1, 2, \dots$ ) or a compound  $f^{\dagger}q^m$  bond. Figure 1 illustrates the nine graph types arising in first order: as usual, field points are denoted by solid circles, and root points by open circles (HMc).

### B. Resummation and truncation to $O(\rho)$

In the next step, Meeron excluded from consideration all diagrams containing simple  $q$ -bond chains (i.e., a sequence of one or more field points linked by  $q^1$  bonds). Thus, the fourth graph in Fig. 1 is excluded when  $m=n=1$  (but is retained if  $m$  or  $n$  exceeds unity). The remaining set of diagrams, say  $\Pi$ , can clearly be used to regenerate the full set of diagrams if each individual  $q$  bond is allowed to be replaced by all possible simple  $q$ -bond chains of lengths  $2, 3, \dots, q$  bonds. By employing the convolution properties of the explicit Fourier transforms of  $q_{\sigma\tau}(r)$ , Meeron was then able to sum over all the possible simple chains in any diagram of  $\Pi$ . At the end, the limit  $\alpha \rightarrow 0$  may be taken safely, leaving only rapidly decaying bond functions.

In total, the complete expansion for  $g_{\sigma\tau}(r)$  is now obtained from  $\Pi$  by replacing each individual  $q$  bond (in a  $q^m$  bond) by a screened Debye bond, or  $w_D$  bond, carrying the factor  $w_{\sigma\tau}^D(\mathbf{r}; T, \rho)$  as defined in Eq. (1.17). On reversing the steps leading to Eq. (2.5) one can collect infinite series of diagrams whose sum represents effective  $f$  bonds carrying factors  $f_{\sigma\tau}^{\text{eff}} \equiv h_{\sigma\tau}^D(\mathbf{r}; T, \rho)$  as defined in Eq. (1.18) with Eq. (1.15).



FIG. 2. Leading “unorderable” diagrams that are expected to contribute to  $g_{\sigma\tau}(r)$  only in orders  $\rho^{3/2}(\ln \rho)^j$  or higher.

At first sight this suggests that one can simply rewrite  $g_{\sigma\tau}(\mathbf{r})$  through the original expansion (2.2) but with an effective short-range interaction potential

$$u_{\sigma\tau}^{\text{eff}}(\mathbf{r}; T, \rho) = u_{\sigma\tau}^{\dagger}(\mathbf{r}) + z_{\sigma} z_{\tau} q_0^2 e^{-\kappa_D r} / D r \quad (2.7)$$

replacing  $u_{\sigma\tau}(\mathbf{r})$ . However, this appealing picture would entail diagrams with  $w_D$ -bond chains which have, in fact, already been included in performing the summations leading to  $w_{\sigma\tau}^D(\mathbf{r})$ . Consequently, Meeron chose to write  $g_{\sigma\tau}(r)$  in terms of  $u_{\sigma\tau}^{\text{eff}}(\mathbf{r})$  and the corresponding  $f$  bonds,  $f_{\sigma\tau}^{\text{eff}} \equiv h_{\sigma\tau}^D(\mathbf{r})$ , but to explicitly subtract off the overcounted diagrams containing  $w_D$  chains. Indeed, the zeroth order term of Meeron’s final expression (1.14) corresponds just to the leading factor in Eq. (2.2) with  $u_{\sigma\tau}$  replaced by  $u_{\sigma\tau}^{\text{eff}}$ . The first-order term, with kernel  $\eta_{\sigma\tau, \nu}^{(1)}(\mathbf{r}, \mathbf{r}'; T, \rho)$  given in Eq. (1.19), contains the anticipated product of two  $f^{\text{eff}}$  bonds but with a two-bond  $w_D$ -chain term subtracted.

The same general structure could have been embodied in Meeron’s expression for  $\eta_{\sigma\tau, \nu, \mu}^{(2)}$ : see Eq. (1.20). However, the formula presented includes only those diagrams with two field points that, after integration over  $\mathbf{r}'$  and  $\mathbf{r}''$ , contribute to  $g_{\sigma\tau}(r)$  up to and including the overall order  $\rho$ . The crucial point is that, on integration, the screening factors  $\exp(-\kappa_D |\mathbf{r}'|)$ , etc., typically lead to factors  $1/\kappa_D \propto 1/\rho^{1/2}$ , so that a given diagram may, in fact, contribute to terms of *lower* order than suggested by the number of its field points.

To check that no diagrams have been overlooked to order  $\rho$  in Eqs. (1.14) and (1.15), Meeron explicitly examined diagrams with an arbitrary number of points in which each field point is connected to no more than three others and also diagrams which are “orderable” in the sense that the corresponding integrals can be related directly to those deriving from diagrams with only two field points, as in Fig. 1. These further diagrams were found to contribute to  $g_{\sigma\tau}(r; T, \rho)$  terms of order at least  $\rho^{3/2}$  or, possibly,  $\rho^{3/2}(\ln \rho)^j$  ( $j = 1, 2, \dots$ ). These conclusions indicate the order of the error term  $\mathcal{E}_{\sigma\tau}$  in Eq. (1.14).

Meeron was actually unable to evaluate definitively the orders in  $\rho$  of various more highly connected diagrams that enter formally in orders  $\rho_{\lambda} \rho_{\mu} \rho_{\nu}$ , etc.: see Fig. 2; but he argued that these cannot contribute to orders below  $\rho^{3/2}(\ln \rho)^j$ . As a further test, he used Eq. (1.14) to calculate the osmotic pressure via the appropriate *virial relation* [25]. His result agrees with expressions derived purely from the thermodynamic expansions to the exactly known second-virial level: see Eq. (1.39), which, however, we derive here via the *compressibility relation* (which is available for a two-component electrolyte) [25].

It is also instructive to switch off the Coulomb interactions by letting  $z_{\sigma} \rightarrow 0$  in order to verify that the proper virial expansion for hard spheres is generated. In this limit we see

from Eq. (1.17) that  $w_{\sigma\tau}^D \rightarrow 0$  so that, by Eq. (1.20),  $\eta_{\sigma\tau, \nu, \mu}^{(2)}$  vanishes identically while Eqs. (1.15) and (1.19) yield

$$g_{\sigma\tau}^D(\mathbf{r}; T, \rho) \rightarrow e^{-\beta u_{\sigma\tau}^{\dagger}(\mathbf{r})}, \quad (2.8)$$

$$\eta_{\sigma\tau, \nu}^{(1)}(\mathbf{r}, \mathbf{r}') \rightarrow f_{\sigma\nu}^{\dagger}(\mathbf{r} - \mathbf{r}') f_{\nu\tau}^{\dagger}(\mathbf{r}'). \quad (2.9)$$

Comparison with Eqs. (2.2) and (2.3) confirms that the short-range expansion for  $g_{\sigma\tau}(r)$  is correctly reproduced to order  $\rho$  (which also corresponds to the second-virial coefficient in the pressure). Notice, however, that no contributions of order  $\rho^2$  are generated despite the apparent order of the third term in Eq. (1.14).

From our analysis of Meeron’s results for  $g_{\sigma\tau}(r; T, \rho)$ , we conclude that expressions (1.14)–(1.22) should be valid for the RPM up to corrections of order  $\rho^{3/2}(\ln \rho)^j$  at fixed  $r$  and  $T$  and, hence, equally when they are integrated over some bounded kernel  $\mathcal{K}(\mathbf{r})$  that decays *sufficiently rapidly* when  $r \rightarrow \infty$ . In our case, however, we take  $\mathcal{K}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}}$  and  $|\mathbf{r}|^n$  so as to obtain  $S_{NN}(k)$ , other Fourier transforms, and various moments. In such cases, as noted above, integration may lead to a loss of order of precision by factors  $1/\kappa_D \propto \rho^{-1/2}$ . Thus, as mentioned in Sec. I, we have used Meeron’s formulation for  $g_{\sigma\tau}(r)$  in the HNC resummation to obtain results for the correlation lengths which are valid up to corrections of order  $\rho^{3/2}(\ln \rho)^j$  or  $\rho \ln \rho$ .

### III. DENSITY-DENSITY STRUCTURE FACTOR

#### A. Symmetry considerations

Now we focus on the RPM, which enjoys a special symmetry beyond the obvious  $(+, -)$  symmetry yielding, e.g.,  $\rho_+ = \rho_- = \frac{1}{2}\rho$ . Specifically, if, as is certainly of interest [11], we assign three distinct hard-core diameters, namely,  $a_{++}$ ,  $a_{+-}$ , and  $a_{--}$ , the RPM has not only  $a_{++} = a_{--} = a$  but also  $a_{+-} = a$ ; see Eq. (1.16). Consequently, as stated in Eq. (1.21),  $f_{\sigma\tau}^{\dagger}$  is independent of  $\sigma$  and  $\tau$ . On the other hand, the DH potential  $w_{\sigma\tau}^D$ , defined in Eq. (1.17), depends on  $\sigma$  and  $\tau$  only through the factor  $z_{\sigma} z_{\tau} = \pm 1$ .

