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BOUNDS, SUCCESSIVE APPROXIMATIONS, AND THERMODYNAMIC LIMITS FOR DISTRIBUTION FUNCTIONS, AND THE QUESTION OF PHASE TRANSITIONS FOR CLASSICAL SYSTEMS WITH NON-NEGATIVE INTERACTIONS

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It is shown rigorously that, for systems with non-negative interactions and integrable Mayer f bonds (e.g., hard spheres), distribution functions and the thermodynamic ratio ρ/z exist in the limit $V\to\infty$, and are analytic functions of the activity z, for $z<1/f$ in the right-hand half-plane, with f the absolute value of the integral of the f bond. Heuristic arguments then indicate that these functions are continuous in z for all $z<\infty$. This would mean that no Ehrenfest phase transitions are possible for such systems.

The problem of bounds for thermodynamic and distribution functions and the existence of thermodynamic limits has aroused considerable interest in recent years.[1] While the problem has been treated successfully for simple thermodynamic functions such as pressure or the thermodynamic ratio ρ/z (with z the activity and ρ the number density),[2] existence of limits for distribution functions has not been proven even at low activities. On the other hand, the question of the thermodynamic significance of singularities obtained from approximate theories for non-negative interactions,[3] and of discontinuities observed in computer calculations,[4] is still unresolved.

In this note, we report the following rigorous results for systems with non-negative interactions: (I) For z real and non-negative, the thermodynamic limits of distribution functions and of the thermodynamic ratio (if they exist) are bounded above and below by the limits of two sequences, monotone decreasing and monotone increasing, respectively. The members of these sequences can be calculated successively in a straightforward manner, thus providing successively better and better approximations to these functions. (II) For z complex in a domain D^* bounded on the right by the semicircle $z<1/f$ (with f the absolute value of the integral of the Mayer f bond), and on the left by the imaginary axis and the semicircle $z<1/ef$ (the Groeneveld lower bound for radii of convergence of cluster expansions[5]), both bounds are regular functions of z. Finally, we show (III) for z within D^* both bounds are equal, thus the thermodynamic limits exist and are regular in z. The physically interesting part of D^*, which includes the part $|z|<1/f$ of the non-negative real z axis, is considerably larger than that defined by the Groeneveld bound. Following these proofs, we present some heuristic arguments for existence of these limits for all $0\leq z<\infty$, and their continuity in z. The latter is tantamount to nonexistence of Ehrenfest[6] phase transitions for the systems under consideration, e.g., hard spheres.

The N-particle interaction potential is written[7]

$$U_N(\underline{N})\equiv U_N(1,2,\cdots,N)\equiv U_N(\vec{r}_1,\cdots,\vec{r}_N)=\sum_{1\leq i<j\leq N}U_{ij};\quad U_{ij}=U_2(\vec{r}_{ij}). \tag{1}$$

We now define Boltzmann factors and f bonds:

$$v_N(\underline{N})\equiv\exp[-U_N(\underline{N})/kT]=\prod_{1\leq i<j\leq N}v_{ij},\quad v_{ij}\equiv\exp(-U_{ij}/kT),\quad f_{ij}\equiv v_{ij}-1. \tag{2}$$

We deal with an open system (grand canonical ensemble) of particles in an s-dimensional domain of volume V. The interaction potential U_{ij} fulfills the conditions

$$U_{ij} \geq 0, \tag{3a}$$

$$f \equiv |\int_\infty f_{ij} d^s r_j| < \infty, \tag{3b}$$

where $\int_\infty$ means integration over V in the limit $V \to \infty$. These conditions include hard-core potentials as special cases; hard cores, however, are not essential for the validity of our theorems.

Our distribution functions are defined by

$$P_n(\underline{n}; z; V) \equiv [L(z; V)]^{-1} \sum_{N=n}^{\infty} [z^{N-n}/(N-n)!] \int_V \prod_{i=1}^{n} \prod_{j=n+1}^{N} v_{ij} v_{N-n}(\underline{N-n}) d(\underline{N-n}); \tag{4}$$

$$\underline{n} \equiv 1, 2, \cdots, n; \quad \underline{N-n} \equiv n+1, \cdots, N; \quad d(\underline{N-n}) \equiv d^s r_{n+1} \cdots d^s r_N.$$

Here $L(z, V)$ is the grand canonical partition function:

$$L(z; V) \equiv \sum_{N=0}^{\infty} (z^N/N!) \int_V v_N(\underline{N}) d(\underline{N}), \quad d(\underline{N}) \equiv d^s r_1 d^s r_2 \cdots d^s r_N. \tag{5}$$

