The moment sum-rules for ionic liquids at criticality

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ABSTRACT

We discuss the first three well known moment charge–charge sum-rules for a general ionic liquid. For the special symmetric case of the Restricted Primitive Model, Das, Kim, and Fisher (2011) has recently discovered, through Monte Carlo simulations, that the Stillinger–Lovett or second-moment sum-rule fails at criticality. We critically discuss a possible explanation for this unexpected behavior. On the other hand the fourth-moment sum-rule turns out to be able to account for the results of the simulations at criticality.

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1. Introduction

It is well known that among all possible long-range pair-potentials, it is only in the Coulomb case that the decay law of the correlations faster then any inverse power is compatible with the structure of equilibrium equations (such as the Born–Green–Yvon). Under the exponential clustering hypothesis for charged fluids, a number of exact sum-rules on the correlation functions can be obtained [1]. Of particular relevance is the Stillinger–Lovett second-moment charge–charge sum-rule which is equivalent to the property that the inverse dielectric function vanishes in the limit of small wavenumbers. When this condition holds the fluid completely shields any external charge inhomogeneity and behaves as a conducting medium.

In a recent work Das, Kim, and Fisher [2,3] found out, through finely discretized grand canonical Monte Carlo simulations, that in the Restricted Primitive Model (RPM) of an electrolyte, the second- and fourth-moment charge–charge sum-rules, typical for ionic fluids, are violated at criticality. For a 1:1 equisized charge-symmetric hard-sphere electrolyte their grand canonical simulations, with a new finite-size scaling device, confirm the Stillinger–Lovett second-moment sum-rule except, contrary to current theory [4], for its failure at the critical point (T_c, ρ_c). Furthermore, the k^4 term in the charge–charge correlation or structure factor $S_{ZZ}(k)$ expansion is found to diverge like the compressibility when $T \to T_c$ at ρ_c. These findings are in evident disagreement with available theory for *charge-symmetric* models and, although their results are qualitatively similar to behavior expected for *charge-asymmetric* systems [4], even a semiquantitative understanding has eluded them.

Starting from the Ornstein–Zernike equation and extending at all densities the small density diagrammatic [5] property for the partial direct correlation functions of behaving as $1/r$ in the $r \to \infty$ limit, it is possible to arrive quickly to the second- and fourth-moment sum rules even if the fourth-moment one will not be expressed in terms of just thermodynamic functions.

The second- and fourth-moment sum-rules are rigorously derived starting from the Born–Green–Yvon equations and the exponential clustering hypothesis by Suttorp and van Wonderen [6–8] for a thermodynamically stable ionic mixture made of pointwise particles of charges all of the same sign immersed in a neutralizing background, the "Jellium". The same

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sum-rules must hold also when we allow in the ionic mixture the presence of mobile charges of *both signs*, which requires to consider a pair-potential regularization in order to prevent opposite charges collapse.

In this work we critically discuss the numerical findings of Das, Kim, and Fisher [2] at the light of the above mentioned analytical work of Suttorp and van Wonderen [6–8] and of a recent result of Santos and Piasecki [9] proving the long range behavior of the n-body correlation functions of a general fluid at his gas–liquid critical point.

2. The ionic fluids model

A multi-component ionic mixture of an electrolyte is made of mobile charges whose μ component (the particles of species μ) has molar fraction x_μ and charge $z_\mu e$, here e is the unit of charge and z_μ are integer numbers. So we may, in general, have charges of both signs. One is generally interested in studying a neutral state (since matter around us is neutrally charged). This can be obtained in the event that $\sum_\mu x_\mu z_\mu = 0$. Otherwise is necessary the addition of a neutralizing uniform background of charge density $-\rho e \sum_\mu x_\mu z_\mu$, with ρ the number density of the system of charges. A particularly simple case id the Restricted Primitive Model (RPM) where we have only two components with $x_1 = x_2 = 1/2$ and $z_1 = -z_2 = 1$ (without a background).

The Hamiltonian of a multi-component ionic mixture consisting of s components, confined in a region $\Omega \subset \mathbb{R}^3$ of volume V, is

