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On the Absence of Intermediate Phases in the Two-Dimensional Coulomb Gas

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For a simple, continuum two-dimensional Coulomb gas (with "soft" cutoff), Gallavotti and Nicoló [*J. Stat. Phys.* **38**:133–156 (1985)] have proved the existence of finite coefficients in the Mayer activity expansion up to order $2n$ below a series of temperature thresholds $T_n = T_\infty[1+(2n-1)^{-1}]$ $(n=1, 2, ...)$. With this in mind they conjectured that an infinite sequence of intermediate, multipole phases appears between the exponentially screened plasma phase above T_1 and the full, unscreened Kosterlitz–Thouless phase below $T_\infty \equiv T_{\mathrm{KT}}$. We demonstrate that Debye–Hückel–Bjerrum theory, as recently investigated for $d=2$ dimensions, provides a natural and quite probably correct explanation of the pattern of finite Mayer coefficients while indicating the total *absence* of any intermediate phases at nonzero density ρ; only the KT phase extends to $\rho > 0$.

KEY WORDS: Coulomb gas; sine-Gordon field theory; two-dimensional Coulomb gases; Kosterlitz–Thouless phase; plasma phase; multipole phases; Bjerrum ion pairs; Debye–Hückel theory; absence of intermediate phases; Mayer coefficients; density and virial expansions; anomalous activity expansions; equation of state in two dimensions; restricted primitive model.

1. INTRODUCTION AND SUMMARY

Consider, for concreteness, the *restricted primitive model* (RPM) of an electrolyte or Coulombic fluid, namely, hard spherical ions in d dimensions (disks when $d=2$) of diameter a in a domain Ω of volume $V=|\Omega|$ with $N_+ \equiv \rho_+ V$ ions carrying charges $q_i = q$ while $N_- \equiv \rho_- V$ carry charges $q_j = -q$. The natural reduced density and temperature variables are

$$\rho^* = \rho a^d \qquad \text{and} \qquad T^* = k_B T a^{d-2}/q^2 \tag{1.1}$$

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where $\rho = (N_+ + N_-)/V$ denotes the total, overall (ionic) density. In $d = 2$ dimensions the Coulombic interaction potential is conveniently taken as

$$\varphi_{ij}(r) = -q_i q_j \ln(r/a) \qquad \text{for} \quad r > a \tag{1.2}$$

[This corresponds to the limit $\epsilon \equiv d - 2 \to 0$ of the general form $\varphi_{ij}(r) = q_i q_j (r^{-\epsilon} - a^{-\epsilon})/\epsilon$ which, apart from a harmless additive constant, reduces to the standard law when $d = 3$.]

Now, celebrated arguments by Kosterlitz and Thouless (KT)[1,2] for two-dimensional Coulomb gases predict[2] the appearance at temperatures below

$$T^*_{\mathrm{KT}} \equiv T^*_\infty = \tfrac{1}{4} \tag{1.3}$$

of a low-density, unscreened phase of "bound charges" which exhibits algebraic decay of correlations.[3] This contrasts with the normal high-temperature, low-density plasma phase, which (for $d \geqslant 2$) displays Debye screening and exponential decay of correlations.

In the standard scenario the KT phase is pictured as consisting of bound dipolar pairs. (The importance of such associated $+/-$ ion pairs was stressed originally for $d = 3$ by Bjerrum.[3]) The density of the ion pairs in the KT phase is $\rho_2 > 0$, while the density of "free ions" ρ_1 vanishes identically, so that the total (ionic) density is just $\rho = 2\rho_2$. Above a transition locus $T_c(\rho)$, which extends to some positive density and satisfies $T_c(\rho) \nearrow T_{\mathrm{KT}}$ as $\rho \to 0$, free ions appear: these result in screening through the normal Debye mechanism in which the correlation length[4] varies as

$$\xi_{\mathrm{D}}(T, \rho) \sim (k_{\mathrm{B}} T / q^2 \rho_1)^{1/2} \tag{1.4}$$

In other words, the plasma phase, with exponentially decaying correlations and

$$\rho_1 > 0, \qquad \rho \equiv \rho_1 + 2\rho_2 \tag{1.5}$$

directly abuts the KT phase.

