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LETTER TO THE EDITOR

Some mathematical properties of classical many-body systems with repulsive interactions

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Abstract. It is shown that, for systems with repulsive (non-negative) interactions, the Yang-Lee zeros of the grand canonical partition function lie on the real z axis. As a result, a series of successively improving lower and upper bounds for the thermodynamic ratio of density to activity is obtained. In addition bounds on the transition activity and density are given in terms of the cluster coefficients.

There is considerable evidence to suggest that the structure of a fluid and the nature of the fluid-solid phase transition are determined primarily by the short-range repulsive part of the intermolecular potential. The long-range attractive component is relatively weak and, as far as the structure of the fluid is concerned, can be treated as a perturbation. As a result much effort has been put into studying the thermodynamic functions of systems with repulsive two-body interactions [1]. A complete description of the fluid phase is provided by the Mayer cluster series in terms of the activity, z. It is desirable to check the mathematical consistency and numerical accuracy of approximate methods and machine computations against the Mayer series. However, in the case of a repulsive interaction, the radius of convergence of the cluster series is determined by a singularity at a point $z=-z_0$, relatively close to the origin, on the negative real axis [2]. As a result the physically relevant region is far outside the radius of convergence of the Mayer series, which provides reliable results only in the extremely low-density regime. Lieb [3] introduced a modified expansion scheme, based on the cluster coefficients, which results in an alternating sequence of upper and lower bounds for the thermodynamic functions. Unfortunately his bounds improve successively only in the circle of convergence, i.e. at low densities. In this letter we extend his method and show that successively improving bounds can be obtained for the entire fluid branch. The location of the dominant singularity (radius of convergence) and the location of the transition activity to another phase can be bounded by using as many coefficients as are available.

We deal with an open system of classical particles interacting via a purely repulsive potential. The Mayer series for the pressure is

$$\beta p=\sum_{n=1}^{\infty} b_n z^n \tag{1}$$

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where $\beta = 1/kT$, and the coefficients $\{b_n\}$ are the Mayer coefficients with $b_1 = 1$ and a non-zero b_2. The number density follows from (1) as

$$\rho(z) = z\frac{\mathrm{d}}{\mathrm{d}z}(\beta p) = \sum_{n=1}^{\infty} nb_n z^n. \tag{2}$$

Consider the symmetric tridiagonal matrix **R** defined by the requirement [4]

$$(\mathbf{R}^n)_{11} = (n+1)|b_{n+1}|. \tag{3a}$$

Then the density is given by

$$\rho(z) = (\mathbf{1}z^{-1} + \mathbf{R})^{-1}_{11} \tag{3b}$$

where $\mathbf{1}$ is the infinite unit matrix. The first matrix elements are given by

$$R_{11} = 2|b_2| \qquad R_{12}^2 = 3b_3 - 2b_2^2 \qquad R_{12}^2 R_{22} = 4|b_4| - R_{11}3b_3 - R_{12}^2 R_{11}.$$

The Lieb lower (upper) bounds are given in terms of **R** by

$$\rho(z)/z \gtrless \left[1 + R_{11}z - R_{12}^2 z^2 \sum_{j=0}^{n} (-1)^j (\mathbf{R}_2^j)_{11} z^j\right]^{-1} \tag{4a}$$

and

$$0 < \rho(z)/z < 1 \tag{4b}$$

with n odd (even), and where $\mathbf{R}_2$ is the first minor of **R**.

The lower bounds are valid for all $z > 0$ but they become useless for large z. The upper bounds are valid for small z only. **R** matrices were constructed using the available information for many lattice models and continuum models [4]. In all cases it was found that all the matrix elements are real and positive. We shall show that this is indeed true. (In the construction process the off-diagonal terms are determined only up to their square; the physical properties are invariant to the choice of the sign of the root.) Let us write the equation for the thermodynamic ratio as a continued fraction,

$$\rho(z)/z = 1/[1 + R_{11}z - R_{12}^2 z r_1(z)] \tag{5a}$$

where $r_1(z)$ is the first remainder. Then

$$r_1(z) = [1 + R_{11}z - z/\rho(z)]/R_{12}^2 z. \tag{5b}$$

Applying the Lieb inequalities to z/ρ one obtains for $r_1(z)$

$$r_1(z) \gtrless \sum_{j=0}^{n} (-1)^j (\mathbf{R}_2^j)_{11} z^{j+1} \qquad \text{and} \qquad 0 < r_1(z) < R_{11}/R_{12}^2. \tag{5c}$$

It is easy to see that $R_{12}^2 > 0$, since this inequality follows immediately from the Groeneveld inequalities [2], and that $R_{22} > 0$. The remainders obey the recursion relation

$$r_n(z) = [1 + R_{nn}z - z/r_{n-1}(z)]/R_{n(n+1)}^2 z. \tag{6}$$

Successive applications of the inequalities (5a) to the remainders result, at least for sufficiently small z, in the inequalities

$$0 < r_n(z) < z \tag{7}$$

for all n. Equation (7) combined with (6) implies that R_{nn} and $R^2_{n(n+1)}$ are positive for all n, and that the matrix $\mathbf{R}$ is a real symmetric matrix with a spectrum of real eigenvalues and positive residues. Thus the Yang-Lee zeros of the grand partition function lie on the real z axis in the two intervals $z < -z_0$ and $z > z_t$, where z_t is the activity of the fluid-solid phase transition, or the termination activity of the fluid phase for a system that undergoes a first-order transition. The rest of the complex z plane is free from zeros. The density is given by the shifted Stieltjes integral

$$\rho(z) = z \sum_{j=1}^{\infty} a_j/(1+\lambda_j z) = z \int_{z_0^{-1}}^{-z_t^{-1}} f(x)/(1+zx)\,\mathrm{d}x. \tag{8a}$$