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m_{\alpha_i}} + U(\mathbf{r}_1, \ldots, \mathbf{r}_N), \tag{2.1}$$

$$U = \frac{1}{2} \sum_{i,j}' z_{\alpha_i} z_{\alpha_j} v_{\alpha_i \alpha_j}(|\mathbf{r}_i - \mathbf{r}_j|), \tag{2.2}$$

with $p = |\mathbf{p}|$ and the pair-potential

$$v_{\mu\nu}(r) = v^c(r) + v^{sr}_{\mu\nu}(r), \tag{2.3}$$

where $r = |\mathbf{r}|$, v^c is the bare Coulomb potential

$$v^c(r) = \frac{e^2}{V} \sum_{\mathbf{k}(\neq \mathbf{0})} \frac{4\pi}{k^2} e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{2.4}$$

and v^{sr} is a short-range regularization assumed integrable on $\mathbb{R}^3$ which includes the local repulsion effect needed to enforce thermodynamic stability [10] when we allow for the presence of particles of opposite charge in the mixture. A first soft regularization can be chosen as

$$v^{sr}_{\mu\nu}(r) = -\frac{e^2}{r} e^{-r/d_{\mu\nu}}, \tag{2.5}$$

where the lengths $d_{\mu\nu}$ control the exponential decay at large distances. A second regularization amounts to introduce hard-cores, namely

$$v^{sr}_{\mu\nu}(r) = \begin{cases} \infty & r < \sigma_{\mu\nu} \\ 0 & r > \sigma_{\mu\nu}, \end{cases} \tag{2.6}$$

where $\sigma_{\mu\nu} = (\sigma_\mu + \sigma_\nu)/2$ and σ_μ is the diameter of the hard-sphere particles of species μ. In Eq. (2.4) we used periodic boundary conditions just to stress the fact that we are interpreting the Monte Carlo simulations of Das, Kim, and Fisher [2], but of course our theoretical arguments apply to the continuous system as well.

The system contains N_μ particles of species μ. We will denote by $\mathbf{q} = (\alpha, \mathbf{r})$ the species α and the position $\mathbf{r}$ of a particle of this species. The particle i of species μ has mass m_{μ_i}, charge $z_{\mu_i} e$ with e the unit of charge and $z_{\mu_i} = 0, \pm1, \pm2, \ldots$, position $\mathbf{r}_i$, and momentum $\mathbf{p}_i$. The symbol $\sum'$ means that one should sum over all particles under the restriction $i \neq j$ when $\alpha_i = \alpha_j$. Periodic boundary conditions have been assumed in the definition of the pair-potential. Each charge in the region Ω is neutralized by a uniform background of opposite charge density. On account of the presence of the neutralizing background the term $\mathbf{k} = \mathbf{0}$ is excluded in Eq. (2.4). The potential energy of Eq. (2.2) is defined up to an additive constant, the Madelung constant $\sum_i z_{\alpha_i}^2 \lim_{r\to 0} [v^c(r) - e^2/r]/2$, which takes into account the interaction of a particle with its own images, and which becomes important in a grand-canonical calculation. We will generally use a Greek index to denote the species label and a Roman index to denote the particle label.

Moreover we impose the constraint

$$Q = Ne \sum_{\mu=1}^{s} x_\mu z_\mu = \text{constant}, \tag{2.7}$$

where $N = \sum_\mu N_\mu$ is the total number of particles and $x_\mu = N_\mu/N$ are the molar fractions of particles of species μ. We also have that $\rho = N/V$ is the particles density and $\rho_\mu = \rho x_\mu$ are the partial densities of the ionic mixture. The neutralizing background has an uniform charge density $-e\rho_Z$ with $\rho_Z = \rho \sum_\mu x_\mu z_\mu$.

Table 1
Critical point estimates for the RPM model from several computer simulation studies. The reduced temperature is $T^* = k_B T \sigma / e^2$, with k_B Boltzmann constant, and the reduced density is $\rho^* = \rho \sigma^3$.

Reference	Year	T_c^*	ρ_c^*
Valleau [12]	1991	0.070	0.07
Panagiotopoulos [13]	1992	0.056	0.04
Orkoulas [14]	1994	0.053	0.025
Caillol [15,16]	1997	0.0488(2)	0.080(5)
Orkoulas [17]	1999	0.0490(3)	0.070(5)
Yan [18]	1999	0.0492(3)	0.062(5)
Caillol [19]	2002	0.04917(2)	0.080(5)

The 1:1 equisized charge-symmetric hard sphere electrolyte, the RPM model, is obtained as the particular case with $s = 2$, $x_1 = x_2 = 1/2$, $\sigma_1 = \sigma_2 = \sigma$, $z_1 = -z_2 = 1$. So that $Q = 0$ and the neutralizing background vanishes.

The RPM has been carefully studied through several computer simulations and the critical point of the gas–liquid coexistence has been given various estimates during the years as summarized in Table 1. On the coexistence spinodal line the isothermal compressibility $\chi_T = (\partial \rho / \partial p)_{\{N_\mu\}, T} / \rho \rightarrow \infty$, with p the pressure of the mixture. On approaching the critical point, the amplitude of density fluctuations increases and local fluctuations become correlated over increasingly long distances. Anomalies in the intensity of light scattered from a fluid near its critical point, particularly the phenomenon known as critical opalescence, were first studied theoretically by Ornstein and Zernike as far back as 1914 [11].

