BREAKDOWN OF EXPONENTIAL SCREENING AT THE CRITICAL POINT OF A CLASSICAL ELECTROLYTE

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OUTLINE

- **A**. SOFT RPM
  1. Definitions
  2. Exponential screening at low density
  3. Liquid-gas transition
- **B**. CRITICAL POINT
  1. Universality class
  2. Screening properties
- **C**. YBG HIERARCHY
  1. Strategy
  2. Equations and validity
  3. Internal charge sum rules
  4. Dielectric constant in terms of a dipole
  5. A plausible model for three-point correlations
  6. Charge and dipole constraints at large distances
  7. Infection mechanism of charge correlations
  8. Algebraic decay of charge correlations
- CONCLUDING COMMENTS

A1.SOFT RPM : Definitions and thermodynamic limit

- Classical symmetric electrolyte, pairwise interactions

$$u_{++}(r) = u_{--}(r) = v_{\mathrm{SR}}(r) + q^2 v_{\mathrm{C}}(r)$$
$$u_{+-}(r) = u_{-+}(r) = v_{\mathrm{SR}}(r) - q^2 v_{\mathrm{C}}(r)$$

with $v_{\mathrm{C}}(r) = 1/r$ and $v_{\mathrm{SR}}(r) = V_0(\sigma/r)^n \mathrm{e}^{-r/\sigma}$ with $n > 1$. (Soft version of the **Restricted Primitive Model** of charged hard spheres).

- **Existence** of the Thermodynamic Limit : **proofs** for [(i) RPM [BRYDGES-FEDERBUSH,1980] (ii) Quantum nuclei-electronic plasma [LIEB-LEBOWITZ,1972]]

- Homogeneous fluid phase **locally neutral** : $\rho_+ = \rho_- = \rho$

Two-point density and charge correlations $(\mathbf{r} = \mathbf{r}_{\mathrm{b}} - \mathbf{r}_{\mathrm{a}})$

$$N(r) = \lim_{\mathrm{TL}} \langle \hat{\rho}(\mathbf{r}_{\mathrm{a}}) \hat{\rho}(\mathbf{r}_{\mathrm{b}}) \rangle = 2\rho\delta(\mathbf{r}) + 2\rho^2 [h_{++}(r) + h_{+-}(r)]$$
$$S(r) = \lim_{\mathrm{TL}} \langle \hat{c}(\mathbf{r}_{\mathrm{a}}) \hat{c}(\mathbf{r}_{\mathrm{b}}) \rangle = 2q^2\rho\delta(\mathbf{r}) + 2q^2\rho^2 [h_{++}(r) - h_{+-}(r)]$$

A2.SOFT RPM : Exponential screening at low density

- Debye theory (**Mean-field**) : $h_{++}(r) = -h_{+-}(r) = -\beta q^2 \phi_{\mathrm{D}}(r)$

$$[\Delta - \kappa_{\mathrm{D}}^2]\phi_{\mathrm{D}}(r) = -4\pi\delta(\mathbf{r}) \quad , \quad \kappa_{\mathrm{D}}^2 = 8\pi\beta q^2 \rho$$

$$\phi_{\mathrm{D}}(r) = v_{\mathrm{C}}(r)\mathrm{e}^{-\kappa_{\mathrm{D}} r}$$

- Systematic **corrections** to Debye theory

Screened Mayer diagrammatic series with bonds

$b_{\mathrm{D}} = -\beta e_\alpha e_\gamma \phi_{\mathrm{D}}(r)$ and $b_{\mathrm{AM}} = \mathrm{e}^{-\beta e_\alpha e_\gamma \phi_{\mathrm{D}}(r)} - 1 + \beta e_\alpha e_\gamma \phi_{\mathrm{D}}(r)$.

Term by term exponential decay of $h_{++}(r)$ and $h_{+-}(r)$

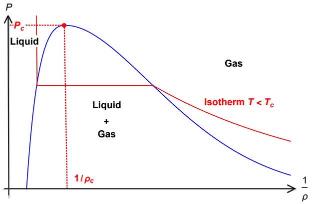
- **Proof** at sufficiently low density and high temperature

[Use of an equivalent field theory model with Sine-Gordon action]

$$|h_{\alpha\gamma}(r)| < C_1 \mathrm{e}^{-C_2 \kappa_{\mathrm{D}} r}$$

A3.SOFT RPM : Liquid-Gas transition

- Neutral systems with Lenard-Jones like potentials (**repulsive** part + **attractive** part)



- Various evidences for a classical electrolyte

Numerical simulations and experimental observations

[Caillol-Leveque,2014] [Das-Kim-Fisher,2012] [Fisher,1994]

- Generation of **effective attractive** interactions

Formation of dimers, trimers,...