[2] Fröhlich and Spencer[15] have rigorously proved the existence of a low-temperature unscreened phase with only power-law decay of correlations in $d = 2$ lattice Coulomb gases. However, they state[15] that their methods extend to "regularized continuum Coulomb gases in two dimensions," which, we presume, include the restricted primitive model. At high temperatures Brydges and Federbush[16] had already proven that exponential screening occurs in $d \geqslant 2$ Coulomb gases. More recently the earlier results have been sharpened[17] to cover all $T < T_{\mathrm{KT}}$ and to prove power-law decay for $d = 2$ lattice Coulomb gases at low enough activity, $z < \bar{z}(T) > 0$.

[3] For *point* ions ($a \equiv 0$) in $d = 2$ dimensions the thermodynamic limit can be defined only for $T > T_1 \equiv 2T_{\mathrm{KT}}$.[12,13,18] For $T < T_1$ the system is often said to "collapse."[18] See also below, following Eq. (2.3).

[4] For *point* ions above $T_1 \equiv 2T_{\mathrm{KT}}$, see ref. 18, Eqs. (4.16)–(4.20), and ref. 19.

However, this scenario has recently been challenged by Gallavotti and Nicoló (GN).[4] They conjecture, instead, that between the high-temperature plasma phase and the low-temperature KT phase an *infinite sequence* of "intermediate" multipole phases is present in the $d=2$ Coulomb gas, the nth phase being associated with a threshold temperature

$$T_n = T_\infty[1+(2n-1)^{-1}], \qquad n=1, 2, ... \tag{1.6}$$

Although GN were not more explicit,[5] this conjecture, to be meaningful, must imply an infinite sequence of *phase boundaries*, say, $T_{c,n}(\rho)$ [or boundary pairs, $T_{n+}(\rho)$ and $T_{n-}(\rho)$, if some or all of the transitions are of first order] each extending to some positive density ρ_n and, presumably, satisfying $T_{c,n}(\rho)$, $T_{n\pm}(\rho) \to T_n$ as $\rho \to 0$. On crossing each phase boundary the pressure (or other thermodynamic potential) would display some *non-analytic* behavior. Of course, the necessary singularities might be quite weak; recall that KT theory predicts only an essential singularity of the form $\sim\exp[-c(\rho)/|t|^{1/2}]$ when $t \equiv 1 - T_c(\rho)/T \to 0\pm$, where $c(\rho)$ is positive.

GN related their conjecture to a theorem[4] they established for a $d=2$ Coulomb gas with a specially chosen smooth ultraviolet cutoff on the interaction potential (1.2). The cutoff scale a may be identified with the hard-core diameter of the RPM (which implies $\varphi_{ij} = +\infty$, $\forall\, i, j$, for $r<a$). Although the behavior of a Coulomb gas at high densities, $\rho^* \gtrsim 1$, must depend strongly on the details of the cutoff, qualitative properties at the

[5] GN[4] title their paper, *The "Screening Phase Transitions" in the Two-Dimensional Coulomb Gas*, and refer to "an infinite number of 'intermediate phases'" in their abstract; but they discuss these conjectured phase transitions otherwise only in Remark (iii) on p. 154 of their paper, there referring to "an infinite sequence of phase transitions passing from the plasma phase" on decreasing the temperature. However, they also cite Benfatto *et al.*,[20] a work entitled, On the Massive Sine-Gordon equation in the First Few Regions of Collapse, and Nicoló,[21] On the Massive Sine-Gordon Equation in the Higher Regions of Collapse. These articles address the "ultraviolet stability problem" for + and − "ions" coupled via the two-dimensional Yukawa interaction. Benfatto *et al.* present the same infinite sequence of temperature thresholds T_n, deriving them heuristically by considering the clustering of n positive and n negative ions. They attribute the discovery of the thresholds to Fröhlich in ref. 18: but in that article Fröhlich seems to mention only T_1 and T_∞ (in our notation). The idea that "at the [inverse] temperatures β_n ..., there should be phase transitions" also appears in Benfatto *et al.*[20] and, seemingly, is subscribed to by Nicoló[21] as well. The counter arguments we present here seem likely to apply equally to the Yukawa gases with repulsive cores, so the conjectured sequence of phase transitions is again to be seriously doubted. However, we postpone a closer investigation to another occasion.

low densities in question here are expected to depend only weakly if at all on the cutoff (which, however, is essential to prevent thermodynamic collapse). In any event, we believe no special significance attaches to the GN choice of cutoff for the point at issue: note, e.g., that the thresholds (1.6) are independent of a.