3. The moment sum-rules

While the thermodynamic stability of the fluid model ensures the existence of the correlation functions in the thermodynamic limit,

$$\rho^{(n)}(\mathbf{q}_1, \ldots, \mathbf{q}_n) = \rho_1 \cdots \rho_n \, g_{\alpha_1 \ldots \alpha_n}^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n)$$
$$= \left\langle \sum_{i_1, \ldots, i_n}' \delta(\mathbf{r}_1 - \mathbf{r}_{i_1}) \delta_{\alpha_1, \alpha_{i_1}} \cdots \delta(\mathbf{r}_n - \mathbf{r}_{i_n}) \delta_{\alpha_n, \alpha_{i_n}} \right\rangle, \quad n = 1, 2, \ldots, \tag{3.1}$$

where $\langle \ldots \rangle$ is a thermal average defined for an infinitely extended system, sum-rules are exact relationships that the correlation functions must obey and can be derived from the microscopic constituent equations like for example the Born–Green–Yvon (BGY) hierarchy [5] under appropriate plausible assumptions.

Sometimes it proves convenient to introduce another set of correlation functions, namely the Ursell's functions $h^{(n)}$,

$$g_{\alpha_1 \alpha_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = h_{\alpha_1 \alpha_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) + 1, \tag{3.2}$$

$$g_{\alpha_1 \alpha_2 \alpha_3}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = h_{\alpha_1 \alpha_2 \alpha_3}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + h_{\alpha_1 \alpha_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) + h_{\alpha_1 \alpha_3}^{(2)}(\mathbf{r}_1, \mathbf{r}_3) + h_{\alpha_2 \alpha_3}^{(2)}(\mathbf{r}_2, \mathbf{r}_3) + 1, \tag{3.3}$$

$$\begin{aligned}
g_{\alpha_1 \alpha_2 \alpha_3 \alpha_4}^{(4)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = {} & h_{\alpha_1 \alpha_2 \alpha_3 \alpha_4}^{(4)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) + h_{\alpha_1 \alpha_2 \alpha_3}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + h_{\alpha_1 \alpha_2 \alpha_4}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_4) \\
& + h_{\alpha_1 \alpha_3 \alpha_4}^{(3)}(\mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_4) + h_{\alpha_2 \alpha_3 \alpha_4}^{(3)}(\mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \\
& + h_{\alpha_1 \alpha_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) h_{\alpha_3 \alpha_4}^{(2)}(\mathbf{r}_3, \mathbf{r}_4) + h_{\alpha_1 \alpha_3}^{(2)}(\mathbf{r}_1, \mathbf{r}_3) h_{\alpha_2 \alpha_4}^{(2)}(\mathbf{r}_2, \mathbf{r}_4) \\
& + h_{\alpha_1 \alpha_4}^{(2)}(\mathbf{r}_1, \mathbf{r}_4) h_{\alpha_2 \alpha_3}^{(2)}(\mathbf{r}_2, \mathbf{r}_3) + h_{\alpha_1 \alpha_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \\
& + h_{\alpha_1 \alpha_3}^{(2)}(\mathbf{r}_1, \mathbf{r}_3) + h_{\alpha_1 \alpha_4}^{(2)}(\mathbf{r}_1, \mathbf{r}_4) \\
& + h_{\alpha_2 \alpha_3}^{(2)}(\mathbf{r}_2, \mathbf{r}_3) + h_{\alpha_2 \alpha_4}^{(2)}(\mathbf{r}_2, \mathbf{r}_4) + h_{\alpha_3 \alpha_4}^{(2)}(\mathbf{r}_3, \mathbf{r}_4) + 1,
\end{aligned} \tag{3.4}$$
$$\cdots$$

It has been shown by Alastuey and Martin [20] that among all possible long-range potentials, it is only the Coulomb case that a decay law of the Ursell correlations faster than any inverse power is compatible with the structure of equilibrium BGY equations. We may then assume, at least far away from a critical point, that these Ursell functions tend to zero faster than any power r_{ij}^{-m} with integer m, if the separation r_{ij} between the positions $\mathbf{r}_i$ and $\mathbf{r}_j$ goes to infinity. This assumption is the usual *exponential clustering hypothesis* for charged systems.