The functions $P_n(\underline{n}; z; V)$ are related to the usual distribution functions and to the thermodynamic ratio by

$$v_n(\underline{n}) P_n(\underline{n}; z; V) = z^{-n} \rho_n(\underline{n}; z; V), \quad \xi(z; V) \equiv \rho(z; V)/z = V^{-1} \int_V P_1(1; z; V) d(1), \tag{6}$$

with $\rho(z; V)$ the average grand canonical ensemble number density. The omission of the direct Boltzmann factor $v_n(\underline{n})$ from the definition (4) results in simplification of subsequent development. For the same reason we define conditional distribution functions

$$F_n(\underline{n}; z; V) \equiv P_n(\underline{n}; z; V)/P_{n-1}(\underline{n-1}; z; V), \quad F_1(1; z; V) \equiv P_1(1; z; V), \tag{7}$$

with $\underline{n-1} = 1, 2, \cdots, n-1$. The thermodynamic limits (here $V \to \infty$) are denoted by $P_n(\underline{n}; z)$, $F_n(\underline{n}; z)$, and $\xi(z) = \rho(z)/z$, respectively.

In order to define our sequences, we introduce exponential coupling[8]:

$$v_{ij}(\lambda_i) \equiv 1 + \lambda_i f_{ij}, \quad 0 \leq \lambda_i \leq 1, \quad i < j; \quad v_{ij}(1) = v_{ij}; \quad v_{ij}(0) = 1. \tag{8}$$

Thus, when $\lambda_i = 0$, the ith particle is effectively removed from interaction with the succeeding particles (in the sense that if, e.g., $i = 4$ then, for $\lambda_4 = 0$, particle 4 does not interact with $5, 6, \cdots, N$, but still interacts with 1, 2, 3). In view of the second equation in (8), we adopt the convention that only coupling parameters different from unity will be indicated explicitly.

We now define coupled distribution functions

$$P(\underline{n}; \underline{\lambda_n}; z; V) \equiv \frac{1}{L(z; V)} \sum_{N=n}^{\infty} \frac{z^{N-n}}{(N-n)!} \int_V \prod_{i=1}^{n} \prod_{j=n+1}^{N} v_{ij}(\lambda_i) v_{N-n}(\underline{N-n}) d(\underline{N-n}). \tag{9}$$

Note that $L(z; V)$ is still defined for the fully coupled system and does not depend on the set of coupling parameters $\underline{\lambda_n} = \lambda_1, \lambda_2, \cdots, \lambda_n$. The same is true for the Boltzmann factors $v_{N-n}(\underline{N-n})$ of the remaining particles in the open system. When all coupling parameters of the set $\underline{\lambda_n}$ are unity, we recover the distribution function $P_n(\underline{n}; z; V)$ for the actual fully coupled system. Finally, we define conditional coupled distribution functions

$$F_n(\underline{n}; \underline{\lambda_n}; z; V) \equiv P_n(\underline{n}; \underline{\lambda_n}; z; V)/P_{n-1}(\underline{n-1}; \underline{\lambda_{n-1}}; z; V), \quad \underline{\lambda_{n-1}} \equiv \lambda_1, \cdots, \lambda_{n-1}. \tag{10}$$

From Eqs. (9) and (10), we have

$$P_n(\underline{n}; \underline{\lambda_n}; z; V)|_{\lambda_n=0} = P_{n-1}(\underline{n-1}; \underline{\lambda_{n-1}}; z; V), \text{ therefore } F_n(\underline{n}; \underline{\lambda_n}; z; V)|_{\lambda_n=0} = 1. \tag{11}$$

With these preliminaries we can now state and prove Theorem I: Given the conditions (3), definitions (8) through (10), and z real and non-negative, there exist two sequences of functions, one monotone increasing, $F_n^{(2m+1)}(\underline{n}; \underline{\lambda_n}; z; V)$, and the other monotone decreasing, $F_n^{(2m)}(\underline{n}; \underline{\lambda_n}; z; V)$, with the following properties:

$$F_n^{(M)}(\underline{n};\underline{\lambda_n};z)=\lim_{V\to\infty}F_n^{(M)}(\underline{n};\underline{\lambda_n};z;V)\text{ exists, all } M<\infty; \tag{12a}$$

$$\lim_{m\to\infty}F_n^{(2m+1)}(\underline{n};\underline{\lambda_n};z)=F_n^{-}(\underline{n};\underline{\lambda_n};z)\leq F_n^{+}(\underline{n};\underline{\lambda_n};z)=\lim_{m\to\infty}F_n^{(2m)}(\underline{n};\underline{\lambda_n};z) \tag{12b}$$

exists for all n, and if the thermodynamic limit $F_n(\underline{n};\underline{\lambda_n};z)$ exists, then

$$F_n^{-}(\underline{n};\underline{\lambda_n};z)\leq F_n(\underline{n};\underline{\lambda_n};z)\leq F_n^{+}(\underline{n};\underline{\lambda_n};z). \tag{12c}$$