More specifically, GN's theorem concerns the nature of the Mayer activity expansion for the pressure p, namely

$$\bar{p} \equiv p/k_{\mathrm{B}}T = \sum_{l=1} b_l(T)\,\lambda^l \tag{1.7}$$

where $\lambda = 2\lambda_+ = 2\lambda_-$ is the activity of the ions. [In a finite neutral system one has $b_l(T; \Omega) \equiv 0$ for all odd l; but it may be convenient to relax neutrality in a finite system.] GN proved[4] (a) that for $T < T_n$ all coefficients $b_l(T)$ up to $l = 2n$ are bounded and well defined in the thermodynamic limit ($\Omega \to \infty$), and (b) that for $T < T_\infty \equiv T_{\mathrm{KT}}$ *all* the $b_l(T)$ are finite. On the other hand, GN also demonstrated (c) that, barring highly unlikely cancellations, the finite-system coefficients $b_{2n}(T; \Omega)$ *diverge* when $\Omega \to \infty$ if $T > T_n$.

These changes in the nature of the Mayer expansion as T drops below the successive thresholds T_n seemed to GN supportive of the infinite sequence of multipole phases described above. (See also footnote 5.) However, we will show, first, that there is a plausible and, indeed, probably correct general form for the full activity expansion for the pressure and for the related density expansion, that reproduces all the GN results for the $b_l(T; \Omega)$ without, however, entailing any type of phase transition across boundaries related to the thresholds T_n. Second, we show how this form of expansion is explicitly generated by the Debye–Hückel-plus-Bjerrum (DHBj) theories for the restricted primitive model[5,6] which we have recently extended to general d and studied explicitly for $d = 2$.[7,8] In particular, the DHBj theory and its various extensions[5–8] predict, for $d = 2$, the existence of a "pure dipole" KT phase separated from the normal screened Debye or plasma phase by an infinite-order critical line in accord with the standard scenario. Even though the thresholds T_n appear naturally in the density and activity expansions predicted by these (approximate) theories, there are no associated intermediate phases whatsoever. Accordingly, we believe that in the absence of significantly improved supporting arguments, no credence should be accorded the GN conjecture.[6]

[6] Or, pending further analysis, to the corresponding conjectures in ref. 20 for the $d = 2$ Yukawa gases: see footnote 5.

2. ACTIVITY AND DENSITY EXPANSIONS

For orientation recall, first, the general relation

$$\rho = \lambda(\partial/\partial\lambda)\,\bar{p}(T, \lambda) \tag{2.1}$$

through which any form of activity expansion for the reduced pressure can be converted to a corresponding density expansion and, employing the ideal limit, *vice versa*. For a fluid with short-range forces, only integral powers λ^l ($l = 1, 2,...$) appear in the activity expansion and the coefficients $b_l(T)$ of the corresponding Mayer series may be computed by the usual graphical methods. Correspondingly, one then has a virial series with only integral powers ρ^n and finite coefficients $B_n(T)$.

However, in three dimensions a Coulombic fluid does *not* possess a regular virial expansion: rather, as first shown by Debye and Hückel,[9,10] it obeys the limiting law

$$\bar{p} = \rho - \mathscr{B}_{3/2}(T)\,\rho^{3/2} + \cdots \tag{2.2}$$

with a coefficient $\mathscr{B}_{3/2}(T) = \sqrt{\pi}\,q^3/3(k_B T)^{3/2}$ that is purely "electrostatic" in origin. Higher-order terms in the expansion for the RPM vary as ρ^2, which includes the hard-core, second-virial excluded-volume contributions, and as $\rho^3 \ln \rho^*$, ρ^3, $\rho^{7/2}$, etc.[10,11] Since in leading order one has $\lambda \sim \rho$ for fully dissociated ions, the activity expansion contains the ideal leading term λ followed by a $\lambda^{3/2}$ term, etc. Although the Mayer coefficients $b_l(T; \Omega)$ in a finite system are always well defined, it is clear that the presence of the $\lambda^{3/2}$ term for $d = 3$ implies the divergence of $b_2(T; \Omega)$ when $\Omega \to \infty$. On the other hand, despite the anomalous nature of the density and activity expansions, the pressure, free energy, etc., are surely analytic functions of T *and* ρ for small enough (positive) ρ. We remark only that the singularity *at* $\rho = 0$ and the divergence (1.4) of $\xi_D(T, \rho)$ as $\rho \sim \rho_1 \to 0$ imply that a Coulombic fluid may be regarded[6] as having a *line* of critical points *at* $\rho = 0$ that continues up to $T = \infty$.