Introducing the notation $\int d\mathbf{q} \ldots = \int d\mathbf{r} \sum_{\alpha=1}^{s} \ldots$ we must have the following normalization properties for the two sets,

$$\lim_{N \rightarrow \infty} \frac{1}{N^n} \int d\mathbf{q}_1 \ldots d\mathbf{q}_n \, \rho^{(n)}(\mathbf{q}_1, \ldots, \mathbf{q}_n) = 1, \tag{3.5}$$

$$\lim_{N \rightarrow \infty} \frac{1}{N^n} \int d\mathbf{q}_1 \ldots d\mathbf{q}_n \, \rho_1 \cdots \rho_n h_{\alpha_1 \ldots \alpha_n}^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n) = 0. \tag{3.6}$$

In the following we will drop the superscript on the correlation functions when not leading to confusion. Note also that $\rho(\mathbf{q}) = \langle \sum_i \delta(\mathbf{r} - \mathbf{r}_i)\delta_{\alpha,\alpha_i} \rangle = \rho_\alpha$ in a homogeneous mixture whereas $h^{(2)}_{\alpha_1\alpha_2}(\mathbf{r}_1, \mathbf{r}_2) = h_{\alpha_1\alpha_2}(|\mathbf{r}_1 - \mathbf{r}_2|)$ in a homogeneous and isotropic mixture.

3.1. The Ornstein–Zernike approach

The Ornstein–Zernike (OZ) equation in reciprocal-space for a fluid mixture is given by

$$\hat{h}_{\mu\nu}(k) = \hat{c}_{\mu\nu}(k) + \rho \sum_\lambda x_\lambda \hat{c}_{\mu\lambda}(k)\hat{h}_{\lambda\nu}(k), \tag{3.7}$$

where $k = |\mathbf{k}|$, $\hat{h}_{\mu\nu}(k)$ is the Fourier transform of the partial total correlation functions $h_{\mu\nu}(r) = g_{\mu\nu}(r) - 1$ with $g_{\mu\nu}$ the partial radial distribution functions

$$g_{\mu\nu}(r) = \frac{1}{N\rho x_\mu x_\nu} \left\langle \sum_{i,j}' \delta_{\mu,\alpha_i}\delta_{\nu,\alpha_j}\delta(\mathbf{r} - \mathbf{r}_i - \mathbf{r}_j) \right\rangle, \tag{3.8}$$

and $\hat{c}_{\mu\nu}(k)$ are the Fourier transform of the partial direct correlation functions [5].

The partial structure factors are defined as

$$S_{\mu\nu}(k) = x_\mu \delta_{\mu\nu} + \rho x_\mu x_\nu \hat{h}_{\mu\nu}(k). \tag{3.9}$$

Given a partial function $f_{\mu\nu}$ we can now introduce the following number–number, number–charge, and charge–charge functions

$$\begin{cases} f_{NN} = \sum_{\mu,\nu} f_{\mu\nu} \\ f_{NZ} = \sum_{\mu,\nu} z_\mu f_{\mu\nu} \\ f_{ZZ} = \sum_{\mu,\nu} z_\mu z_\nu f_{\mu\nu} \end{cases} \tag{3.10}$$

where in the RPM case $f_{NZ} = 0$.

We can moreover introduce the following definitions

$$\begin{cases} \tilde{h}_{\mu\nu} = \sqrt{x_\mu x_\nu}\hat{h}_{\mu\nu} \\ \tilde{c}_{\mu\nu} = \sqrt{x_\mu x_\nu}\hat{c}_{\mu\nu} \\ \tilde{S}_{\mu\nu} = S_{\mu\nu}/\sqrt{x_\mu x_\nu} = \delta_{\mu\nu} + \rho\tilde{h}_{\mu\nu} \end{cases} \tag{3.11}$$

with which the OZ equation can be written in a simple matrix form

$$\tilde{\mathbf{S}} - \mathbf{I} = \rho\tilde{\mathbf{S}}\tilde{\mathbf{c}}, \tag{3.12}$$

where $\mathbf{I}$ is the identity matrix. Eq. (3.12) can also be rewritten as follows

$$\tilde{\mathbf{S}} = (\mathbf{I} - \rho\tilde{\mathbf{c}})^{-1}. \tag{3.13}$$

It is natural [5] to separate the direct correlation functions into a short-range and a Coulombic part

$$\hat{c}_{\mu\nu}(k) = \hat{c}^{sr}_{\mu\nu}(k) - \frac{4\pi\beta z_\mu z_\nu e^2}{k^2}, \tag{3.14}$$

where $\hat{c}^{sr}_{\mu\nu}(k)$ is a regular function in the $k \to 0$ limit. We then see, after some algebra, that in the small k limit, it must be $S_{NN} \sim k^0$, $S_{NZ} \sim k^2$, and $S_{ZZ} \sim k^2$. Moreover, It is a simple algebraic task, starting from the matrix form $\tilde{\mathbf{S}} = k^2(k^2\mathbf{I} - \rho k^2\tilde{\mathbf{c}})^{-1}$, to show that for the RPM case