B1. CRITICAL POINT: Universality Class

- Critical exponents for thermodynamic singularities

$$(T \to T_c^+ \quad \text{at fixed} \quad \rho = \rho_c)$$

  - Neutral fluids with short-range attractive interactions: ISING
  - Neutral fluids with power-law attractive interactions: ISING-like
  - Electrolyte : ISING-like rather than Mean-Field (long-standing controversy)

- Exponent for the long-range behavior of density correlations

$(T = T_c, \rho = \rho_c : N(r) \sim A/r^{1+\eta}$ when $r \to \infty)$

  - $\eta = 0$ for short-range attractive interactions
  - $\eta > 0$ for power-law attractive or Coulomb interactions

NO FIRMLY ESTABLISHED RESULTS FOR COULOMB

B2. CRITICAL POINT: Screening properties

- **Algebraic infection** of charge correlations ?

(various contradictory answers)

- ▶ NO (diagrammatic representations of direct correlations in terms of $h_{\alpha\gamma}$) [Stell,1995] ; (solvable symmetric Mean-Spherical-Model) [Aqua-Fisher,2004]
- ▶ YES (solvable assymmetric Mean-Spherical-Model) [Aqua-Fisher,2004]

BUT

VIOLATION of the Stillinger-Lovett sum rule

(Finite-size scaling Monte Carlo simulations) [Das-Kim-Fisher,2011]

$$\int \mathrm{d}\mathbf{r}\ r^2\ S(r) \neq -\frac{3}{2\pi\beta} \quad \Longleftrightarrow \quad \varepsilon < \infty$$

Dielectric behavior, no perfect screening of external charges

C1. YBG HIERARCHY: Strategy

Assumptions and **inputs** at the critical point

- Particle correlations decay as $1/r^{1+\eta}$
- Charge correlations decay faster than $1/r^{4+\delta}$ $(\delta > 0)$
- No oscillations in leading large-distance behaviors
- YBG equations are valid
- Violation of the Stillinger-Lovett sum rule

IMPLY

ALGEBRAIC decay of charge correlations

C2. YBG HIERARCHY: Equations and validity

- Combination of YBG hierarchy equations for h_{++} , h_{+-} :

$$\nabla S(\mathbf{r}) = \beta S(\mathbf{r})\mathbf{F}_{\mathrm{SR}}(\mathbf{r}) + 2\beta q^2 \int \mathrm{d}\mathbf{x} H^{(3)}_{\mathrm{cd}}(\mathbf{0},\mathbf{r},\mathbf{x})\mathbf{F}_{\mathrm{SR}}(\mathbf{r}-\mathbf{x})$$
$$+ \beta q^4 N(\mathbf{r})\mathbf{F}_{\mathrm{C}}(\mathbf{r}) + 2\beta q^2 \rho \int \mathrm{d}\mathbf{x} S(\mathbf{x})\mathbf{F}_{\mathrm{C}}(\mathbf{r}-\mathbf{x})$$
$$+ 2\beta q^4 \int \mathrm{d}\mathbf{x} H^{(3)}_{\mathrm{cc}}(\mathbf{0},\mathbf{r},\mathbf{x})\mathbf{F}_{\mathrm{C}}(\mathbf{r}-\mathbf{x}) \; .$$

$$H^{(3)}_{\mathrm{cd}} = \rho^3 \left[h^{(3)}_{+++} + h^{(3)}_{++-} - h^{(3)}_{+-+} - h^{(3)}_{+--} \right]$$
$$H^{(3)}_{\mathrm{cc}} = \rho^3 \left[h^{(3)}_{+++} + h^{(3)}_{+-+} - h^{(3)}_{++-} - h^{(3)}_{+--} \right] \; ,$$

- Each integral **converges**: suggests VALIDITY YBG

(**proof** at low density [Fontaine-Martin,1984])

C3. YBG HIERARCHY: Internal charge sum rules

- **Integrable** decay of charge correlations ensures the perfect screening of internal charges [Martin,1988]

Remark : Guarantees a minimal decoupling between charge and density correlations

- Perfect screening of a **single fixed** charge

$$\rho \int \mathrm{d}\mathbf{x}[h_{++}(\mathbf{0},\mathbf{x}) - h_{+-}(\mathbf{0},\mathbf{x})] = -1$$