These conclusions extend to general $d > 2$ since one easily sees[7,8] that the singular $\rho^{3/2}$ term in (2.2) is replaced by $\rho^{d/2}$ (with logarithmic factors possible when $\frac{1}{2}d$ is an integer), while regular virial terms $B_n(T)\,\rho^n$ appear up to order $n < \frac{1}{2}d$. Clearly, the activity expansion behaves similarly, so that the $b_l(T; \Omega)$ have finite thermodynamic limits for $l < \frac{1}{2}d$, but diverge for $l > \frac{1}{2}d$. [Here it is convenient, grand canonically, to allow deviations from neutrality in constructing the $b_l(T; \Omega)$.]

The situation in $d = 2$ dimensions is somewhat different. For a system of *point* charges in which (1.2) holds for all $r > 0$, Salzberg and Prager[12] have shown that the equation of state is simply

$$\bar{p} = [1 - (T_\infty/T)]\,\rho \qquad \text{provided} \qquad T > T_1 = 2T_\infty \tag{2.3}$$

The condition $T > T_1$ is essential since the partition function for point ions is undefined for $T \leqslant T_1$.[12] (A later note by May[13] overlooks the need for a limitation with $T_1 > T_\infty$, although May was subsequently corrected by Knorr.[14),7]) Now it seems very likely (although we know of no proof) that this result remains true asymptotically for general two-dimensional Coulomb gases with hard cores or other reasonable short-distance cutoffs in the limit $\rho^* \to 0$. In that case there will always be a finite first virial coefficient (when $T > T_1$). However, the activity expansion for $T > T_1$ must then take the strongly anomalous form

$$\bar{p}(T, \lambda) = b_\psi(T)\, \lambda^{2\psi(T)}[1 + e(T, \lambda)] \tag{2.4}$$

where the temperature-dependent exponent is

$$2\psi(T) = [1 - (T_\infty/T)]^{-1} \tag{2.5}$$

which satisfies $\psi < 1$ for $T > T_1$.[8] To ensure a proper correction factor $[1 + E(\rho, T)]$ in (2.3) with $E(\rho, T) = o(1)$ we must also have $e(T, \lambda)$, $\lambda(\partial e/\partial \lambda) = o(1)$. Clearly, a form like (2.4) cannot derive simply from the standard finite-size expansions!

Finally, let us address the situation *below* T_1 where GN anticipated an infinite sequence of phase transitions. With their concrete results for the activity series and the previous discussions in mind, consider the ansatz

$$\bar{p}(T, \lambda) = b_\psi(T)\, \lambda^{2\psi(T)}[1 + e(T, \lambda)] + \sum_{k=1}^{\infty} \bar{b}_{2k}(T)\, \lambda^{2k} \tag{2.6}$$

where $\psi(T)$ is still given by (2.5) and so remains finite for $T > T_\infty$. Furthermore, we suppose now that $b_\psi(T)$ and $\bar{b}_{2k}(T)$ ($\forall\, k$) are analytic for $T \geqslant T_\infty$, that, similarly, $e(T, \lambda)$ is analytic in $T > T_\infty$ *and* in $\lambda > 0$, and that the power series in λ converges for small enough $\rho(>0)$ and $T \geqslant T_\infty$. These conditions ensure that $\bar{p}(T, \lambda)$ exhibits no singularities for $T > T_\infty$ and small $\lambda > 0$ and, hence, that there are *no* intermediate phase boundaries for $T > T_\infty$. Furthermore, (2.6) is clearly consistent with the form (2.4) when $T > T_1$.

Now notice that $\psi(T)$ rises monotonically as T decreases and, furthermore, that at the thresholds T_n defined in (1.6) we have $\psi(T_n) = n = 1, 2, \ldots$.

[7] Neither May[13] nor Knorr[14] in 1967–1968 nor Fröhlich[18] in 1976 shows awareness of the earlier pioneering work of Salzberg and Prager,[12] although in 1974 Deutch and Lavaud[22] cite Salzberg and Prager, May, and Knorr. They[22] also provide other informative background references and perspectives on the pre-Kosterlitz–Thouless era.