$$S_{ZZ}(k) = \frac{k^2}{(k_D/\bar{z}_2)^2} + \left(\frac{\rho}{4}\hat{c}^{sr}_{ZZ}(0) - 1\right)\frac{k^4}{(k_D/\bar{z}_2)^4} + O(k^6), \tag{3.15}$$

where $k_D = \sqrt{4\pi\beta\rho\bar{z}_2^2 e^2}$ is the Debye wave-number with $\bar{z}_2^2 = \sum_\mu x_\mu z_\mu^2$. In the RPM $\bar{z}_2^2 = 1$. Since we have $S_{ZZ}(k) = \sum_\mu x_\mu z_\mu^2 + \rho \sum_{\mu,\nu} x_\mu x_\nu z_\mu z_\nu \hat{h}_{\mu\nu}(k)$, using spherical symmetry, from Eq. (3.15) follow the following first three charge–charge

moment sum-rules

$$\rho \sum_{\mu,\nu} x_\mu x_\nu z_\mu z_\nu \int d\mathbf{r}\, h_{\mu\nu}(r) = -\bar{z}_2^2 \tag{3.16}$$

$$\rho \sum_{\mu,\nu} x_\mu x_\nu z_\mu z_\nu \int d\mathbf{r}\, r^2 h_{\mu\nu}(r) = -\frac{6}{(k_D/\bar{z}_2)^2} \tag{3.17}$$

$$\rho \sum_{\mu,\nu} x_\mu x_\nu z_\mu z_\nu \int d\mathbf{r}\, r^4 h_{\mu\nu}(r) = -\frac{120}{(k_D/\bar{z}_2)^4} \left(1 - \frac{\rho}{4}\hat{c}_{ZZ}^{sr}(0)\right). \tag{3.18}$$

The first identity, the zeroth-moment sum-rule, is a consequence of the normalization conditions of the correlation functions (3.8)

$$\rho \sum_{\mu} x_\mu z_\mu \int d\mathbf{r}\, h_{\mu\nu}(r) = \sum_{\mu} z_\mu \frac{\langle N_\mu N_\nu\rangle - \langle N_\mu\rangle\langle N_\nu\rangle - \delta_{\mu\nu}\langle N_\mu\rangle}{\langle N_\nu\rangle} = -z_\nu \tag{3.19}$$

and reflects internal screening (or bulk elecroneutrality). The second, the second-moment sum-rule, is commonly known as the Stillinger–Lovett (SL) condition [21] and reflects external screening. The third is the fourth-moment sum-rule.

In view of the exponential clustering expected to hold in ionic fluids away from criticality (see next section) we may assume the following small k expansions

$$S_{NN}(k)/S_{NN}(0) = 1 + \sum_{p\geq 1} (-)^p \xi_{N,p}^{2p}(T,\rho) k^{2p}, \tag{3.20}$$

$$S_{ZZ}(k)/\bar{z}_2^2 = 0 + \xi_{Z,1}^2 k^2 - \sum_{p\geq 2} (-)^p \xi_{Z,p}^{2p}(T,\rho) k^{2p}, \tag{3.21}$$

where working in the grand-canonical ensemble [5] $S_{NN}(0) = \chi_T/\chi_T^0$ with $\chi_T^0 = \beta/\rho$ the isothermal compressibility of the ideal gas.

Das, Kim, and Fisher [2] has calculated through grand-canonical Monte Carlo simulations the second S_2 and fourth S_4 moments: $S_{ZZ}(k)/\bar{z}_2^2 = 0 + S_2 k^2 - S_4 k^4 + \cdots$ for the RPM, and found a deviation of about 16% on the SL condition, $S_2 = 1/k_D^2$, at criticality. Moreover S_4 appears to diverge to $+\infty$ upon approaching the RPM critical point. At criticality, density correlations are long ranged and [11] $S_{NN}(k) \sim 1/k^{2-\eta}$ for $k \to 0$ with $0 < \eta < 1$ the anomalous critical-point decay exponent [22] (equal to zero in the Ornstein–Zernike theory) [23]. Equivalently, in real-space, in three dimensions, $\sum_{\mu,\nu} x_\mu x_\nu h_{\mu\nu}(r) \sim 1/r^{1+\eta}$ for $r \to \infty$. Then according to Proposition 1 of Ref. [24] we cannot say anything about the SL sum-rule; the fact that the SL sum rule is found to fail means that the density correlations must decay as $1/r^5$ or slower. Evidently the development of clustering or association amongst the particles of the mixture upon approaching the critical point inhibits the external screening. Or in other words, the diverging density fluctuations that characterize criticality destroy perfect screening at (T_c, ρ_c).