- Perfect screening of **two fixed** charges with polarization cloud

$$Q^{(3)}_{++}(\mathbf{x}|\mathbf{0},\mathbf{r}) = q[\frac{\rho^{(3)}_{+++}(\mathbf{0},\mathbf{r},\mathbf{x}) - \rho^{(3)}_{++-}(\mathbf{0},\mathbf{r},\mathbf{x})}{\rho^{(2)}_{++}(\mathbf{0},\mathbf{r})} + \delta(\mathbf{x}-\mathbf{r}) + \delta(\mathbf{x})]$$

$$\int \mathrm{d}\mathbf{x} Q^{(3)}_{++}(\mathbf{x}|\mathbf{0},\mathbf{r}) = 0 \Longleftrightarrow$$

$$\rho \int \mathrm{d}\mathbf{x} \left[h^{(3)}_{+++}(\mathbf{0},\mathbf{r},\mathbf{x}) - h^{(3)}_{++-}(\mathbf{0},\mathbf{r},\mathbf{x})\right] = -2h_{++}(\mathbf{0},\mathbf{r})$$

C4. YBG HIERARCHY: Dielectric constant in terms of a dipole

STEP 1: Express the second moment of $S(r)$ in terms of $h^{(3)}$ (inspired by [Martin-Gruber,1983])

[(i) calculate $\int \mathrm{d}\mathbf{r}_1(\mathbf{r}_1 - \mathbf{r}_2)\nabla_2 S(\mathbf{r}_1,\mathbf{r}_2)$ (ii) translational/rotational invariance (iii) $\int \mathrm{d}\mathbf{r}_1 \int \mathrm{d}\mathbf{x} ... \to \int \mathrm{d}\mathbf{x} \int \mathrm{d}\mathbf{r}_1 ...$ (iv) internal perfect screening rules]

STEP 2: Express $1/\varepsilon$ in terms of $\int \mathrm{d}\mathbf{r} r^2 S(r)$ within linear response theory

IMPLY

$$\frac{1}{\varepsilon} = \frac{2\pi\beta\rho q}{3} \int \mathrm{d}\mathbf{r}[1 + h_{-+}(r)][\mathbf{F}_{\mathrm{C}}(\mathbf{r}) \cdot \mathbf{p}^{(3)}_{-+}(\mathbf{0},\mathbf{r})]$$

[Alastuey-Cornu,1992]

Dipole $\mathbf{p}^{(3)}_{-+}(\mathbf{0},\mathbf{r})$ carried by the charge distribution $Q^{(3)}_{-+}(\mathbf{x}|\mathbf{0},\mathbf{r})$ **does not identically vanishes** since $\varepsilon < \infty$.

Key Inputs

1. Correlations between two sets of particles with respective centers of mass $\mathbf{R}_1$ and $\mathbf{R}_2$ decay as $1/|\mathbf{R}_1 - \mathbf{R}_2|^{1+\eta}$
2. Correlations between a set of particles and the charge density at $\mathbf{x}$ decay at least as $1/|\mathbf{x} - \mathbf{R}_1|^{4+\delta}$

- Two-point correlations:

$$h_{++}(r) \sim h_{+-}(r) \sim \frac{A}{r^{1+\eta}} \quad ; \quad |h_{++}(r) - h_{+-}(r)| < \frac{\mathrm{cst}}{r^{4+\delta}}$$

- Three-point correlations ($\mathbf{R}_{\alpha\gamma} = (\mathbf{r}_1 + \mathbf{r}_2)/2$, $\mathbf{n}_\mathbf{x} = (\mathbf{x} - \mathbf{R}_{\alpha\gamma})/|\mathbf{x} - \mathbf{R}_{\alpha\gamma}|$)

$$h^{(3)}_{\alpha\gamma\omega}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{x}) \sim \frac{A_{\alpha\gamma}(\mathbf{r}_2 - \mathbf{r}_1; \mathbf{n}_\mathbf{x})}{|\mathbf{x} - \mathbf{R}_{\alpha\gamma}|^{1+\eta}}$$

$$|A_{++}(\mathbf{r}; \mathbf{n}_\mathbf{x}) - A_{+-}(\mathbf{r}; \mathbf{n}_\mathbf{x})| < \frac{\mathrm{cst}}{r^{4+\delta}}$$

C6. YBG HIERARCHY: Charge and dipole constraints at large r

- Charge sum rule for $Q^{(3)}_{++}$ for r large $\rightarrow$

$$\rho \int \mathrm{d}\mathbf{y}[A_{++}(\mathbf{y};\mathbf{n}) - A_{+-}(\mathbf{y};\mathbf{n})] = -A$$