In (8a) the eigenvalues are bounded by $-1/z_t < \lambda_j < 1/z_0$. The normalised weight function $f(x) > 0$ for all x in the interval. The pressure is given by a similar integral,

$$\beta p(z) = \int_{z_0^{-1}}^{-z_t^{-1}} [f(x)/x] \ln(1+zx)\,\mathrm{d}x. \tag{8b}$$

For a system that does not undergo a phase transition, i.e. $1/z_t = 0$, the matrix $\mathbf{R}$ is positive definite, and the cluster coefficients form a series of Stieltjes. In the general case the matrix $(\mathbf{1}z^{-1} + \mathbf{R})$ is positive definite for $0 < z < z_t$ or, equivalently, all the remainders $r_n(z)$ are positive there. It is therefore possible to construct in this interval two sequences of bounds for the density, a monotone increasing sequence of lower bounds and a monotone decreasing sequence of upper bounds, which converge to a common limit. The set of lower bounds is formed by successive truncations of the continued fraction. The first lower bound

$$\rho_1(z) = z/(1+R_{11}z) \tag{9a}$$

is identical to the first lower bound of Lieb. But the second one

$$\rho_2(z) = z[1 + R_{11}z - R_{12}z^2/(1+R_{22}z)]^{-1} \tag{9b}$$

is larger than the corresponding Lieb bound for all $0 < z < z_t$. Divergence of a lower bound due to the existence of a pole at some z' indicates that $z' > z_t$. More precisely the existence of a negative eigenvalue for any sub-matrix of $\mathbf{R}$ implies that the system undergoes a phase transition and $z_t < -\lambda_{\min}^{-1}$, provided that $\lambda_{\min} < 0$.

The construction of the sequence of upper bounds is based on the fact that z_t is the largest point for which the matrix $(\mathbf{1}z^{-1} + \mathbf{R})$ is positive definite. An upper bound is formed by a truncation followed by a replacement of the term R_{nn} by the term R'_{nn},

$$R'_{nn} = -1/z_t + R^2_{n(n-1)} D_{n-2}/D_{n-1} \tag{10a}$$

where D_n is the determinant of the truncated matrix $(\mathbf{1}z_t^{-1} + \mathbf{R}_n)$. The upper bounds depend, through R'_{nn}, on z_t whose value is usually not known; they are therefore not very useful as numerical bounds on the density. The positivity of the R'_{nn} is, however, used to provide a sequence of improving lower bounds for z_t. The first of these z_1 is given by

$$z_1 = [R_{11} + (R_{11}^2 + 4R_{12}^2)^{1/2}]/2R_{12}. \tag{10b}$$

To our knowledge the best previous lower bound for z_t is that of Meeron [5] $z_t > R_{11}$ which is smaller even than z_1. All the available information can be used to obtain a lower bound for z_t and then, by performing an appropriate truncation of the continued fraction, to obtain a lower bound for the transition density.

The exact location of z_0, the radius of convergence of the Mayer expansion, is an interesting mathematical problem in itself, but it may also have a physical significance. The physically relevant properties of the system are screened by the dominant singularity at $-z_0$. A suitable conformal mapping results in a new expansion whose radius of convergence is determined by z_t, and the point $-z_0$ is mapped to the exterior of the new circle of convergence. The efficiency of the mapping increases with the accuracy of the estimates of z_0. Groeneveld [2] showed that z_0 obeys the inequalities

$$1/R_{11}e < z_0 < 1/R_{11}. \tag{11}$$

These are the best possible general bounds on z_0 that depend only on b_2. Ree [6] improved these bounds by introducing the effect of b_3 on the higher cluster coefficients. The set of largest eigenvalues of the upper sub-matrices of $\mathbf{R}$ forms a sequence of improving upper bounds for z_0. The cluster coefficients themselves are bounded by

$$(m+1)|b_{m+1}| \geq \sum_{j=1}^{n} a_j(n)\lambda_j^m(n) \tag{12}$$

where $a_j(n)$ and $\lambda_j(n)$ are the jth residue and eigenvalue of the $n \times n$ upper sub-matrix of $\mathbf{R}$. For $(m+1) \leq 2n$ the inequality is an equality.

It is worthwhile investigating the asymptotic behaviour of the elements of the $\mathbf{R}$ matrix and their effect on the onset of the transition. Let μ be the absolute value of the smallest negative eigenvalue of $\mathbf{R}$. Then

$$\det(\mathbf{R}+\mu\mathbf{1}) = (R_{11}+\mu)\det(\mathbf{R}_2+\mu\mathbf{1}) - R_{12}^2\det(\mathbf{R}_3+\mu\mathbf{1}) = 0.$$

By assuming $\det(\mathbf{R}_2+\mu\mathbf{1}) \neq 0$ one obtains

$$(R_{11}+\mu)/R_{12}^2 = r_1(1/\mu) \leq R_{11}/R_{12}^2.$$

Thus either a negative eigenvalue does not exist or $\det(\mathbf{R}_2+\mu\mathbf{1}) = 0$. The latter implies that the determinants of all the other minors vanish too. The minors of an infinite Toeplitz [7] matrix have this property. Indeed, based on numerical inspection, it was conjectured [4] that for all repulsive systems the matrix elements converge to constants along the diagonals, forming a Toeplitz-like matrix.

Finally we would like to conjecture that the addition of an attractive component to the potential does not change the above results, provided the temperature is higher than the critical temperature. The Yang–Lee zeros are still located on the real z axis, z_t is shifted towards the origin, while the singularity at $-z_0$ moves towards lower z values as the temperature decreases. Complex Yang–Lee zeros start to appear only for $T \leq T_c$.

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