3.2. The Born–Green–Yvon approach [6–8]

Suttorp and van Wonderen [6] study a thermodynamically stable ionic mixture with pointwise mobile charges all of the same sign ($z_\mu \leq 0$ for all μ) with the pair-potential of Eq. (2.3) without the short-range term v^{sr}. Starting from the Born–Green–Yvon hierarchy [5] and using the hypothesis of exponential clustering of the Ursell's functions they are able to show that independently of the statistical ensemble used to describe the ionic liquid the internal screening and SL conditions (3.16)–(3.17) hold. In order to make progress for subsequent relationships one has to specify the ensemble. In a grand-canonical ensemble with the constraint (2.7) the independent variables are β, V, the $s-1$ chemical potentials, and $q = Q/V$. They are able to prove the following additional sum-rules for the partial pair Ursell's functions

$$\rho \sum_{\mu,\nu} x_\mu x_\nu \int d\mathbf{r}\, h_{\mu\nu}(r) = \frac{2}{3}\frac{\beta}{\rho}\frac{\partial\rho}{\partial\beta} - 2\frac{q}{\rho}\frac{\partial\rho}{\partial q} + 1, \tag{3.22}$$

$$\rho \sum_{\mu,\nu} x_\mu x_\nu z_\mu \int d\mathbf{r}\, r^2 h_{\mu\nu}(r) = -\frac{6}{(k_D/\bar{z}_2)^2} e\frac{\partial\rho}{\partial q}, \tag{3.23}$$

$$\rho \sum_{\mu,\nu} x_\mu x_\nu z_\mu z_\nu \int d\mathbf{r}\, r^4 h_{\mu\nu}(r) = -\frac{120}{(k_D/\bar{z}_2)^4} \frac{e^2\beta\rho}{q}\frac{\partial p}{\partial q}, \tag{3.24}$$

where p is the pressure and in the partial derivatives all others independent variables are kept constant. For example, we see that from Eq. (3.22) follows

$$S_{NN}(0) = \frac{\chi_T}{\chi_T^0} = \frac{2}{3}\frac{\beta}{\rho}\frac{\partial\rho}{\partial\beta} + 2\left(1 - \frac{q}{\rho}\frac{\partial\rho}{\partial q}\right). \tag{3.25}$$
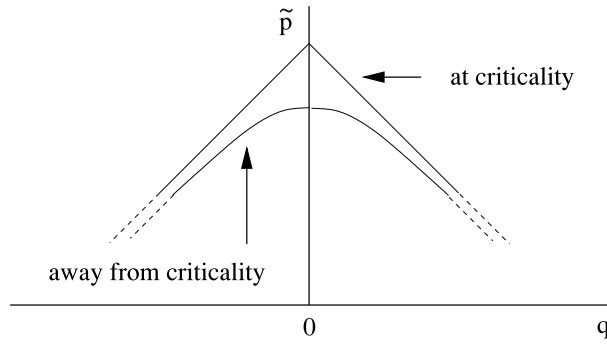
Fig. 1. Sketch of $\tilde{p}(q)$ near $q = 0$ upon approaching criticality.

For an ionic mixture with positive and negative mobile charges, made thermodynamically stable by the addition of the short-range pair-potential v^{sr}, the zeroth-moment of Eqs. (3.22) and (3.16) clearly continue to hold as well as the second-moment SL sum-rule of Eqs. (3.18)–(3.23) as it is shown in Ref. [24]. Note that in order to derive the SL sum-rule a weaker condition than the exponential clustering hypothesis is actually needed as shown in Ref. [24]. That is, one just needs to require a certain short-range behavior of the Ursell functions. For the fourth-moment condition of Eq. (3.24) we also expect there to be no effect due to the short-range regularization as shown in Refs. [25–27] and in Appendix. So we can say that the Suttorp and van Wonderen sum-rules hold generally for the more general ionic liquid model of a mixture with positive and negative mobile charges opportunely regularized.

On the other hand from the work of Santos and Piasecki [9] follows that the Ursell functions of any order have a long-range behavior on a critical point, thus violating the exponential clustering hypothesis necessary to prove the Suttorp and van Wonderen sum rules. In this sense the numerical result found by Fisher et al. of the violation of the second and fourth moment of the charge–charge structure factor of the Restricted Primitive Model at criticality, is not in contradiction with the result of Suttorp and van Wonderen. But is instead telling us something that goes beyond the analysis of the sum-rules based on the exponential clustering hypothesis.