Proof: On differentiating both sides of Eq. (9) with respect to λ_n, dividing by $P_n(\underline{n};\underline{\lambda_n};z;V)$, noting that $P_{n-1}(\underline{n-1};\underline{\lambda_{n-1}};z;V)$ is independent of λ_n, and reintegrating we obtain the hierarchy

$$F_n(\underline{n};\underline{\lambda_n};z;V)=\exp[-z\overline{A}_{n,V}\cdot F_{n+1}(\underline{n+1};\underline{\lambda_n};z;V)], \tag{13}$$

with the operators $\overline{A}_{n,V}$ defined by

$$\overline{A}_{n,V}\cdot F_{n+1}(\underline{n+1};\underline{\lambda_n};z;V)\equiv-\int_0^{\lambda_n}d\lambda_n\int_V d^s r_{n+1}[f_{n,n+1}\prod_{i=1}^{n-1}v_{i,n+1}\cdot F_{n+1}(\underline{n+1};\underline{\lambda_n};z;V)]\geq 0. \tag{14}$$

The inequality follows from (3a) and (2). We now define our sequence by setting $F_k^{(0)}(\underline{k};\underline{\lambda_k};z;V)\equiv 1$, for all k and all values of the λ_i's and coordinates, and

$$F_n^{(M)}(\underline{n};\underline{\lambda_n};z;V)\equiv\exp[-z\overline{A}_{n,V}\cdot F_{n+1}^{(M-1)}(\underline{n+1};\underline{\lambda_n};z;V)]. \tag{15}$$

Now, we have $\lim_{V\to\infty}(\overline{A}_{n,V}\cdot 1)=\overline{A}_n\cdot 1<\infty$, remembering (3b) and noting that all $v_{ij}\leq 1$; thus (12a) follows immediately by induction. To prove (12b) we obtain by induction, remembering the inequality in (14), and using $\overline{A}_n$ instead of $\overline{A}_{n,V}$ in (15),

$$F_n^{(2k+1)}\leq F_n^{(2k+3)}\leq F_n^{(2m+2)}\leq F_n^{(2m)},\text{ all } k,m<\infty, \tag{16}$$

abbreviating $F_n^{(M)}(\underline{n};\underline{\lambda_n};z)$ by $F_n^{(M)}$. The odd sequence is monotone increasing, and the even one monotone decreasing. Since $F_n^{(2k+1)}\leq F_n^{(2m)}$ for any k,m, both sequences are bounded; therefore both converge to some limits (not necessarily equal). This is precisely Eq. (12b). To prove (12c) we only need note that, if $F_n(\underline{n};\underline{\lambda_n};z)$ exists, it decreases monotonically with increasing λ_n. Equation (11) thus yields a generalization of the Groeneveld inequality[9] $F_n(n;\underline{\lambda_n};z)\leq 1$. This, when used in (15), yields $F_n^{(2k+1)}\leq F_n(\underline{n};\underline{\lambda_n};z)\leq F_n^{(2m)}$, by induction. This last inequality, and (12b), then yields (12c). The proof of Theorem I is thus completed.

We now assert Theorem II: Given the conditions (3a), (3b), and $z=re^{i\theta}$ complex, the limits F_n^{+} and F_n^{-} are regular functions of z in the open domain D: $r<1/f$, $|\theta|<\pi/2$. To prove this, it suffices to prove (a) each $F_n^{(M)}$ is regular for $z\in\overline{D}$: $r\leq 1/f$, $|\theta|\leq\pi/2$, and (b) each $|F_n^{(M)}|\leq K$, $z\in\overline{D}$. Since Theorem I means that the sequence converges at a set of points clustering at an interior point of $\overline{D}$ (here along the entire positive real axis), Theorem II follows from Vitali's convergence theorem.[10]

Defining $F_n\equiv R_n\exp(-i\varphi_n)$, $R_n^{(0)}\equiv 1$, $\varphi_n^{(0)}\equiv 0$, the sequence equivalent to (15) becomes (of course, in the limit $V\to\infty$),

$$R_n^{(M)}=\exp\{-r\overline{A}_n\cdot[R_{n+1}^{(M-1)}\cos(\theta-\varphi_{n+1}^{(M-1)})]\}, \tag{17a}$$

$$\varphi_n^{(M)}=r\overline{A}_n\cdot R_{n+1}^{(M-1)}\sin(\theta-\varphi_{n+1}^{(M-1)}). \tag{17b}$$