[8] For point ions (with $T > T_1$) this form has been proven by Fröhlich[18] with $e(T, \lambda) \equiv 0$.

It is then evident that (2.6) represents a Mayer expansion with finite coefficients $b_l(T) \equiv \bar{b}_l(T)$ up to order $l = 2n$ provided $T < T_n$. Conversely, when T exceeds T_n but not T_{n-1}, an anomalous term $b_\psi \lambda^{2\psi}$ with $n-1 < \psi < n$ intervenes so that the finite-system Mayer coefficient $b_{2n}(T; \Omega)$ must diverge when $\Omega \to \infty$. In addition, $\psi(T)$ becomes infinite at $T = T_\infty \equiv T_{\mathrm{KT}}$, so that below T_∞ one is left with a complete Mayer expansion. [However, analyticity of $\bar{p}(T, \lambda)$ for $T < T_\infty$ is neither implied not expected: rather, the nonanalytic KT transition line $T_c(\lambda)$ should be encountered below T_∞ when $\lambda > 0$.] Thus our ansatz is fully consistent with the theorem of Gallavotti and Nicoló and with the associated results summarized in (a)–(c) following (1.7) above.

In summary, the expression (2.6) (together with the stated conditions) constitutes a realistic possibility for the equation of state of a two-dimensional Coulomb gas. It is consistent with the GN behavior of the activity series, but implies the *absence* of all low-density phase transitions above T_∞. Consequently, it represents a strong counterexample to the GN conjecture of an infinite sequence of intermediate phases lying above the KT phase.

From (2.6) a corresponding density expansion can be derived straightforwardly. In the next section we show that a density expansion essentially consistent with (2.6) is, in fact, implied by DHBj theories. Indeed it seems likely that (2.6) represents the correct general result for Coulomb gases when $d = 2$.

3. THE EQUATION OF STATE ACCORDING TO DEBYE–HÜCKEL–BJERRUM THEORIES

We outline briefly here the relevant aspects of the Debye–Hückel and Bjerrum theories (and various extensions) in $d = 2$ dimensions: the reader desiring more details should consult refs. 7 and 8. The DHBj theories[5–7] postulate that a Coulombic fluid in thermal equilibrium can be regarded as an interacting mixture of three distinct chemical species, free + and − ions, and neutral, associated +/− ion pairs or Bjerrum dipoles, of densities ρ_+, $\rho_- = \rho_+ = \frac{1}{2}\rho_1$, and ρ_2, respectively. (Further multi-ion species, charged and neutral, can be incorporated in an essentially straightforward manner, but are expected to produce only relatively minor, quantitative effects.) The charged species alone contribute to the screening via the standard Debye mechanism that yields the correlation (alias screening) length ξ_{D} as in (1.4).[5–7,9,10] The total Helmholtz free-energy density $f = -F/V$ is then constructed as a sum of specific physical contributions[5–7]: (i) ideal-gas terms f_j^{Id} for each species ($j = +, -, 2$); (ii) hard-core repulsion terms f^{HC} which admit a virial expansion in ρ_1 and ρ_2;

(iii) the ionic excess free energy computed according to DH theory, which for $d=2$ is found to be[7,8]

$$f^{\mathrm{DH}}(\rho_1; T) = (k_B T/2\pi a^2) \ln[(a/\xi_D) K_1(a/\xi_D)] \tag{3.1}$$

where $K_1(z)$ is the standard modified Bessel function and $a^2/\xi_D^2 = 2\pi\rho_1^*/T^*$; and (iv) a dipole–ionic fluid solvation free energy $f^{\mathrm{DI}}(\rho_1, \rho_2; T) \propto \rho_1 \rho_2 \ln(a/\xi_D)$ $(d=2)$, which, however, plays no essential role in the present considerations. Various further refinements of the theory, in particular to incorporate the Kosterlitz–Thouless picture of smaller dipoles modifying the effective dielectric constant for larger dipoles, etc., may be contemplated, but seem unlikely to alter the basic features relevant here.