Note that we can write the partial derivative on the right hand side of Eq. (3.23) as follows

$$
\begin{aligned}
\frac{\partial \rho}{\partial q} &= \frac{\partial(\rho, \mu_1, T, V)}{\partial(q, \mu_1, T, V)} \\
&= \frac{\partial(\rho, \mu_1, T, V)}{\partial(N_1, N_2, T, V)} \frac{\partial(N_1, N_2, T, V)}{\partial(q, \mu_1, T, V)} \\
&= \frac{1}{V}\left[\left(\frac{\partial \mu_1}{\partial N_2}\right)_{N_1} - \left(\frac{\partial \mu_1}{\partial N_1}\right)_{N_2}\right]_{T,V}\left[\left(\frac{\partial N_1}{\partial q}\right)_{\mu_1}\left(\frac{\partial N_2}{\partial \mu_1}\right)_q - \left(\frac{\partial N_1}{\partial \mu_1}\right)_q\left(\frac{\partial N_2}{\partial q}\right)_{\mu_1}\right]_{T,V}.
\end{aligned}
\tag{3.26}
$$

So that for the symmetric RPM where $\mu_1 = \mu_2$, using the $1 \leftrightarrow 2$ symmetry, we find $\partial \rho/\partial q = 0$, since the first Jacobian vanishes. Whereas, for a one component system, where $q = e\rho$, we find $\partial \rho/\partial q = 1/e$.

From the analysis of Suttorp and van Wonderen we also deduce that

$$
\bar{z}_2^2 S_4 = \left(\frac{\bar{z}_2}{k_D}\right)^4 \frac{e^2 \beta \rho}{q} \frac{\partial p}{\partial q} = -\left(\frac{\bar{z}_2}{k_D}\right)^4 e^2 \beta \rho \frac{\partial^2 \tilde{p}}{\partial q^2},
\tag{3.27}
$$

where $\tilde{p} = p - q\tilde{\mu}_q$ with $\tilde{\mu}_q = -\partial \tilde{p}/\partial q$ the Lagrange multiplier which takes into account of the constraint (2.7). The RPM results of Das, Kim, and Fisher [2] show how $(k_D/\bar{z}_2)^4 \bar{z}_2^2 S_4 \to 0$ for $\rho \to 0$ (their Fig. 3). This is easily explained observing that as $\rho \to 0$ we must have $\beta p \to \rho$ so that from Eq. (3.27) follows

$$
(k_D/\bar{z}_2)^4 \bar{z}_2^2 S_4 \to e^2 \frac{\partial \rho^2}{\partial q^2} = 0.
\tag{3.28}
$$

This result also implies that, in view of Eq. (3.18), $\rho \hat{c}_{ZZ}^{sr}(0) \to 4$.

Moreover from Das, Kim, and Fisher [2] Fig. 4, follows that in the RPM we must have

$$
\lim_{q \to 0} \frac{\partial^2 \tilde{p}}{\partial q^2} = -\infty
\tag{3.29}
$$

when one approaches the critical point. Notice that by charge symmetry we must have that both p and $\tilde{p}$ are even functions of q. So a sketch of $\tilde{p}(q)$ near $q = 0$ must look as in Fig. 1. The figure aims to give a very qualitative sketch of $\tilde{p}(q)$ only in a very narrow neighborhood of $q = 0$. Away from criticality we must have $\partial p/\partial q|_{q=0} = 0$ and S_4 is finite. But near

criticality $\partial p/\partial q|_{q=0} > 0$ and S_4 diverges. This means that near criticality there is a non negligible variation of the pressure of the fluid upon switching on a charge asymmetry ($q \neq 0$) keeping overall neutrality with the neutralizing background. So notwithstanding the fact that the exponential clustering hypothesis breaks down near criticality the results of Das, Kim, and Fisher [2] do not tell us anything about the failure of the fourth-moment sum-rule. On the other hand their Figs. 1 and 2 indicate the failure of the SL condition upon approaching the critical point, as already observed in the previous section.

4. Conclusions

We studied a general ionic mixture with particles of different mass, diameter, and charge immersed in a neutralizing background so that the mixture is globally neutral. When we allow for the presence of mobile charges of opposite sign we need to add either a soft- or a hard-core regularization to the pair-potential in order to make the mixture thermodynamically stable.

We derived a series of sum-rules on the first three moments of the charge–charge correlation functions starting from the Ornstein–Zernike theory [5]. Then we showed that the sum-rules derived by Suttorp and van Wonderen [6] for an ionic mixture made of particles all of the same sign immersed in a neutralizing background remain valid if one allows the particles to carry charges of opposite sign and adds a soft or a hard-core repulsion in order to ensure thermodynamic stability. In particular they remain valid for the symmetric RPM case when the neutralizing background vanishes. Suttorp and van Wonderen derivation relies on the assumption of the exponential clustering in the mixture [1].