In Eqs. (17a), (17b), and from now on, we take the upper limits of integration over λ_n's, Eq. (14), to be 1. Lemma (a) follows immediately by induction. To prove Lemma (b) we show that $R_n^{(M)}\leq 1$, $z\in\overline{D}$, all $k,M<\infty$. From (17a) we see that this will hold if $\cos(\theta-\varphi_{n+1}^{(M-1)})\geq 0$, that is, if $|\theta-\varphi_{n+1}^{(M-1)}|\leq\pi/2$. We see that this condition holds for $M=1,2$. For any M this condition holds by induction if $r\overline{A}_k\cdot 1\leq 1$, any k. Now, we have, for any k, $\overline{A}_k\cdot 1\leq\overline{A}_1\cdot 1=f$, from (14) and (3a), (3b). This completes Lemma (b) and thus Theorem II.

Theorem III reads: For $z\in D$, the thermodynamic limits $F_n(\underline{n};\underline{\lambda_n};z)$ exist, and are regular functions of z. This theorem will follow from Lemma (c): The limits $F^{-}(\underline{n};\underline{\lambda_n};z)$ and $F^{+}(\underline{n};\underline{\lambda_n};z)$ are given by the same hierarchy of integral equations; from Groeneveld's lower bound for radii of convergence of cluster expansions[5]; and from Theorem II. The latter, together with Groeneveld's result, means that

F_n^- and F_n^+ are both regular in the domain D^* consisting of D (bounded by semicircle of radius $1/f$ to the right, and by the imaginary axis to the left) combined with D_0 (bounded by semicircle of radius $1/fe$ to the left). Therefore both bounds can be expanded around any point within D^*, in any domain contained in D^*. Lemma (c) then means that the expansion coefficients of F_n^- and F_n^+ are identical, thus $F_n^- = F_n^+$. Theorem III then follows from (12c), Theorem I. To prove the lemma, we note that the proof of Theorem I also leads to the following equations for the two bounds:

$$F_n^- = \exp(-z\bar{A}_n \cdot F_{n+1}^+), \quad F_n^+ = \exp(-z\bar{A}_n \cdot F_{n+1}^-). \tag{18}$$

Substituting the corresponding equations for F_{n+1}^+ and F_{n+1}^- we obtain

$$F_n^* = \exp[-z\bar{A}_n \cdot \exp(-z\bar{A}_{n+1} \cdot F_{n+2}^*)], \text{ where } * = + \text{ or } -. \tag{19}$$

Lemma (c) and Theorem III are thus proven.

In view of the relation between discontinuities in distribution functions and orders of (Ehrenfest) phase transitions,[11] Theorem III means that no such phase transitions of any order are possible for systems with non-negative interactions at activities lower than $1/f$. A heuristic argument to the effect that this statement may be valid for all finite activities stems from the following proof of the alternative Theorem IIIa: For z real, $0 \leq z \leq 1/f$, the thermodynamic limits $F_n(\underline{n}; \underline{\lambda_n}; z)$ exist and are continuous functions of z. This proof proceeds as follows: It is easy to show that the M sequences converge uniformly with respect to z in any closed interval $0 \leq z \leq c < \infty$. Since each member of the sequence is continuous in z, this means that the limits F_n^- and F_n^+ are both continuous functions of z. On the other hand, it is easily seen that the functions F_n given by (13) are components of a vector $\vec{F}$ in Banach function space, and the operators $\bar{Q}_n = \exp(-z\bar{A}_n)$ are components of the corresponding vector $\vec{Q}$ in this space. It is easy to show that, for $z \leq 1/f$, the operator $\vec{Q}$ is a contraction (that is, $\|\vec{Q}\cdot\vec{f} - \vec{Q}\cdot\vec{g}\| \leq \|\vec{f} - \vec{g}\|$, with $\vec{f}$, $\vec{g}$ arbitrary functions in Banach space[12]). This means that the vector operator equation $\vec{Q}\cdot\vec{F} = \vec{F}$ can have at most one solution; thus $F_n^+ = F_n^-$ and, from (12c), F_n exists and is continuous in z for $z \leq 1/f$.

Now, if one calculates using an explicit form for interaction potentials (hard spheres), one finds that IIIa is valid for $z \leq c_k$, with $c_{k+1} > c_k > 1/f$, but proof that c_∞ can be arbitrarily large is lacking as yet. Work in this direction is in progress.

In closing, we note that the M-sequence method is not limited to non-negative interactions. For potentials consisting of positive core and an attractive part it leads to some rather remarkable factorization theorems for distribution functions. These and other matters will be reported in the full article.

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