Consider now the  $\eta_{\sigma\tau, \nu, \mu}^{(2)}$  kernel defined in Eq. (1.20), and note that in the basic results (1.14) and (1.22) for the correlation functions, the indices  $\nu$  and  $\mu$  are summed over. The two terms in Eq. (1.20) thus yield contributions to  $h_{\sigma\tau}$  proportional to

$$S_1 = \sum_{\nu, \mu} z_{\sigma} z_{\nu} z_{\mu} z_{\tau} = z_{\sigma} z_{\tau} \left( \sum_{\nu} z_{\nu} \right)^2, \quad (3.1)$$

$$S_2 = \sum_{\nu, \mu} z_{\sigma} z_{\nu} (z_{\nu} z_{\mu})^2 z_{\mu} z_{\tau} = z_{\sigma} z_{\tau} \left( \sum_{\nu} z_{\nu}^3 \right)^2. \quad (3.2)$$

But both of these *vanish identically*. Consequently the  $\eta^{(2)}$  term in Eq. (1.20) makes *no* contribution to  $h_{\sigma\tau}(r)$  for the RPM. However, it will enter for a 1:1 electrolyte as soon as  $u_{+-}^{\dagger}(r)$  differs from  $u_{++}^{\dagger}(r)$  or  $u_{--}^{\dagger}(r)$  even if  $u_{++}^{\dagger}$

$=u_{-}^{\dagger}$  [11]. It remains to analyze the two leading terms in Eq. (1.14): no comparable simplification is implied for the  $\eta^{(1)}$  term in Eq. (1.19).

### B. Correlation functions in Fourier space

We calculate the density-density structure factor  $S_{NN}(k)$  by first computing the Fourier transforms  $\hat{h}_{\sigma\tau}(\mathbf{k})$  using Eqs. (1.14), (1.18), and (1.19). To that end, note the relations

$$\hat{g}_{\sigma\tau}^D(\mathbf{k}) = (2\pi)^3 \delta(\mathbf{k}) + \hat{h}_{\sigma\tau}^D(\mathbf{k}), \quad (3.3)$$

and, via the convolution theorem,

$$\int d\mathbf{r} g(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} \int d\mathbf{r}' h(\mathbf{r}-\mathbf{r}') j(\mathbf{r}') \\ = \int \frac{d\mathbf{k}'}{(2\pi)^3} \hat{g}(\mathbf{k}-\mathbf{k}') \hat{h}(\mathbf{k}') \hat{j}(\mathbf{k}'). \quad (3.4)$$

Thus we obtain the basic expression

$$\hat{h}_{\sigma\tau}(\mathbf{k}) = \hat{h}_{\sigma\tau}^D(\mathbf{k}) + \sum_{\nu} \rho_{\nu} [\hat{h}_{\sigma\nu}^D(\mathbf{k}) \hat{h}_{\nu\tau}^D(\mathbf{k}) - \hat{w}_{\sigma\nu}^D(\mathbf{k}) \hat{w}_{\nu\tau}^D(\mathbf{k})] \\ + \sum_{\nu} \rho_{\nu} \int \frac{d\mathbf{k}'}{(2\pi)^3} \hat{h}_{\sigma\tau}^D(\mathbf{k}-\mathbf{k}') [\hat{h}_{\sigma\nu}^D(\mathbf{k}') \hat{h}_{\nu\tau}^D(\mathbf{k}') - \hat{w}_{\sigma\nu}^D(\mathbf{k}') \hat{w}_{\nu\tau}^D(\mathbf{k}')] + \rho^{-1} \tilde{\mathcal{E}}_{\sigma\tau}(k\xi_D; T, \rho), \quad (3.5)$$

where for the RPM the symmetric sum of the error term  $\tilde{\mathcal{E}}_N(k\xi_D; T, \rho)$  is of order  $\rho^{3/2}(\ln \rho)^j$  at fixed  $k$  when  $\rho \rightarrow 0$ .

To handle the Fourier transforms it is convenient to use the dimensionless variables

$$x = \kappa_D a \quad \text{and} \quad q = ka, \quad (3.6)$$

and to analyze  $\hat{h}_{\sigma\tau}^D(\mathbf{k})$  via Eq. (1.15) by expanding in powers of  $w_{\sigma\tau}^D = -z_{\sigma} z_{\tau} b e^{-\kappa_D r}/r$ . We then find

$$\hat{w}_{\sigma\tau}^D(\mathbf{k}) = -4\pi a^3 z_{\sigma} z_{\tau} / T^* (x^2 + q^2), \quad (3.7)$$

and need to study the integrals

$$I_0(q; x) = \hat{f}^{\dagger}(q) / 4\pi a^3 = (q \cos q - \sin q) / q^3, \\ = -\frac{1}{3} + \frac{1}{30} q^2 - \frac{1}{840} q^4 + \dots, \quad (3.8)$$

$$I_1(q; x) = \frac{1}{q} \int_1^{\infty} \sin(qy) e^{-xy} dy, \\ = e^{-x} [\cos q + (x/q) \sin q] / (x^2 + q^2), \quad (3.9)$$

and, for  $n \geq 2$ ,

$$I_n(q; x) = \frac{1}{q} \int_1^{\infty} dy \sin(qy) e^{-nxy/y^{n-1}} \\ = \frac{1}{2iq} [E_{n-1}(nx - iq) - E_{n-1}(nx + iq)], \quad (3.10)$$

where the exponential integrals are given by [22]

$$E_n(v) = \int_1^{\infty} du e^{-uv} / u^n = v^{n-1} \Gamma(1-n, v), \quad (3.11)$$

for all  $n$ , with  $\Gamma(\alpha, v)$  the incomplete  $\lambda$  function. In terms of these integrals we have

$$\hat{h}_{\sigma\tau}^D(k) = 4\pi a^3 \sum_{n=0}^{\infty} \frac{1}{n!} I_n(q; x) \left( \frac{-z_{\sigma} z_{\tau}}{T^*} \right)^n. \quad (3.12)$$

Now employing Euler's constant  $\gamma_E = -\psi(1) \approx 0.5772 \dots$  and the logarithmic derivative of the gamma function

$$\psi(n) = \sum_{l=1}^{n-1} l^{-1} - \gamma_E, \quad (3.13)$$

the exponential integrals have the expansions [22]

$$E_n(v) = \frac{(-v)^{n-1}}{(n-1)!} [\psi(n) - \ln v] - \sum_{m=0}^{\infty} \frac{(-v)^m}{m!(m-n+1)!} \quad (3.14)$$

for  $n \geq 1$ , where the prime on the sum denotes omission of the formally infinite term which, in this case, corresponds to  $m = n - 1$ . For  $n \geq 2$  we can thus write

$$I_n(q; x) = \left[ A_{n-2} \left( \frac{q}{nx} \right) \ln(nx)^{-1} - B_n \left( \frac{q}{nx} \right) \right] \frac{(-nx)^{n-3}}{(n-2)!} \\ - \sum_{m=1}^{\infty} A_m \left( \frac{q}{nx} \right) \frac{(-nx)^{m-1}}{m!(m-n+2)!}, \quad (3.15)$$

where the momentum variable  $q/x = k/\kappa_D$  ( $\equiv ns$ ) enters via

$$A_n(s) = (1+s^2)^{n/2} \sin[n\bar{s}(s)]/s, \quad (3.16)$$

$$B_{n+2}(s) = \{\tilde{s} \cos(n\tilde{s}) + [\frac{1}{2} \ln(1+s^2) - \psi(n+1)] \sin(n\tilde{s})\} \tan^{-1} s = \tilde{s}(s) = s - \frac{1}{3}s^3 + \dots \quad (3.18)$$

$$\times (1+s^2)^{n/2}/s, \quad (3.17) \quad \text{For use later we quote the expansions}$$

where, for brevity, we write

$$A_n(s) = n - \binom{n}{3}s^2 + \binom{n}{5}s^4 + O(s^6), \quad (3.19)$$

$$B_n(s) = 1 - (n-2)\psi(n-1) + \left[ \binom{n-2}{3} \psi(n-1) - \frac{1}{2}n^2 + 3n - 4 \frac{1}{3} \right] s^2$$

$$- \left[ \binom{n-2}{5} \psi(n-1) - \frac{1}{24}n^4 + \frac{2}{3}n^3 - \frac{31}{8}n^2 + \frac{29}{3}n - 8 \frac{7}{10} \right] s^4 + O(s^6). \quad (3.20)$$

### C. Analysis of the density structure factor

To obtain  $S_{NN}(k)$  we now focus on calculating  $\hat{h}_N(k)$  by summing  $\hat{h}_{\sigma\tau}(k)$  over  $\sigma, \tau$ : see Eqs. (1.4) and (1.5). In addition, we consider the sum over the field point labeled  $\nu$  in Eq. (3.5). The leading term in Eq. (3.5), together with Eq. (3.7) and expansion (3.12), entails the valence sums

$$\mathcal{S}_{n,0,0} = \frac{1}{4} \sum_{\sigma,\tau} (z_\sigma z_\tau)^n = \frac{1}{2} [1 + (-1)^n]. \quad (3.21)$$

