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Classical Hard-Sphere Fluid in Infinitely Many Dimensions

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The equation of state of the fluid phase of the classical hard-sphere system in infinitely many dimensions has been obtained exactly. Only the first two virial coefficients are nonvanishing. The upper bound for the coefficients of the Mayer series for nonnegative interaction potentials is reached by this system.

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Hard spheres[1] provide a useful model for fluids at sufficiently high temperatures and possibly their transitions to solids. Despite its apparent simplicity, this model has not been solved. However, as we will show in this Letter, considerable simplifications occur in the limit of infinitely many space dimensions, and we are able to give an equation of state for the thermodynamic properties of the hard-sphere fluid.

For any finite dimension D, the grand partition function Ξ for the system of hard spheres can be written as a power series in the activity $z=\Lambda^{-D}\exp(\mu\beta)$ $[\Lambda=(h^2/2\pi mkT)^{1/2}$, $\beta=1/kT$, and μ is the chemical potential] as

$$\Xi=\sum_{n=0}^{\infty}(z^n/n!)\int d^Dx_n\cdots d^Dx_n\prod_{i<j}^{n}[1-\Theta(\alpha-|\mathbf{x}_i-\mathbf{x}_j|)]=\exp(\beta pV) \qquad (1)$$

in the thermodynamic limit. In (1), α is the diameter of the hard sphere, Θ is the Heaviside unit step function, p is the pressure, and V is the volume of the system. The linked-cluster theorem then yields[1,2] the Mayer series

$$pV/kT=v\sum_{n=1}^{\infty}b_nz^n,\quad \langle N\rangle=v\sum_{n=1}^{\infty}nb_nz^n, \qquad (2)$$

where $\langle N\rangle$ is the expected number of hard spheres. The b_n are the sum of all possible connected graphs on n labeled points multiplied by their respective weights [which are integrals over the $\Theta(\alpha-|\mathbf{x}_i-\mathbf{x}_j|)$'s]. The natural scale of volume is $v=\pi^{D/2}a^D/\Gamma(1+\frac{1}{2}D)$, the volume of a sphere of radius a.[2] The Mayer series (2) has the alternating bond property, $(-1)^{n-1}b_n\geqslant 0$, as befits repulsive intersphere potentials.[2]

The crucial observation is that as $D\rightarrow\infty$ the evaluation of the b_n's requires only the contribution of tree diagrams. Contributions from other diagrams containing one or more loops are smaller by a factor of $(1/\sqrt{D})\alpha^{-D}$, $\alpha\simeq 4/3^{3/2}<1$. This is because $v/a^D\rightarrow 0$ and the cross section between spheres vanishes in the limit $D\rightarrow\infty$. Thus one finds,[3,4] using the number of labeled tree graphs of order n, n^{n-2},[3]

$$pv/kT=-\sum_{n=1}^{\infty}(n^{n-2}/n!)(-zv)^n[1+O((1/\sqrt{D})(4/3^{3/2})^D)], \qquad (3)$$

$$\rho v=-\sum_{n=1}^{\infty}(n^{n-1}/n!)(-zv)^n[1+O((1/\sqrt{D})(4/3^{3/2})^D)], \qquad (4)$$

with ρ the number density. For $D \to \infty$, the radius of convergence of these series is $zv = 1/e$. For $0 < zv < e^{-1}$ one finds, on reversion of (4) and substitution in (3) (see Ref. 1, Chap. 8), that

$$p/\rho kT = 1 + \tfrac{1}{2} v\rho. \tag{5}$$

Higher-order virial coefficients vanish identically at $D = \infty$.

Specifically, one can show that, for $|zv| < 1/e$, the Mayer series (4) is the *unique* root of the implicit equation (in ρ)[5]

$$\rho v e^{\rho v} = zv. \tag{6}$$

This equation yields

$$d(\rho v)/d(zv) = e^{-(\rho v)}/(1+\rho v),$$

whereas the Mayer series (3) and (4) imply that $zv\, d(pv/kT)/d(zv) = \rho v$, and thus

$$\frac{d(pv/kT)}{d(\rho v)} = \frac{\rho v}{zv\, d(\rho v)/d(zv)}.$$

Combining these two expressions with Eq. (6), we obtain $d(pv/kT)/d(\rho v) = 1 + \rho v$, and hence (5).