The dipoles and ions are maintained in mutual chemical equilibrium so that their densities are related by[5–8]

$$\rho_2^* = \tfrac{1}{4} K(T) \rho_1^{*2} \exp[(2\mu_1^{\mathrm{Ex}} - \mu_2^{\mathrm{Ex}})/k_B T] \tag{3.2}$$

where $K(T)$ is an association constant for the ion $\rightleftharpoons$ dipole reaction, while the excess chemical potentials are given by

$$\mu_i^{\mathrm{Ex}}(\rho_1, \rho_2) = -\frac{\partial f^{\mathrm{Ex}}}{\partial \rho_i} \qquad (i = 1, 2) \tag{3.3}$$

$$f^{\mathrm{Ex}}(\rho_1, \rho_2) = f^{\mathrm{DH}} + f^{\mathrm{DI}} + f^{\mathrm{HC}} \tag{3.4}$$

The precise form of the association constant $K(T)$ is a matter of some delicacy.[5,8,23] Clearly, however, it should be positive and vary analytically with $T > 0$: beyond that its behavior will not matter for the points at issue. Nevertheless, we mention that for low temperatures $(T < T_1,\ d=2)$ it varies as $2\pi a^2 T^*/(1 - 2T^*)$.[7,8]

Now the crucial feature of the DH theory in $d=2$ dimensions, which is unique to that dimension, is that the excess chemical potential μ_1^{Ex} entering (3.2) varies as $-\frac{1}{2} q^2 \ln(a/\xi_D) \approx -\frac{1}{4} q^2 \ln \rho_1^*$ when $\rho_1 \to 0$. Consequently the equilibrium condition takes the unusual low-density form

$$\rho_2 \approx \bar{K}(T) \rho_1^{*2 - 1/2T^*} \tag{3.5}$$

where factors analytic in T have been combined with K to yield the effective association constant $\bar{K}$, while an overall factor $[1 + G_0(\rho_1, \rho_2; T)]$ and a similar factor $[1 + G_1(\rho_1, \rho_2; T)]$ in the exponent of ρ_1^* have been omitted for clarity: the G_i are analytic in T, vanish with ρ_1 and ρ_2, and have expansions (in powers $\rho_1^j \rho_2^k \ln^l \rho_1$ with $l \leqslant j+1$) convergent for small enough densities and so enter below only beyond leading orders.

The corresponding logarithmic ρ_1 dependence in f^{DH} leads to the equation of state

$$\bar{p}(\rho, T) = \left(1 - \frac{1}{4T^*}\right)\rho_1 + \rho_2 + \sum_{\substack{j+k \geqslant 2 \\ l \leqslant j}} B_{jkl}(T)\, \rho_1^j \rho_2^k \ln^l \rho_1 \qquad (3.6)$$

where $B_{111} \equiv 0$ and, of course, ρ_1 and ρ_2 are related to $\rho = \rho_1 + 2\rho_2$ via (3.5). Now $T_\infty^* = \frac{1}{4}$, so that, if ρ_2 may be neglected relative to $\rho_1 \approx \rho$, this DHBj equation of state has, asymptotically, precisely the previous form (2.3), known for point ions and expected to be generally valid provided $T > T_1 = 2T_\infty$; but recall $T_1^* = \frac{1}{2}$, so that by (3.5) we indeed have

$$\rho_2/\rho_1 \sim \rho_2/\rho \sim \rho^{*1-(T_1/T)} \to 0 \qquad (\rho \to 0,\ T > T_1) \qquad (3.7)$$

Thus DHBj theory is also consistent with the anomalous activity expansion (2.4).

Just *at* the first threshold T_1 the result (3.6) reduces to

$$\bar{p}(\rho, T_1) = \tfrac{1}{2}\rho + \sum_{\substack{k \geqslant 2 \\ l \leqslant k}} B_{kl}^{(1)} \rho^k \ln^l \rho \qquad (3.8)$$

where, clearly, the $B_{kl}^{(1)}$ can be expressed in terms of $\bar{K}(T_1)$, the coefficients $B_{jkl}(T_1)$, and the functions $G_i(\rho_1, \rho_2; T_1)$.

On the other hand, for all $T_\infty < T < T_1$ we find

$$\frac{\rho_1}{\rho_2} \sim \frac{\rho_1}{\rho} \sim \rho^{*\theta(T)} \qquad \text{with} \quad \theta(T) = \frac{T_1 - T}{2(T - T_\infty)} > 0 \qquad (3.9)$$

when $\rho \to 0$. It follows from these considerations that for $T > T_\infty$ and ρ small enough but nonzero, the pressure $\bar{p}(\rho, T)$ is analytic in $T > T_\infty$ and in ρ for ρ positive and hence displays *no* phase transitions.