The second or  $\hat{h}^D \hat{h}^D$  term in Eq. (3.5) generates

$$\rho \mathcal{S}_{0,p,r} = \frac{1}{4} \sum_{\sigma,\tau,\nu} \rho_\nu (z_\sigma z_\nu)^p (z_\nu z_\tau)^r$$

$$= \frac{1}{4} \rho [1 + (-1)^p] [1 + (-1)^r], \quad (3.22)$$

since  $\rho_+ = \rho_- = \frac{1}{2}\rho$ . The third term, involving  $\hat{w}^D \hat{w}^D$ , entails only  $\rho \mathcal{S}_{0,1,1} = 0$  and so does not contribute to  $\hat{h}_N(k)$ . The fourth term, with three  $\hat{h}^D$  factors, yields

$$\rho \mathcal{S}_{n,p,r} = \frac{1}{4} \sum_{\sigma,\tau,\nu} \rho_\nu (z_\sigma z_\tau)^n (z_\sigma z_\nu)^p (z_\nu z_\tau)^r$$

$$= \frac{1}{4} \rho [1 + (-1)^{n+p} + (-1)^{p+r} + (-1)^{n+r}]. \quad (3.23)$$

Finally, the last term, containing  $\hat{h}^D \hat{w}^D \hat{w}^D$ , leads to

$$\rho \mathcal{S}_{n,1,1} = \frac{1}{4} \sum_{\sigma,\tau,\nu} \rho_\nu (z_\sigma z_\tau)^n (z_\sigma z_\nu) (z_\nu z_\tau)$$

$$= \frac{1}{2} \rho [1 + (-1)^{n+1}]. \quad (3.24)$$

Overall we thus find that the density-density structure factor takes the form

$$S_{NN}(k) = 1 + \rho \hat{h}_N^D(k) + [\rho \hat{h}_N^D(k)]^2 + \mathcal{R}_N^M(k), \quad (3.25)$$

where, recalling Eq. (3.6),

$$\hat{h}_N^D(k) = 4\pi a^3 \sum_{n=0}^{\infty} \left( \frac{\mathcal{S}_{n,0,0}}{n! (T^*)^n} \right) I_n(ka, \kappa_D a), \quad (3.26)$$

$$\mathcal{R}_N^M(k; T, \rho) = 8a^6 \rho^2 \left[ \sum_{n,p,r=0}^{\infty} \left( \frac{\mathcal{S}_{n,p,r}}{n! p! r! (-T^*)^{n+p+r}} \right) \int d\mathbf{q}' I_n(\mathbf{q} - \mathbf{q}') I_p(q') I_r(q') \right.$$

$$\left. - \sum_{n=0}^{\infty} \left( \frac{\mathcal{S}_{n,1,1}}{n! (-T^*)^{n+2}} \right) \int d\mathbf{q}' \frac{I_n(\mathbf{q} - \mathbf{q}')}{(x^2 + q'^2)^2} \right] + \tilde{\mathcal{E}}_N(k \xi_D; T, \rho), \quad (3.27)$$

while  $\mathcal{S}_{n,p,r}$  selects terms  $\hat{h}^D$  according to the simple rule

$$\mathcal{S}_{n,p,r} = 1 \quad \text{for } n, p, r \text{ all even or all odd} \\ = 0 \quad \text{otherwise.} \quad (3.28)$$

To extract  $\xi_{N,1}$  and  $\xi_{N,2}$  we now expand  $\hat{h}_N^D(k)$  in powers

of  $k$  and collect the contributions in  $\rho$  of lowest order using Eqs. (3.26), (3.8), and (3.15)–(3.20). This yields

$$\rho \hat{h}_N^D(k) = H_0 + H_2 k^2 + H_4 k^4 + O(k^6), \quad (3.29)$$

where the  $H_0$  term reproduces result (1.38) for  $S_{NN}(0)$  while

$$H_2 = \frac{-b}{48\kappa_D} - \frac{\kappa_D b^3}{576} - \frac{2\pi\rho a^5}{3} \sum_{n=0}^{\infty} \frac{1}{(2n)!(2n-5)(T^*)^{2n}} + O(\rho^{3/2} \ln \rho), \quad (3.30)$$

$$H_4 = \frac{b}{320\kappa_D^3} + \frac{b^3}{4^5 \times 90\kappa_D} + \frac{\kappa_D b^5}{6^4 \times 20^2} + \frac{\pi\rho a^7}{30} \sum_{n=0}^{\infty} \frac{1}{(2n)!(2n-7)(T^*)^{2n}} + O(\rho^{3/2} \ln \rho). \quad (3.31)$$

Thence we obtain

$$S_{NN}(0) \xi_{N,1}^2 = \frac{b}{3 \times 2^4 \kappa_D} + \frac{b^2}{3 \times 2^5} + O(\rho^{1/2} (\ln \rho)^j), \quad (3.32)$$

$$S_{NN}(0) \xi_{N,2}^4 = \frac{b}{5 \times 2^6 \kappa_D^3} + \frac{23b^2}{45 \times 2^8 \kappa_D^2} + O(\rho^{-1/2} (\ln \rho)^j), \quad (3.33)$$

which yield the results for  $\xi_{N,1}(T, \rho)$  and  $\xi_{N,2}(T, \rho)$  quoted in Eq. (1.33) and (1.34).

Note that we are limited to the orders in  $\rho$  shown here by our neglect of the contributions from the infinite set of graphs contributing to  $\tilde{\mathcal{E}}_N(k)$  in Eq. (3.27), which derives from  $\tilde{\mathcal{E}}_{\sigma r}(k)$  in Eq. (3.5). Indeed, from Meeron's analysis of  $g_{\sigma r}(r)$  we know that  $\hat{\mathcal{E}}_N(0)$  contributes to  $S_{NN}(0)$  in order  $\rho^{3/2} (\ln \rho)^j$ . Moreover, as indicated in Sec. II C, we find  $\tilde{\mathcal{E}}_N(k)$  contributes to  $S_{NN}(0) \xi_{N,1}^2$  and  $S_{NN}(0) \xi_{N,2}^4$  in orders  $\rho^{1/2} (\ln \rho)^j$  and  $\rho^{-1/2} (\ln \rho)^j$ , respectively. We also show in Appendix A that the integrals entering the remainder function  $\mathcal{R}_N^M$  in Eq. (3.27) do not contribute to  $S_{NN}(0)$ ,  $\xi_{N,1}$  and  $\xi_{N,2}$  to the orders in  $\rho$  displayed in Sec. I. We do this by studying the integrals

$$\Phi_{npr}(q; x) = \int d\mathbf{q}' I_n(\mathbf{q} - \mathbf{q}') I_p(q') I_r(q'), \quad (3.34)$$

defined via Eqs. (3.8)–(3.10) with the expansions (3.15)–(3.20).

As an example, we analyze here the integral  $\Phi_{npr}(0; x)$  which contributes to  $S_{NN}(0; T, \rho)$  via Eqs. (3.25) and (3.27). For this we have

$$\Phi_{npr}(0; x) = -2\pi^2 \int_1^\infty du \int_1^\infty du' \int_1^\infty du'' \frac{e^{-x(nu+pu'+ru'')}}{u^{n-1}(u')^{p-1}(u'')^{r-1}} \zeta(u, u', u''), \quad (3.35)$$

where, with  $\text{sgn}(y) = y/|y|$  ( $y \neq 0$ ), one finds

$$\begin{aligned} \zeta(u, u', u'') &= -\frac{2}{\pi} \int_0^\infty dq \frac{\sin(qu) \sin(qu') \sin(qu'')}{q} \\ &= \frac{1}{4} [\text{sgn}(u+u'+u'') - \text{sgn}(u+u'-u'') \\ &\quad - \text{sgn}(u-u'+u'') + \text{sgn}(u-u'-u'')]. \end{aligned} \quad (3.36)$$

Evidently one has  $|\zeta(u, u', u'')| < 1$  so that, on letting  $x = \kappa_D a \rightarrow 0$ , we obtain

$$|\Phi_{npr}(0; 0)| < 2\pi^2 \int_1^\infty \frac{du}{u^{n-1}} \int_1^\infty \frac{du'}{(u')^{p-1}} \int_1^\infty \frac{du''}{(u'')^{r-1}}, \quad (3.37)$$

which is bounded for  $n, p, r \geq 3$ . Consequently, the contribution to  $\mathcal{R}_N^M(0)$  and  $S_{NN}(0)$  coming from such integrals is at worst of order  $\rho^2$ , which is of higher order than considered in the present analysis. In Appendix A, we explicitly bound  $\Phi_{npr}(q; x)$  for all  $n, p$ , and  $r$  using similar methods, thereby justifying the neglect of  $\mathcal{R}_N^M$  for the results stated.