Although the equation of state (5) is analytic, the original series (3) and (4) have a singularity at $zv = -1/e$. Notwithstanding the fact that the implicit equation (6) has more than one root outside the circle of convergence of the Mayer series $|zv|e = 1$, an analytic continuation of the series can be performed as follows. The Mayer coefficients are well approximated and bounded by Stirling's approximation, $n^{n-1}/n! < e^n (2\pi)^{-1/2} n^{-3/2}$. The approximate series,

$$\rho v \simeq -(2\pi)^{-1/2} \sum_{n=1}^{\infty} \frac{(-zve)^n}{n^{3/2}},$$
$$\frac{pv}{kT} \simeq -(2\pi)^{-1/2} \sum_{n=1}^{\infty} \frac{(-zve)^n}{n^{5/2}} \tag{7}$$

(which have the same radius of convergence, and the same divergence at $zve = -1$ as the original series), can be analytically continued in the complex z plane, cut along $-\infty < z < -1/ev$, by use of Appell's integral[6]

$$-\sum_{n=1}^{\infty} \frac{(-zev)^n}{n^{3/2}} = \frac{zev}{\Gamma(3/2)} \int_0^{\infty} dt \frac{t^{1/2}}{e^t + zev}, \tag{8}$$

which is an analytic function of z everywhere in the cut complex z plane. We conclude that there are no premonitory signs of a phase transition in the fluid phase described by the Mayer series (3) and (4) or the equation of state (5). This is, however, not sufficient to rule out a phase transition in the $D = \infty$, classical hard-sphere system. Computer simulations have established the existence of a first-order phase transition for $D = 3$.[7]

The simple form of the equation of state (5) is due to fluctuations becoming less important as the dimensionality of the system increases. Indeed, the mean-field theory of critical phenomena becomes exact above the upper critical dimension (which is 4 for fluids), for the same reason. The decreasing importance of fluctuations as $D \to \infty$, together with a *finite* nontrivial virial coefficient in Eq. (5), suggest the presence of a phase transition, despite the lack of any premonition in the fluid phase. The precise structure of a sufficiently dense solid phase in the $D = \infty$ hard-sphere system is unknown[8] (only bounds[9] are known), so that neither the solid branch of the equation of state, nor nucleation into the solid phase, can be studied independently.

We note that the space-filling density, by which the pressure must have diverged, is infinite as $D = \infty$, since $v/a^D \to 0$ as $D \to \infty$. Thus, the so-called "random close packing" divergence[10] occurs at $\rho v = \infty$ for $D = \infty$, as do the Rogers bounds for dense packing of spheres.[9] On the other hand, hypercubic $[\rho v = v(2a)^{-D}]$ and body-centered hypercubic densities are vanishingly small, well within the fluid phase, and below the density and pressure corresponding to the radius of convergence of the Mayer series

$$(\rho v)^* \simeq (2\pi)^{-1/2} \eta(\tfrac{3}{2}) = 0.305,$$
$$(pv/kT)^* \simeq (2\pi)^{-1/2} \eta(\tfrac{5}{2}) = 0.346,$$

where $\eta(s) = -\sum_{n=1}^{\infty} (-n)^{-s}$ is the modified Riemann zeta function. Note that $(p/\rho kT)^* = 1.134$ is only one order of magnitude below the value at which computer simulations in three (and two) dimensions indicate a phase transition.[7]

A general theorem for hard-sphere systems[2] gives bounds for the Mayer coefficients,

$$\frac{1}{n} \leq |b_n| \leq \frac{n^{n-2}}{n!}, \tag{9}$$

and, accordingly, for the radius of convergence of the Mayer series. Our classical system of hard spheres at $D = \infty$ realizes the upper bound [or the lower bound for the radius of convergence R, which is also related to that of the finite-volume Mayer expansion, $R(V) \geq R = \lim_{V \to \infty} R(V)$ [11,12]]. The lower bound is realized by the Ford model,[13] a grand partition function constructed *ad hoc* as an example of the Yang-Lee phase transition,[14] and for which no physical potential has been found. In the Ford model, no pressure maxima have been obtained by Padé-approximant analysis of the virial series, indicating the failure of the equation of the fluid phase to supply any information about the condensed phase,[10] exactly as in the present $D = \infty$ hard-sphere model.

Although the classical $D = \infty$ hard-sphere fluid is nonideal [finite second virial coefficient in Eq. (5)], its quantum mechanical counterpart behaves like an ideal Bose gas at low temperatures,[4] with a Bose-Einstein condensation.

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