This is a central conclusion. However, to understand the appearance of the GN thresholds we need to study the behavior as $\rho \to 0$ below T_1. To this end we may expand $\rho_2 = \frac{1}{2}(\rho - \rho_1)$ in powers of ρ_1/ρ when $T < T_1$ and reorganize the series (3.5) to obtain

$$\bar{p} = \tfrac{1}{2}\rho + \tfrac{1}{2}\left(1 - \frac{T_1}{T}\right)\rho_1 + \sum_{\substack{i+k \geqslant 2 \\ l \leqslant i}} \bar{B}_{ikl}(T)\, \rho_1^i \rho^k \ln^l \rho_1 \qquad (3.10)$$

$$= \tfrac{1}{2}\rho + \sum_{l \geqslant 2} \bar{B}_l(T)\, \rho^l + \rho^{*\psi(T)} B_\psi(T)[1 + E(\rho, T)] \qquad (3.11)$$

where $\psi(T)$ is just as defined in (2.5), while $B_\psi(T) = \frac{1}{2}[1 - (T_1/T)] \times [2\bar{K}(T)]^{-\psi(T)}$, and $E(\rho, T)$ is analytic in $\rho > 0$ and $T > T_\infty$ and of order

$(\rho^{\psi(T)} \ln^2 \rho, \rho)$ as $\rho \to 0$. As written, this form is valid even for $T = T_1$ when $\psi = 1$; but one should note that, in general, $B_{k0}^{(1)} \neq \bar{B}_k(T_1)$.

Now we see that for $T_1 > T > T_\infty$, the DHBj virial coefficients, $B_l \equiv \bar{B}_l$ in (3.11), are evidently well defined up to order $l = n$ when $T < T_n$ and, presumably, can be computed from finite-system expressions by taking $\Omega \to \infty$. However, the thermodynamic limit of $B_n(T; \Omega)$ must diverge if $T > T_n$. When $T \to T_\infty$ a complete virial expansion appears. Of course, these properties are just the density analogs of the GN results for the activity series and, indeed, it is easy to see that (3.11) is quite consistent with the activity expansion (2.6) which embodies the GN properties [but, again, (3.11) exhibits no intermediate phases].

Lastly, we remark that an expansion of $\bar{p}(T, \rho)$ for $T > T_1$ in powers of ρ alone can also be obtained in an analogous fashion using (3.5) and (3.7) in (3.6). The leading behavior is

$$\bar{p} = \left(1 - \frac{T_\infty}{T}\right)\rho + \left(\frac{T_1}{T} - 1\right)\bar{K}(T)\rho^{*2-(T_1/T)} + O(\rho^{*3-2(T_1/T)}, \rho^2 \ln^2 \rho) \quad (3.12)$$

so that a second virial coefficient is never well defined. The different form of this expansion for $T > T_1$ from (3.11) for $T < T_1$ might be thought to indicate the presence of a phase boundary of some sort at $T = T_1$: however, one can see directly from (3.6) with (3.5) that, as already stated, $\bar{p}(\rho, T)$ is indeed analytic across $T = T_1$. Nevertheless, one could well regard $(\rho, T) = (0, T_1)$ as locating a *multi*critical point on the DH critical line at $\rho = 0$, since the screening length ξ_D diverges in normal DH fashion[9] as $1/(\rho^*)^{1/2}$ when $\rho \to 0$ for $T \geqslant T_1$, whereas $\xi_D \sim 1/(\rho^*)^{\psi(T)/2}$ when $T < T_1$. Below T_∞, where $\psi \to \infty$, one is in the KT phase when $\rho \to 0$ and then $\xi_D \equiv \infty$.

Finally, we mention again that the DHBj theories *do* automatically generate a pure dipole or KT phase (with $\rho_1 \equiv 0$) below a critical line $T_c(\rho) \leqslant T_\infty$ across which the pressure and free energy exhibit essential singularities while $\ln[\xi_D(T, \rho)/a]$ diverges as a power of $T - T_c(\rho)$.[7,8] We conclude, once more, that there are no reasonable grounds for accepting the GN scenario of many intermediate phases.

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[9] As found also for point ions.[18,19]

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