As remarked in Sec. I, the approximate density-density structure factor (1.36), derived from the leading terms of the HNC approximation, leads precisely to the leading low density results for  $\xi_{N,1}$  and  $\xi_{N,2}$  presented in Eqs. (1.33) and

(1.34) [missing the  $O(\rho \ln^j \rho)$  terms]. We can see why this is so for all the leading contributions, as in Eq. (1.37), by first rewriting Eq. (3.25) as

$$S_{NN}(k) \approx [1 - \rho \hat{h}_N^D(k)]^{-1}. \quad (3.38)$$

From Eqs. (3.15)–(3.20), we find the leading contribution to  $\rho \hat{h}_N^D(k)$  when  $\rho \rightarrow 0$  comes from the  $n=2$  term of Eq. (3.26), which yields

$$\hat{h}_N^D(k) \approx \frac{4\pi a^3}{2(T^*)^2} I_2(q, x) + \dots, \quad (3.39)$$

with  $I_2(q, x) \approx \tan^{-1}(q/2x)/q + \dots$ . Then Eq. (3.38) precisely yields the HNC-derived result, Eq. (1.36).

#### D. Density structure factor from HNCM

It is instructive to check that the HNCM approach gives precisely the same result for  $S_{NN}(k)$ , namely, Eq. (1.23), as the ‘‘Meeron only’’ route. We may relate  $S_{NN}(k)$  to the direct correlation function

$$\hat{c}_N(k) = \frac{1}{2} [\hat{c}_{++}(k) + \hat{c}_{+-}(k)], \quad (3.40)$$

by using Eq. (1.4) and the OZ equation (1.26). For the RPM, one finds the simple relation

$$S_{NN}(k) = [1 - \rho \hat{c}_N(k)]^{-1}. \quad (3.41)$$

From Eqs. (1.27), (1.30), (1.17), and (3.40) we thus find that the HNCM result,

$$\begin{aligned} S_{NN}(k) &= [1 - \rho \hat{h}_N^D(k) - \rho \hat{\mathcal{R}}_N(k)]^{-1} \\ &= 1 + \rho \hat{h}_N^D(k) + [\rho \hat{h}_N^D(k)]^2 + O(\rho \hat{\mathcal{R}}_N(k)), \end{aligned} \quad (3.42)$$

is exactly the same as that derived using Meeron's  $g_{\sigma\tau}(r)$  directly up to and including terms of relative order  $\rho$ : compare with Eqs. (1.23) and (3.25). Note that the relevant combination  $\rho \hat{\mathcal{R}}_N(k)$  contributes in relative order  $\rho^{3/2}(\ln \rho)^j$  and may therefore be neglected in this analysis.

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$$\begin{aligned} \mathcal{D}_{n,p,r} &= 1 \quad \text{for } n \text{ even with } p, r \text{ odd, or } n \text{ odd with } p, r \text{ even} \\ &= 0 \quad \text{otherwise,} \end{aligned} \quad (4.4)$$

and substituting  $\hat{\xi}_Z(k)$  for  $\hat{\xi}_N(k)$ . On expanding Eq. (4.1) in powers of  $k$ , we find that Meeron's analysis yields

$$S_{ZZ}(0) = O(\rho \ln \rho), \quad (4.5)$$

$$\xi_{Z,1} = \xi_D [1 + O(\rho \ln \rho)], \quad (4.6)$$

$$\xi_{Z,2} = \xi_D [1 + O(\rho \ln \rho)], \quad (4.7)$$

so that the SL zeroth and second moment sum rules are satisfied but only up to possible deviations of order  $\rho \ln \rho$ . This must be regarded as a serious defect of the approach. Accordingly, we turn to the HNCM formulation which ensures the validity of both sum rules to all orders in  $\rho$ , i.e.,  $S_{ZZ}(0) \equiv 0$  and  $\xi_{N,1} = \xi_D$ . Furthermore, as reported,  $\xi_{Z,2}$  can then be found to be correct to relative order  $\rho$ .

### B. Charge correlations via HNCM

Following Sec. III D, we first relate  $S_{ZZ}(k)$  to the direct correlation function

$$\hat{c}_Z(k) = \frac{1}{2} [\hat{c}_{++}(k) - \hat{c}_{+-}(k)] \quad (4.8)$$

via Eq. (1.9) and the OZ relation (1.26). For the RPM, one finds

$$S_{ZZ}(k) = [1 - \rho \hat{c}_Z(k)]^{-1}. \quad (4.9)$$

Then, with the aid of Eqs. (1.27)–(1.31), we obtain the

## IV. CHARGE-CHARGE STRUCTURE FACTOR

### A. Analysis following Meeron

Following essentially the same steps that lead to expression (3.25) for  $S_{NN}(k)$  but now for the charge correlations, we find

$$S_{ZZ}(k) = 1 + \rho \hat{h}_Z^D(k) + \rho^2 [(\hat{h}_Z^D(k))^2 - (\hat{w}_Z^D(k))^2] + \mathcal{R}_Z^M(k), \quad (4.1)$$

where

$$\hat{h}_Z^D(k) = -4\pi a^3 \sum_{n=0}^{\infty} \frac{1}{(2n+1)!} I_{2n+1}(q;x) \left(\frac{1}{T^*}\right)^{2n+1}, \quad (4.2)$$

$$\hat{w}_Z^D(k) = -4\pi a^3 / T^* (x^2 + q^2), \quad (4.3)$$

while  $\mathcal{R}_Z^M(k)$  is found from Eq. (3.27) by replacing  $\mathcal{S}_{n,p,r}$  (and  $\mathcal{S}_{n,1,1}$ ) by

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HNCM result for  $S_{ZZ}(k)$  reported in Eq. (1.32). This enjoys the small  $k$  expansion

$$\begin{aligned} S_{ZZ}(k) &= \xi_D^2 k^2 \{1 + [1 - \rho(\hat{h}_Z^D(0) - \hat{w}_Z^D(0) + \hat{\mathcal{R}}_Z(0))] \xi_D^2 k^2 \\ &\quad + O(k^4)\}. \end{aligned} \quad (4.10)$$

The required  $k=0$  terms follow directly from Eqs. (4.2) and (4.3) with the aid of Eqs. (3.8)–(3.20), as

$$\begin{aligned} \rho[\hat{h}_Z^D(0) - \hat{w}_Z^D(0)] &= \frac{1}{2} x^2 + \frac{1}{6} (\kappa_D b)^2 [\ln x + e_2 - Y(T^*)] \\ &\quad + O(\rho^{3/2} \ln \rho), \end{aligned} \quad (4.11)$$

where  $e_2$  and  $Y(T^*)$  are defined in Eqs. (1.43) and (1.45), respectively. Finally, Appendix B establishes that  $\rho \hat{\mathcal{R}}_Z(0)$  is of order  $\rho^{3/2}(\ln \rho)^j$ . In total, the analysis thus justifies results (1.40) and (1.41) for  $\xi_{Z,1}$  and  $\xi_{Z,2}$ .

### C. Lebowitz length

We may now use the expression (1.32) for  $S_{ZZ}(k)$  and the relation (1.13) to calculate  $\xi_L(T, \rho)$ . We begin by expanding in powers of  $\rho(\hat{h}_Z^D - \hat{w}_Z^D)$  to obtain

$$S_{ZZ}(k) \approx \frac{k^2}{k^2 + \kappa_D^2} \left\{ 1 + \frac{\rho k^2}{k^2 + \kappa_D^2} [\hat{h}_Z^D(k) - \hat{w}_Z^D(k)] + \dots \right\}. \quad (4.12)$$

Then, employing Eqs. (3.6)–(3.12) and integrating on  $k$  leads to

$$\xi_L(T, \rho) \approx \frac{2a}{\pi} \left[ \frac{\pi}{2x} - x^2 \sum_{n=0}^{\infty} \frac{(T^*)^{-2n}}{(2n+1)!} \Xi_L^{(2n+1)}(x) + \dots \right], \quad (4.13)$$

where, for  $m \geq 1$ ,

$$\Xi_L^{(m)}(x) = \int_0^{\infty} dq \frac{q^2}{(x^2 + q^2)^2} \left[ I_m(q; x) - \frac{\delta_{m,1}}{x^2 + q^2} \right]. \quad (4.14)$$

We find the contribution of leading order in  $x$  from these integrals as follows. For  $m=1$  we put  $q=ux$  and expand to find

$$[I_1(q; x) - (x^2 + q^2)^{-1}]_{q=ux} = -\frac{1}{2}(u^2 + 1)x^2 + O(x^3), \quad (4.15)$$

which yields

$$\Xi_L^{(1)}(x) = -(\pi/8x) + O(x^0). \quad (4.16)$$

For  $m \geq 2$  we use the integral form (3.10) and interchange orders of integration to obtain

$$\begin{aligned} \Xi_L^{(m)}(x) &= \int_1^{\infty} dy \frac{e^{-mxy}}{y^{m-1}} \int_0^{\infty} dq \frac{q \sin(qy)}{(x^2 + q^2)^2} \\ &= \frac{\pi}{4x} \int_1^{\infty} dy \frac{e^{-(m+1)xy}}{y^{m-2}} = \frac{\pi}{4x} E_{m-2}(mx+x). \end{aligned} \quad (4.17)$$

Collecting all terms up to and including those of order  $x$ , recalling the expansion (3.14), and appealing to Appendix B for a bound on  $\hat{\mathcal{R}}_Z(k)$ , finally establishes the result for  $\xi_L(T, \rho)$  given in Eq. (1.42).