We interpreted recent results of Das, Kim, and Fisher [2] reporting the failure of the charge–charge second-moment sum-rules for the RPM of a ionic liquid at criticality and the divergence of the charge–charge fourth-moment at criticality. In particular the divergence of the fourth moment S_4 at the critical point of the RPM seems to still be in agreement with the fourth-moment sum-rule (even if the exponential clustering of the Ursell's function breaks down there as shown in Ref. [9]) if one assumes that at criticality there is a non negligible variation of the pressure of the fluid upon switching on a charge asymmetry ($q \neq 0$) keeping overall neutrality with the neutralizing background. The observed violation of the second-moment sum-rule on the other hand seems to indicate that at criticality the clustering phenomenon occurring in the ionic mixture is responsible for the break down of the external screening and the system behaves as an insulator [1]. At criticality we do not have anymore an exponential or short-range clustering but a long-range clustering as shown by the results of Ref. [9].

Our results could be helpful to a better understanding of Refs. [28,29] and Refs. [30–32]. Moreover our results could give some insights to study the critical behavior of more complex fluids such as the ones described in Refs. [33–45].

Acknowledgments

Appendix. Invariance in form of the moment sum-rules under the addition of a hard-core

Let us call PWE the point-wise particle electrolyte considered by Suttorp and van Wonderen [6] and HSE the hard-sphere electrolyte obtained by our model of Eqs. (2.1)–(2.6). The configurations space of PWE is Ω^N whereas the one of HSE is $\mathcal{O}_N = \{\mathbf{R} \equiv (\mathbf{r}_1, \ldots, \mathbf{r}_N) \in \Omega^N | \quad \forall i, j \neq i \quad |\mathbf{r}_i - \mathbf{r}_j| > \sigma_{\alpha_i \alpha_j}\} \subset \Omega^N$. In particular it is well known from electrostatics that HSE is equivalent to the PWE restricted to the configuration space $\mathcal{O}_N$. We then conclude that the sum-rules of Eqs. (3.23) and (3.24) must hold also for the HSE. In any case the thermodynamic quantities on both sides of the sum-rule will remain unchanged after the restriction. Infact, calling the complementary set $\mathcal{O}_N^c = \Omega^N - \mathcal{O}_N = \{\mathbf{R} \equiv (\mathbf{r}_1, \ldots, \mathbf{r}_N) \in \Omega^N | \quad \exists i, j \neq i \quad |\mathbf{r}_i - \mathbf{r}_j| \leq \sigma_{\alpha_i \alpha_j}\}$ we have for a generic thermal average of an everywhere finite physical observable

$$
\begin{aligned}
\langle \ldots \rangle_{\text{PWE}} &= \frac{\int_{\Omega^N} \ldots e^{-\beta U} d\mathbf{R}}{\int_{\Omega^N} e^{-\beta U} d\mathbf{R}} = \frac{\int_{\mathcal{O}_N} \ldots e^{-\beta U} d\mathbf{R} + \int_{\mathcal{O}_N^c} \ldots e^{-\beta U} d\mathbf{R}}{\int_{\mathcal{O}_N} e^{-\beta U} d\mathbf{R} + \int_{\mathcal{O}_N^c} e^{-\beta U} d\mathbf{R}} \\
&= \frac{\int_{\mathcal{O}_N} \ldots e^{-\beta U} d\mathbf{R} \left(1 + \int_{\mathcal{O}_N^c} \ldots e^{-\beta U} d\mathbf{R} / \int_{\mathcal{O}_N} \ldots e^{-\beta U} d\mathbf{R}\right)}{\int_{\mathcal{O}_N} e^{-\beta U} d\mathbf{R} \left(1 + \int_{\mathcal{O}_N^c} e^{-\beta U} d\mathbf{R} / \int_{\mathcal{O}_N} e^{-\beta U} d\mathbf{R}\right)} \\
&\to \frac{\int_{\mathcal{O}_N} \ldots e^{-\beta U} d\mathbf{R}}{\int_{\mathcal{O}_N} e^{-\beta U} d\mathbf{R}} = \langle \ldots \rangle_{\text{HSE}},
\end{aligned}
\tag{A.1}
$$

in the thermodynamic limit $\Omega \to \mathbb{R}^3$ and $N = \rho V$. Since the measure of $\mathcal{O}_N$ is an infinite of higher order than the measure of $\mathcal{O}_N^c$. This does not mean of course that the Ursell functions themselves will be equal for the PWE and the HSE and in fact they will be different generally.

This argument suggests that Suttorp and van Wonderen analysis [6] continues to hold also for an ionic mixture with mobile charges of opposite sign opportunely regularized. This has recently been proved semi-heuristically by Alastuey and Fantoni [27] for the fourth moment of the charge–charge structure factor of such an ionic mixture.

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