- Dipole sum rule for $Q^{(3)}_{-+}$ for r large ($\mathbf{n} = \mathbf{r}/r$) $\rightarrow$

$$q\rho \int \mathrm{d}\mathbf{x}\, \mathbf{x}[A_{++}(\mathbf{x};\mathbf{n}) - A_{+-}(\mathbf{x};\mathbf{n})]$$

$$= -\frac{1}{2} \lim_{r\rightarrow\infty} \{r^{1+\eta}\mathbf{p}^{(3)}_{-+}(\mathbf{0},\mathbf{r})\} = -\frac{1}{2}\mathbf{P}_{-+}$$

C7. YBG HIERARCHY: Infection mechanism of charge correlations

In the YBG equation for $\nabla S(r)$, two ALGEBRAIC slowest contributions :

1. Direct coupling term with $N(r)$

$$\mathbf{R}_{\mathrm{DC}}(\mathbf{r}) = \beta q^4 N(\mathbf{r}) \mathbf{F}_{\mathrm{C}}(\mathbf{r}) \sim \frac{4\beta q^4 \rho^2 A}{r^{3+\eta}} \mathbf{n}$$

2. Contribution of the region $\mathbf{x}$ close to $\mathbf{0}$ in $\mathbf{R}_{\mathrm{C}}^{(3)}(\mathbf{r})$:

$$\mathbf{R}_{\mathrm{C}}^{(3)}(\mathbf{r}) = 2\beta q^4 \int \mathrm{d}\mathbf{x} H_{\mathrm{cc}}^{(3)}(\mathbf{0}, \mathbf{r}, \mathbf{x}) \mathbf{F}_{\mathrm{C}}(\mathbf{r} - \mathbf{x})$$

$$\sim 4\beta q^4 \rho^3 \int \mathrm{d}\mathbf{x} \frac{[A_{++}(\mathbf{x}, \mathbf{n}_{\mathbf{x}}) - A_{+-}(\mathbf{x}, \mathbf{n}_{\mathbf{x}})]}{|\mathbf{r} - \mathbf{x}/2|^{1+\eta}} \mathbf{F}_{\mathrm{C}}(\mathbf{r} - \mathbf{x})$$

$$\mathbf{R}_{\mathrm{DC}}(\mathbf{r}) + \mathbf{R}_{\mathrm{C}}^{(3)}(\mathbf{r}) \sim \frac{\mathrm{cst}}{r^{4+\eta}}$$

[Use (i) Taylor expansion with respect to $(\mathbf{x}/r)$ of $\mathbf{n}_{\mathbf{x}}$, $1/|\mathbf{r} - \mathbf{x}/2|^{1+\eta}$, $\mathbf{F}_{\mathrm{C}}(\mathbf{r} - \mathbf{x})$ (ii) charge and dipole sum rules for the $A_{\alpha\gamma}$'s]

C8. YBG HIERARCHY: Algebraic decay of charge correlations

Charge correlations necessarily decay algebraically, $S(r) \sim \mathrm{cst}/r^s$, since the mean-field term

$$\mathbf{R}_{\mathrm{MF}}(\mathbf{r}) = 2\beta q^2 \rho \int \mathrm{d}\mathbf{x} S(\mathbf{x}) \mathbf{F}_{\mathrm{C}}(\mathbf{r}-\mathbf{x}) \sim \frac{\mathrm{cst}}{r^{s-1}}$$

MUST CANCEL the leading behavior of $[\mathbf{R}_{\mathrm{DC}}(\mathbf{r}) + \mathbf{R}_{\mathrm{C}}^{(3)}(\mathbf{r})]$ in the YBG equation, namely

$$s = 5 + \eta$$

REMARKS : (i) All density-charge correlations decay as $1/r^s$ (ii) $\int \mathrm{d}\mathbf{r} r^4 S(r) = \infty$ ($s < 7$) as observed in MC simulations [Das-Kim-Fisher,2011] (iii) algebraic scenario consistent with YBG equation for $N(r)$

CONCLUDING COMMENTS

- A priori assumption of MONOTONIC decays (possible oscillations are excluded)
- Is η identical to the similar exponent for Lennard-Jones fluids ? Only a RENORMALIZATION GROUP approach can answer...**VERY HARD**!
- Derivation of an approximate closure for $h^{(3)}_{\alpha\gamma\delta}$ in the YBG hierarchy which preserves the essential mechanisms at work

BEWARE

In critical phenomena, you never find what you expect!

[Michael FISHER]

STATISTICAL MECHANICS OF COULOMB SYSTEMS

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(Presses Polytechniques Universitaires Romandes, 2023)

Contents:

- Classical and quantum systems
- Rigorous proofs and solvable models
- Diagrammatic expansions
- Equilibrium correlations and equation of state