#### D. Analysis of the generalized DH predictions

The pure GDH (generalization of the DH theory) approximation for  $S_{ZZ}(k)$  is

$$S_{ZZ}^{\text{GDH}}(k) = \frac{q^2}{x^2 + q^2 + g_0(x; q)}, \quad (4.18)$$

where, from Eqs. (1) and (2) of Ref. [29],

$$\begin{aligned} g_0(x; q) &= x^2(\cos q - 1) - [2 \ln(1+x) - 2x + x^2] \\ &\quad \times (\cos q - \sin q/q). \end{aligned} \quad (4.19)$$

Clearly GDH theory satisfies the zeroth and second moment SL sum rules. Expanding for small  $q=ka$  yields

$$\begin{aligned} \xi_{Z,2}^{\text{GDH}} &= \xi_D [1 + \frac{2}{3} \ln(1+x) - \frac{2}{3}x - \frac{1}{6}x^2]^{1/4} \\ &= \xi_D / [1 + \frac{1}{8}x^2 - \frac{1}{18}x^3 + \frac{31}{384}x^4 + O(x^5)]. \end{aligned} \quad (4.20)$$

As regards the Lebowitz length, the form (1.13) gives

$$\xi_L^{\text{GDH}} = \frac{2a}{\pi} \int_0^{\infty} dq \frac{1}{x^2 + q^2 + g_0(q; x)}, \quad (4.21)$$

which on expansion in powers of  $g_0$  yields a sum over the integrals

$$\mathcal{J}_n(x) = \frac{1}{\pi} \int_0^{\infty} dq \frac{[-g_0(q; x)]^n}{(x^2 + q^2)^{n+1}}. \quad (4.22)$$

Then one has  $\mathcal{J}_0(x) = 1/2x$  and evaluation using Eq. (4.19) gives

$$\mathcal{J}_1(x) = -\frac{1}{8}x + \frac{5}{36}x^2 - \frac{11}{96}x^3 + \frac{43}{480}x^4 + O(x^5), \quad (4.23)$$

$$\mathcal{J}_2(x) = \frac{3}{64}x^3 - \frac{1}{10}x^4 + O(x^5), \quad (4.24)$$

while  $\mathcal{J}_n(x) = O(x^{2n-1})$  for  $n \geq 3$ . Collecting terms yields the GDH prediction

$$\xi_{Z,2}^{\text{GDH}} = \xi_D [1 + \frac{1}{4}x^2 - \frac{5}{18}x^3 + \frac{31}{96}x^4 + O(x^5)]. \quad (4.25)$$

Comparing this with the exact low-density result (1.42), one sees that GDH theory generates the exact leading behavior and one of the correction terms of relative order  $\rho$ , namely,  $\frac{1}{4}x^2$ . Similarly, comparing Eqs. (4.20) and (1.41), one finds that the theory predicts the leading behavior of  $\xi_{Z,2}$  as well as the  $\frac{1}{8}x^2$  correction. However, the dominant  $O(\rho \ln \rho)$  term does *not* appear.

Why this is so is most easily understood by comparing  $S_{ZZ}^{\text{GDH}}(k)$  in Eq. (4.18) with  $S_{ZZ}(k)$  as represented in Eq. (1.32). By using Eq. (3.7) for  $\hat{w}_Z^D(k)$  and retaining only the first two terms in the expansion of  $\hat{h}_Z^D(k)$  in Eq. (3.12), one may write  $S_{ZZ}(k)$  in the GDH form, but with  $g_0(q, x)$  replaced by

$$\begin{aligned} \tilde{g}_0(q, x) &= q^2 x^2 [I_1(q; x) - (x^2 + q^2)^{-1}] \\ &= x^2(\cos q - 1) + O(x^3). \end{aligned} \quad (4.26)$$

But one then observes that  $g_0(q; x)$  has precisely the same small- $x$  expansion. Thus, in effect, GDH theory generates the first term in the full expansion of  $\hat{h}_Z^D(k) - \hat{w}_Z^D(k)$ : see Eqs. (4.2) and (4.3). However, the dominant  $O(\rho \ln \rho)$  correction actually comes from the *next* term in this expansion, namely, from  $I_3(q; x)$ , which GDH theory does not produce.

From this discussion and the success of GDH theory in predicting the correct density-density correlation lengths (including leading correction terms), we conclude that the approximation essentially reproduces the correct low-density, fixed- $k$  behavior of  $S_{ZZ}(k)$  and  $S_{NN}(k)$  that arises from the first two terms in the expansion (3.12) of the Debye correlation function.

## V. RESULTS FROM THE KM ANALYSIS

### A. Direct correlation function expression

Kjellander and Mitchell [27] have constructed a formally exact theory for primitive model Coulomb fluids in terms of a Poisson-Boltzmann equation *linear* in the average electrostatic potential for “dressed ions.” The nonlinear contributions appear in a nonlocal dielectric response function, in effective values for the ionic charges, namely,

$$q_\sigma^* = q_\sigma + \sum_\tau q_\tau \rho_\tau \hat{h}_{\sigma\tau}^0(i\kappa_\infty), \quad (5.1)$$

and in the true screening length  $\kappa_\infty^{-1} \equiv \xi_{Z,\infty}$  given by

$$\kappa_\infty^2 = 4\pi\beta \sum_\sigma q_\sigma q_\sigma^* \rho_\sigma / D, \quad (5.2)$$

where  $q_\sigma = z_\sigma q_0$  while  $\hat{h}_{\sigma\tau}^0(k)$  is defined in terms of the short-range part of the direct correlation function  $c_{\sigma\tau}^0(r)$  in Eq. (1.27) via the “reduced” OZ relation

$$h_{\sigma\tau}^0(r) = c_{\sigma\tau}^0(r) + \sum_\nu \rho_\nu \int c_{\sigma\nu}^0(|\mathbf{r}-\mathbf{r}'|) h_{\nu\tau}^0(r') d\mathbf{r}'. \quad (5.3)$$

KM studied  $c_{\sigma\tau}^0(r)$ —and thence  $h_{\sigma\tau}^0(r)$ —using the HNC resummation (1.28) including  $b_{\sigma\tau}(r)$ , the bridge diagram corrections: see Ref. [27(a)] for details. They focused explicitly on the *long-distance decay* of  $c_{\sigma\tau}^0(r)$  and  $h_{\sigma\tau}^0(r)$  at low densities by searching for the poles and branch-cut singularities of  $\hat{c}_{\sigma\tau}^0(k)$  in the complex  $k$  plane that lie closest to the real axis. One can extract a corresponding low-density expression for  $\hat{c}_N^0(k)$  for the RPM, defined similarly to  $\hat{c}_N(k)$  in Eq. (3.40), by using Eqs. (C21), (B5a), (C23), (C15), and (C17) of Ref. [27(a)]. This is found to be

$$\rho \hat{c}_N^0(k) \approx \frac{1}{4} \kappa_D b s(k/2\kappa_D) \left[ 1 - \frac{1}{8} (\kappa_D b)^2 s(k/2\kappa_D) \right]^{-1} + \dots, \quad (5.4)$$

where, as before,  $s(y) = (\tan^{-1}y)/y$ .

### B. Comparison with KM results

We can find a corresponding KM expression for  $S_{NN}(k)$  by using Eqs (5.4), (3.41), and (1.27). On expanding the result for small  $k$ , we discover that the KM direct correlation function (which includes leading bridge function corrections), although constructed only to ensure accurate behavior for  $r \rightarrow \infty$ , gives precisely the same results for  $\xi_{N,1}$  and  $\xi_{N,2}$  reported in Eqs. (1.33) and (1.34), respectively. Moreover,

analysis of the dominant pole of the corresponding expression for  $S_{NN}(k)$  also yields the true density-correlation decay length

$$\xi_{N,\infty} = \frac{1}{2} \xi_{Z,\infty} \left[ 1 + 2 \exp \left\{ \frac{-8}{\kappa_D b} \left( 1 - \frac{1}{2} \kappa_D b + \dots \right) \right\} + \dots \right]. \quad (5.5)$$

By comparing this with the GDH result, Eq. (12) of Ref. [14(a)], we see that it is the bridge function that generates the  $\frac{1}{2} \kappa_D b$  correction, although the most essential features of  $\xi_{N,\infty}$  at low densities are captured by the GDH approach.

Finally, we compare with the KM result (1.46) for  $\xi_{Z,\infty} \equiv 1/\kappa_\infty$  by using the small  $\rho$  expansion of  $\rho[\hat{h}_Z^D(0) - \hat{w}_Z^D(0)]$  presented in Eq. (4.11), in  $S_{ZZ}(k)$ , as given in Eq. (1.32), and solving  $S_{ZZ}^{-1}(i\kappa_\infty) = 0$  with neglect of the remainder  $\hat{\mathcal{R}}_Z$ . We find

$$\xi_{Z,\infty} = \xi_D \left[ 1 - \frac{1}{12} (\kappa_D b)^2 \ln x + O(\rho) \right], \quad (5.6)$$

which agrees with the KM result (1.46) when evaluated for the RPM. As remarked in Sec. I, the KM expression contains the factor  $\ln \kappa_D b$ , since KM took  $b$  as a lower cutoff whereas we explicitly find  $\ln \kappa_D a$  as written.

In summary, the KM analysis provides a complementary verification of our principal results and, in so doing, reveals a comforting degree of uniformity (with respect to long-distance behavior and low- $k$  variation) in the restricted primitive model at low densities. The same high degree of uniformity should not be expected for charge and/or hard-core *nonsymmetric* primitive models [11].

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## APPENDIX A: ANALYSIS OF INTEGRALS IN THE MEERON REMAINDER

In this appendix we analyze the integrals and integral differences appearing in the Meeron remainder terms  $\mathcal{R}_N^M(k; T, \rho)$  and  $\mathcal{R}_Z^M(k; T, \rho)$  [see Eqs. (3.27) and (4.1)–(4.4)]; of course, these derive from the term  $h_{\sigma\tau}^D(r) \eta_{\sigma\tau}(r)$  in the original expressions (1.14), (1.18), and (1.22). In particular, we expand in powers of  $q^\alpha k$  all the integrals  $\Phi_{npr}(q; x)$ , defined in Eq. (3.34) as a convolution over the exponential integrals  $I_n(q; x)$  introduced in Eqs. (3.8)–(3.11). Thus,

writing

$$\begin{aligned} \Phi_{npr}(q;x)/2\pi^2 &= -\Phi_{npr}^{(0)}(x) + \frac{1}{3!} q^2 \Phi_{npr}^{(2)}(x) \\ &\quad - \frac{1}{5!} q^4 \Phi_{npr}^{(4)}(x) + O(q^6), \end{aligned} \quad (\text{A1})$$

we aim to determine the low-density ( $x \propto \rho^{1/2} \rightarrow 0$ ) behavior of the integrals appearing in  $\Phi_{npr}^{(m)}$  for  $m=0, 2$ , and  $4$ .

Now by using the convolution relation in bipolar coordinates, namely,

$$\begin{aligned} \int d\mathbf{q}' f(|\mathbf{q}-\mathbf{q}'|) g(q') \\ = \frac{2\pi}{q} \int_0^\infty du f(u) u \int_{|u-q|}^{u+q} dv g(v) v, \end{aligned} \quad (\text{A2})$$

together with Eqs. (3.8)–(3.10) we may rewrite Eq. (3.34) in the compact form

$$\Phi_{npr}(q;x) = \frac{2\pi}{q} \int_1^{\Theta_n} du \int_1^{\Theta_p} du' \int_1^{\Theta_r} du'' \frac{e^{-x(nu+pu'+ru'')}}{u^{n-1}(u')^{p-1}(u'')^{r-1}} \Upsilon(q;u,u',u''), \quad (\text{A3})$$

with  $n, p, r \geq 0$ , where  $\Theta_0=0$  but  $\Theta_n=\infty$  for  $n \geq 1$ ; the integrand factor becomes

$$\Upsilon(q;u,u',u'') = \int_0^\infty dv \sin(vu) \Psi(q;v,u',u''), \quad (\text{A4})$$

where, with  $u_- = u' - u''$  and  $u_+ = u' + u''$ , we have

$$\Psi(q;v;u',u'') = \frac{1}{2} \int_{|v-q|}^{v+q} \frac{dw}{w} (\cos u_- w - \cos u_+ w). \quad (\text{A5})$$

This kernel can be expanded as

$$\Psi(q;v;u',u'') = \frac{2q}{v} \sin(vu') \sin(vu'') + \sum_{n=1}^{\infty} [\Psi_{2n+1}(u_-;v) - \Psi_{2n+1}(u_+;v)] \frac{q^{2n+1}}{(2n+1)!}, \quad (\text{A6})$$

with coefficients

$$\Psi_{2n+1}(u;v) = (-1)^{n+1} \int_0^u z^{2n} \sin(vz) dz. \quad (\text{A7})$$

Performing the various trigonometric integrals then leads to

$$\begin{aligned} \Upsilon(q;u;u',u'') &= -\pi q \left[ 1 - \frac{1}{3!} (qu)^2 + \frac{1}{5!} (qu)^4 \right. \\ &\quad \left. + O(q^6) \right] \zeta(u,u',u''), \end{aligned} \quad (\text{A8})$$

where the step function  $\zeta(u,v,w)$  has already appeared in Eq. (3.36).

Substitution in Eq. (A3) yields integral expressions for the desired coefficients in Eq. (A1). By using the trivial bounds  $|\zeta| \leq 1$  and  $\int_0^1 u^m du \leq 1$ , one is then led to

$$|\Phi_{npr}^{(m)}(x)| < \tilde{\Phi}_{npr}^{(m)}(x), \quad (\text{A9})$$

where, since the integrals in Eq. (A3) now factorize, the bounds can be written [using the exponential integrals (3.11)] in the compact form

$$\begin{aligned} \tilde{\Phi}_{npr}^{(m)}(x) &= [\delta_{n,0} + \bar{\delta}_{n,0} E_{n-m-1}(nx)] [\delta_{p,0} + \bar{\delta}_{p,0} E_{p-1}(px)] \\ &\quad \times [\delta_{r,0} + \bar{\delta}_{r,0} E_{r-1}(rx)], \end{aligned} \quad (\text{A10})$$

where  $\delta_{n,m}$  is the Kronecker delta and  $\bar{\delta}_{n,m} \equiv 1 - \delta_{n,m}$ .

Finally, by employing the expansion (3.14) of the exponential integrals for  $n \geq 1$  (and noting that the integrals are elementary for  $n \leq 0$ ), we may bound the orders of the contributions that a particular combination  $\rho^2 \Phi_{npr}(q;x)$  makes to  $\mathcal{R}_N^M(k)$  and  $\mathcal{R}_Z^M(k)$ . As an example, consider  $(n,p,r) = (3,1,1)$  and  $m=0$ ; we find that the leading order behavior when  $\rho \rightarrow 0$  is given by

$$\rho^2 \tilde{\Phi}_{311}^{(0)}(x) = \rho^2 E_2(3x) [E_0(x)]^2 \sim \rho^2 x^0 (x^{-1})^2 \sim \rho. \quad (\text{A11})$$

Of course, the bound on the behavior of  $\Phi_{n,p,r}(x)$  as  $\rho \rightarrow 0$  obtained this way need not be optimal. However, it may be adequate if it is of higher order in  $\rho$  than the terms explicitly retained in our various results. This will be the case (form  $=0, 2$ , and  $4$ ) provided  $\rho^2 \tilde{\Phi}_{n,p,r}$  proves to be of order  $\rho^{(3-m)/2} (\ln \rho)^j$  or higher. Evidently, however, Eq. (A11) is *not* adequate. Now, by careful tabulation one finds that the only inadequate cases arise (a) from the integrals  $\Phi_{n,1,1}(x)$

for all  $n \geq 0$ , and (b) from  $\Phi_{1,p,1}(x)$  and  $\Phi_{1,1,r}(x)$  for  $p, r \geq 3$ . [Note that the definition (3.34) implies  $\Phi_{1,p,1}(x) = \Phi_{1,1,p}(x)$ .]

Now, in diagrammatic terms, the integrals  $\Phi_{n,1,1}(x)$  implicitly contain a two-bond  $w_D$  chain which (since it is already included in the Mayer resummation, as discussed in Sec. II) is subtracted off explicitly in the full expressions for  $h_{\sigma\tau}^D \eta_{\sigma\tau}$ : see Eq. (1.19). Consequently, by recalling Eq. (3.7) for  $\hat{w}_{\sigma\tau}^D(k)$ , we see that the relevant contributions to  $\mathcal{R}_N^M(k)$  and  $\mathcal{R}_Z^M(k)$  are the differences

$$\Delta_n(q;x) \equiv \Phi_{n,1,1}(q;x) - \int \frac{I_n(\mathbf{q}-\mathbf{q}';x)}{(x^2+q'^2)^2} d\mathbf{q}'. \quad (\text{A12})$$

To analyze the  $\Delta_n$ , it is useful to define a rescaled version of the integrals  $I_n(q,x)$  defined in Eq. (3.10): thus we put  $\mathbf{q} = x\mathbf{s}$  and  $y = u/x$  to obtain

$$I_n(q;x) = J_n(s;x) \equiv \frac{x^{n-3}}{s} \int_x^{\Theta_n} \frac{du}{u^{n-1}} \sin(su) e^{-nu}, \quad (\text{A13})$$

where  $\Theta_n$  is defined as in Eq. (A3). We may now write

$$\Delta_n^{(0)}(x) \approx \frac{2x}{\pi} \int_0^\infty du J_n(u;x) u^2 / (1+u^2), \quad (\text{A18})$$

$$\Delta_n^{(2)}(x) \approx \frac{4}{\pi x} \int_0^\infty du J_n(u;x) u^2 (3-u^2) / (1+u^2)^3, \quad (\text{A19})$$

$$\Delta_n^{(4)}(x) \approx \frac{48}{\pi x^3} \int_0^\infty du J_n(u;x) u^2 (5-10u^2+u^4) / (1+u^2)^5, \quad (\text{A20})$$

for  $x \rightarrow 0$ . On substituting with Eq. (A13) and evaluating the infinite integrals on  $u$ , we obtain

$$\Delta_n^{(m)}(x) \approx \int_1^{\Theta_n} du e^{-(n+1)xu} / u^{n-m-1}, \quad (\text{A21})$$

so that, as  $x \rightarrow 0$ ,  $\Delta_n^{(m)} = O(1)$  for  $n=0$  or  $n > m+2$ , while  $\Delta_n^{(m)} = O(x^{-m-2+n})$  for  $1 \leq n < m+2$  and  $\Delta_{m+2}^{(m)} = O(\ln x)$ . Thus the lowest order behavior derives from  $n=1$ . Consequently, one finds from Eq. (A17) that the contributions from  $\rho^2 \Delta_n^{(m)}(x)$  are at worst of order  $\rho^{(3-m)/2}$  for  $m=0, 2$ , and  $4$ . This is of higher order than the expected error terms,  $O(\rho^{(3-m)/2} (\ln \rho)^j)$ , in the  $k$  expansion of  $\mathcal{R}_N^M(k)$  and  $\mathcal{R}_Z^M(k)$ , and so may be neglected.

Finally, we analyze the leading behavior of the integrals  $\Phi_{1,p,1}(s;x)$  for  $p \geq 3$  which we again write in terms of  $J_n(s;x)$ , as introduced in Eq. (A13), to find

$$\Delta_n(sx, x) = x^3 \int ds' J_n(|\mathbf{s}-\mathbf{s}'|;x) \Gamma(s';x), \quad (\text{A14})$$

where we have simply

$$\Gamma(s,x) = \frac{[\cos(sx) + \sin(sx)/s]^2 e^{-2x} - 1}{x^4(1+s^2)^2}, \quad (\text{A15})$$

which, when  $x \rightarrow 0$ , can be represented as

$$\Gamma(s,x) = -x^{-2}/(1+s^2)[1+O(x)]. \quad (\text{A16})$$

In parallel with Eq. (A1) we may write the expansion

$$\Delta_n(sx;x)/2\pi^2 = -\Delta_n^{(0)} + \frac{1}{3!} s^2 x^2 \Delta_n^{(2)}(x) - \dots. \quad (\text{A17})$$

On neglecting the  $O(x)$  term in Eq. (A16), and appealing again to the bipolar convolution theorem (A2), we can express the coefficients here as

$$\Phi_{1,p,1}(sx;x) = x^3 \int ds' J_1(\mathbf{s}-\mathbf{s}') J_p(\mathbf{s}') J_1(\mathbf{s}'). \quad (\text{A22})$$

Following essentially the same steps as above, we appeal to Eq. (A2), and expand  $J_1(\mathbf{s}';x)$  here for small  $x$ . Then we expand for small  $s$  and compare with Eq. (A1) to discover that the dominant contribution arises from  $\Phi_{1,3,1}^{(m)}(x) = O(\rho^{-(m+1)/2} \ln \rho)$ . [Note that this replaces an inadequate bound of order  $\rho^{1-(m/2)}$  following from Eq. (A10).] Finally, therefore, the most relevant terms satisfy  $\rho^2 \Phi_{1,p,1}^{(m)}(x) = O(\rho^{(3-m)/2} \ln \rho)$  (for  $m=0, 2$ , and  $4$ ) which is of higher order than concerns us.

In conclusion, all the terms contained in the Meeron remainders can be correctly neglected to the orders claimed in the text.

## APPENDIX B: ANALYSIS OF INTEGRALS IN THE HNCM REMAINDER

In Appendix A we actually bounded the orders of the leading contributions to  $\mathcal{R}_{\sigma\tau}(\mathbf{k})$ , namely, the integrals

derived from  $h_{\sigma\tau}^D(r)\eta_{\sigma\tau}(r)$ : see Eqs. (1.31) and (1.32) *et seq.* For completeness we now analyze the next most important terms, namely, the bridge integral  $\hat{b}_Z(0)$  and the dominant quadratic terms  $[\hat{\eta}_Z(0)]^2$  appearing in the

sum in Eq. (1.31). As seen from Eq. (4.10), both these contribute to the charge correlation length  $\xi_{Z,2}(T,\rho)$ .

We begin with the leading bridge diagram which has five  $h_{\sigma\tau}$  bonds [26,27(a)], so that

$$b_{\sigma\tau}(r) = \frac{1}{2} \sum_{\mu} \sum_{\nu} \rho_{\mu} \rho_{\nu} \int d\mathbf{r}' \int d\mathbf{r}'' h_{\sigma\mu}(r') h_{\sigma\nu}(r'') h_{\nu\tau}(|\mathbf{r}-\mathbf{r}''|) h_{\nu\mu}(|\mathbf{r}'-\mathbf{r}''|) h_{\mu\tau}(|\mathbf{r}-\mathbf{r}'|) + \dots \quad (\text{B1})$$

We then employ the leading low-density contribution to  $h_{\sigma\tau}(r)$ , namely,  $h_{\sigma\tau}^D(r)$ , arising via Eqs. (1.14)–(1.18). The expansion of  $h_{\sigma\tau}(r)$  in powers of  $w_{\sigma\tau}^D(r)$  may be rewritten conveniently as

$$h_{\sigma\tau}(r) \approx f^{\dagger}(r) + \sum_{m=1}^{\infty} (-z_{\sigma} z_{\tau} b)^m \phi_m(r)/m!, \quad (\text{B2})$$

where we recall Eq. (1.21) and have set

$$\phi_m(r) = e^{-\beta u^{\dagger}(r)} e^{-m\kappa_D r/r^m}. \quad (\text{B3})$$

The leading contributions to the required combination

$$b_Z(r) = \frac{1}{4} \sum_{\sigma,\tau} z_{\sigma} z_{\tau} b_{\sigma\tau}(r), \quad (\text{B4})$$

follow by substitution in Eq. (B1). The coefficient of  $\phi_j \phi_l \phi_m \phi_n \phi_p$  in the resulting integrand entails the valence sums

$$\begin{aligned} \mathcal{S}_3(j,l,m,n,p) &= \sum_{\sigma,\tau} \sum_{\mu,\nu} z_{\sigma}^{j+l+1} z_{\tau}^{m+p+1} z_{\mu}^{j+n+p} z_{\nu}^{l+m+n} \\ &= [1 + (-1)^{j+l+1}] [1 + (-1)^{m+p+1}] [1 + (-1)^{j+n+p}] [1 + (-1)^{l+m+n}]. \end{aligned} \quad (\text{B5})$$

The dominant terms in  $\rho$  require  $\mathcal{S}_3 \neq 0$ , and are found to arise from  $(j,l,m,n,p) = (2,1,2,1,1)$  and  $(1,2,1,1,2)$ , which both make the same contribution to  $\hat{b}_Z(0)$ . Adding these yields, after some rearrangement,

$$\hat{b}_Z^{(1)}(0;x) = -\frac{1}{4} \rho^2 b^7 \int d\mathbf{r} \int d\mathbf{r}' \phi_1(r') \phi_2(|\mathbf{r}-\mathbf{r}'|) \int d\mathbf{r}'' \phi_2(r'') \phi_1(|\mathbf{r}-\mathbf{r}''|) \phi_1(|\mathbf{r}'-\mathbf{r}''|), \quad (\text{B6})$$

where we will neglect the corresponding higher order contributions  $\hat{b}_Z^{(n)}(0;x)$ .

Now we may decouple  $\mathbf{r}'$  and  $\mathbf{r}''$  in the last factor in Eq. (B6) by using the trivial bound  $\phi_m(r) \leq a^{-m}$ , where  $a$  is the hard-core diameter. Then we can call again on the convolution relation (3.4), now with  $\mathbf{k} = \mathbf{0}$  while  $g(\mathbf{r})$  itself is a convolution. This yields the bound

$$|\hat{b}_Z^{(1)}(0;x)| \leq \frac{\rho^2 b^7}{4a} \int \frac{d\mathbf{k}}{(2\pi)^3} [\hat{\phi}_1(\mathbf{k})]^2 [\hat{\phi}_2(\mathbf{k})]^2 = 8\pi b^7 a^2 \rho^2 \Phi_{1,2}(x), \quad (\text{B7})$$

in which the integral can be written in terms of the  $I_n(q;x)$  defined in Eqs. (3.9)–(3.11) via

$$\Phi_{n,m}(x) = \int d\mathbf{q} [I_n(q;x)]^2 [I_m(q;x)]^2. \quad (\text{B8})$$

On substituting the forms (3.9) and (3.10), the integral over  $\mathbf{q}$  can be performed to obtain

$$\Phi_{n,m}(x) = \int_1^\infty du \int_1^\infty du' \int_1^\infty du'' \int_1^\infty du''' \frac{e^{-x[n(u+u') + m(u''+u''')]} }{u^{n-1}(u')^{n-1}(u'')^{m-1}(u''')^{m-1}} \zeta(u, u', u'', u'''), \quad (\text{B9})$$

where, with the aid of machine algebra (*Mathematica* and *Maple*), we find

$$\zeta(u, u', u'', u''') = \int_0^\infty dq \frac{1}{q^2} \sin(qu) \sin(qu') \sin(qu'') \sin(qu''') = -\frac{1}{16} \pi \sum_{\pm, \pm, \pm} (\pm)(\pm)(\pm) |u \pm u' \pm u'' \pm u'''|. \quad (\text{B10})$$

For  $u, u' \dots \geq 1$ , as required, a simple bound is

$$|\zeta(u, \dots)| < \frac{1}{2} \pi (u + u' + u'' + u'''). \quad (\text{B11})$$

With this and Eq. (3.11) (including the cases  $n \leq 0$ ) we find that  $|\Phi_{n,m}(x)|/\pi$  is bounded by

$$\begin{aligned} \tilde{\Phi}_{n,m}(x) &= E_{n-2}(nx) E_{n-1}(nx) [E_{m-1}(mx)]^2 \\ &+ E_{m-2}(mx) E_{m-1}(mx) [E_{n-1}(nx)]^2. \end{aligned} \quad (\text{B12})$$

The small  $x$  expansion (3.14) (for  $n \geq 1$ ) then yields

$$\tilde{\Phi}_{1,2}(x) = x^{-3} \ln x [\ln x + O(1)], \quad (\text{B13})$$

which shows that the relevant combination  $\rho \hat{b}_Z(0)$  contributes to  $\rho \mathcal{R}_Z(0)$  only in order  $\rho^{3/2} (\ln \rho)^2$  or higher, and can thus be neglected in the present analysis.

In order to bound the leading order contributions to

$$\hat{\eta}_Z^2(0) = \frac{1}{4} \sum_{\sigma, \tau} \int d\mathbf{r} z_\sigma z_\tau \eta_{\sigma\tau}^2(r), \quad (\text{B14})$$

we may follow essentially the same steps which led to Eq. (B7) and to the bounds (B12) and (B13). Using Eqs. (B2), (1.19), and (1.22) in Eq. (B14) [and recalling that the  $\eta^{(2)}$  term in Eq. (1.20) makes no contribution for the RPM] leads to the sums

$$\begin{aligned} S_4(j, l, m, p) &= \sum_{\sigma, \tau} \sum_{\mu, \nu} z_\sigma^{j+m+1} z_\tau^{l+p+1} z_\nu^{j+l} z_\mu^{m+p} \\ &= [1 + (-1)^{j+m+1}] [1 + (-1)^{l+p+1}] \\ &\times [1 + (-1)^{j+l}] [1 + (-1)^{m+p}], \end{aligned} \quad (\text{B15})$$

as coefficients of  $\phi_j \phi_l \phi_m \phi_p$  in the expansion of the product of four  $h_{\sigma\tau}^D$  factors.

The leading order low-density contributions to the  $h^D h^D h^D h^D$  term which, excluding the effects of the  $w^D w^D$  term in Eq. (1.19), we denote by  $\hat{\eta}_Z^H(\mathbf{k}; x)$ , arise from the

smallest values of  $j, l, m$ , and  $p$  ( $\geq 1$ ) for which  $S_4 \neq 0$ . The dominant contributions are found to derive from  $(j, l, m, p) = (1, 1, 2, 2)$  and  $(2, 2, 1, 1)$  which yield equivalent expressions so that

$$\begin{aligned} \hat{\eta}_Z^H(\mathbf{0}) &\approx \frac{1}{2} \rho^2 b^6 \int d\mathbf{r} \int d\mathbf{r}' \phi_1(|\mathbf{r} - \mathbf{r}'|) \phi_1(r') \\ &\times \int d\mathbf{r}'' \phi_2(|\mathbf{r} - \mathbf{r}''|) \phi_2(r''). \end{aligned} \quad (\text{B16})$$

With the aid, once more, of the convolution relation (3.4), this reduces to

$$\hat{\eta}_Z^H(0; x) \approx 16 \pi b^6 a^3 \rho^2 \Phi_{1,2}(x), \quad (\text{B17})$$

with  $\Phi_{1,2}$  still defined in Eq. (B8). The bound (B13) applies equally, and we conclude that  $\rho \hat{\eta}_Z^H$  contributes to  $\rho \mathcal{R}_Z(0)$  in no order lower than  $\rho^{3/2} (\ln \rho)^2$ .

The  $w^D w^D$  factor so far neglected in Eq. (1.19) yields products  $h^D h^D w^D w^D$  leading to a contribution, say,  $\hat{\eta}_Z^W(\mathbf{k}; x)$ . But each  $w^D$  factor corresponds, essentially, to an index of  $j, l, m$ , or  $p = 1$ . The same method thus suffices to establish that  $\rho \hat{\eta}_Z^W$  contributes to  $\rho \mathcal{R}_Z(0)$  only in order  $\rho^{3/2} (\ln \rho)^2$  or higher. To complete the discussion of the  $[\hat{\eta}_Z(0)]^2$  term we note that the fourfold products  $w^D w^D w^D w^D$  are eliminated by the valence sums  $S_4$  which vanish identically for these products. We conclude that the overall corrections arising from  $[\hat{\eta}_Z]^2$  are no worse than  $\rho^{3/2} (\ln \rho)^2$ . Actually, more explicit calculations which allow for cancellations arising in  $\eta^{(1)} \propto (h^D h^D - w^D w^D)$  indicate that  $\rho \hat{\eta}_Z(0)$  is, in reality, only of order  $\rho^{5/2} \ln \rho$ .

Some further work is needed to bound the orders of the corrections to results (4.12)–(4.17) for the Lebowitz length. In fact, the (unwritten) correction term  $\hat{\mathcal{R}}_Z(k)$  entering Eq. (4.12) and derived, in leading order, from  $h_{\sigma\tau}^D(r) \eta_{\sigma\tau}(r)$ , must enter the expression (4.13) for  $\xi_L(T, \rho)$  as a sum over  $n, p$ , and  $r$  of integrals

$$\Phi_{npr}^L(x) = \frac{2x}{\pi} \int_0^\infty dq \frac{q^2}{(x^2+q^2)^2} \Phi_{npr}(q;x), \quad (\text{B18})$$

in parallel to Eq. (4.14), where  $\Phi_{npr}(q;x)$  remains as expressed in Eqs. (A3)–(A8).

If Eq. (A8) is now written in the closed form

$$Y(q;u,u',u'') = -\pi \sin(qu) \zeta(u,u',u'')/u, \quad (\text{B19})$$

and used in Eqs. (A3) and (B18), one obtains the same integral as evaluated in Eq. (4.17) (with, merely,  $y$  replaced by  $u$ ). This then yields

$$\Phi_{npr}^L(x) = -\pi^2 \int_1^{\Theta_n} du \int_1^{\Theta_p} du' \int_1^{\Theta_r} du'' \frac{e^{-x[(n+1)u+pu'+ru'']}}{u^{n-1}(u')^{p-1}(u'')^{r-1}} \zeta(u,u',u''), \quad (\text{B20})$$

which can be bounded following the analysis of the integrals  $\Phi_{npr}^{(m)}(x)$  in Eq. (A9). Indeed, the extra factor  $e^{-xu}$  in Eq. (B20) relative to Eq. (A3) has no sensible effect so that, up to constant factors, precisely the same bounds are found for  $\Phi_{npr}^L$  as established for  $\Phi_{npr}^{(0)}(x)$  in Appendix A.

Beyond the terms thus adequately bounded one must examine the  $(h^D - w^D)$  difference integrals entailing the  $\Delta_n(q;x)$  introduced in Eq. (A12). These lead to corresponding corrections for  $\xi^L$ , namely,

$$\Delta_n^L(x) = \frac{2x}{\pi} \int_0^\infty dq \frac{q^2}{(x^2+q^2)^2} \Delta_n(q;x). \quad (\text{B21})$$

In leading order in  $\rho$  one can show that these exhibit the same behavior as the  $\Delta_n(0;x)$ . Consequently, one can retrace the analysis of Appendix A for bounding the behavior of the  $\Phi_{npr}(0;x)$  and  $\Delta_n(0;x)$ , and thereby conclude that  $\rho \hat{\mathcal{R}}_Z(k)$  contributes to  $\xi_L(T,\rho)$  no more than the terms of order  $\rho^{3/2}(\ln \rho)^j$  displayed in the result (1.42).

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