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Padé approximants and the random close packing of hard spheres and disks

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arried out studies of momentum densities for atoms ith atomic numbers ranging from two to ten using ingle zeta, double zeta, and near Hartree–Fock wave unctions.[1] With single zeta basis sets, $\rho(p)$ is found to e monotonic in all cases. Using double zeta or more ccurate basis sets, nonmonotonic behavior is found in arbon, nitrogen, oxygen, fluorine, and neon in their ground states. Momentum densities in boron, helium, lithium, and beryllium atoms are found to be monotonically decreasing. Thus, an application of the bounds among $\langle p^n\rangle$ values in Refs. 2 and 3 requires a preliminary investigation of the monotonic nature of $\rho(p)$. In case such an *a priori* check is not feasible, the inequalities can be used to obtain semiempirical estimates of unknown $\langle p^n\rangle$ expectation values. These estimates should be reasonably accurate, although not necessarily upper bounds, since the deviation from monotonicity of $\rho(p)$ is generally small.

If rigorous bounds for $\langle p^n\rangle$ are desired for all systems, slightly weaker but general inequalities can be employed. These can be derived from the general Gram inequality

$$\left| \int f_m(x) f_n(x)\, dx \right|_{m,n=1,2,\ldots,N} > 0 \ . \tag{1}$$

Specifically, the bounds corresponding to Eqs. (2b), (3b), (4b), and (5b) given in Ref. 2 can be replaced by

$$\langle p\rangle\langle p^{-1}\rangle > 1 \ , \tag{2}$$

$$\langle p\rangle\langle p^{3}\rangle < \langle p^{2}\rangle^{2} \ , \tag{3}$$

$$\langle p^{2}\rangle > \langle p\rangle^{2} \ , \tag{4}$$

and

$$\langle p^{-2}\rangle > \langle p^{-1}\rangle^{2} \ , \tag{5}$$

which are weaker than their counterparts by about 12%, 4%, 6%, and 33%, respectively.

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Padé approximants and the random close packing of hard spheres and disks

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It is well known[1] that successive virial coefficients become increasingly difficult to calculate, even for classical gases as simple as that of hard spheres or disks. For both these systems only the first seven coefficients have been determined.[2] In spite of this, it is common knowledge[3] that Padé approximants,[4] constructed solely from the first six or seven coefficients of the density expansion, have provided excellent representations of the equation of state as determined by "computer experiments" such as "molecular dynamics" (MD)[3] or "Monte Carlo" (MC)[5] techniques.

Assuming that for densities *beyond* the crystallization density[6] of about 2/3 times the regular (fcc or hcp) close-packing density the virial series continues to describe the metastable fluid branch, it is somewhat disappointing as well as puzzling that *none* of the equations of state extrapolated beyond low density available in the literature diverge at the *random* (or irregular) close-packing density (ρ_0) of the hard sphere gas, as one would expect on physical grounds, with the exception of the extrapolant of Ref. 9 which however contains an *ad hoc* constraint. The random close-packing density, as determined from actual experiments with ball bearings is 0.8597 times the regular close-packing value. Computer-generated close packings,[8] on the other hand, have thus far fallen about 3% too short of reproducing this empirical value. However, LeFevre's[9] analysis of both MC and MD data clearly points to the Scott–Kilgour[7] value of 0.8597 ρ_0 as the density where the pressure diverges. But the divergence in the published extrapolants for the equation of state occurs *at*[10] regular close packing or even *beyond* [11] as, e.g., with both the "scaled-particle theory"[12] and the Carnahan–Starling[13] equations of state, as well as the Padé approximant in Ref. 14. In some cases the pole of the extrapolant occurs for imaginary density as in the Padé approximant labeled $P(3,3)$ in Ref. 2.

We have carefully recalculated all the Padé approximants using Kratky's[14] recent recalculation of the higher-order virial coefficients and find, apparently for the first time, more than one such approximant diverging very near the empirical irregular close-packing density of Scott and Kilgour. This result is offered as a criterion for selecting the best fluid equation of state for hard spheres.

The virial expansion as known to date, taking

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TABLE I. Value x_0 of density, in units of regular close-packing density $\rho_0 \equiv \sqrt{2}/c^3$, for which different Padé approximants (2), constucted on the basis of the virial expansion (1) with $\epsilon_5 = \epsilon_6 = 0$, diverge. The empirical value (Ref. 7) is 0.8597.

L, M	3, 3	2, 4	2, 3	3, 1	4, 2	4, 1
x_0	0.8618	0.8624	0.8731	0.8787	0.9587	0.9569

TABLE II. Coefficients p_i and q_i of the three best Padé approximants (2) to the virial expansion (1).

L, M	3, 3	2, 4	2, 3
p_1	0.617 895 415 5	0.678 739 183 7	0.671 469 870 8
p_2	0.627 934 820 3	0.668 789 577 5	0.680 867 409 1
p_3	−0.041 426 538 8	···	···
q_1	−2.344 026 543 4	−2.283 182 775	−2.290 452 088
q_2	2.087 644 956	1.948 285 220	1.981 894 189
q_3	−0.828 667 618 1	−0.708 081 707 6	−0.767 770 383 3
q_4	···	−0.046 714 043 2	···

Kratky's[14] value, is

$$\frac{PV}{NkT} \equiv Z(x) = 1 + \sum_{n=1}^{6} A_n x^n ,$$

$$A_1 = 2.961\,921\,959, \quad A_2 = 5.483\,113\,556, \quad A_3 = 7.456\,363\,357,$$

$$A_4 = 8.485\,568\,085, \quad A_5 = 8.867\,836\,122 \pm \epsilon_5,$$

$$A_6 = 9.250\,436\,707 \pm \epsilon_6, \quad \epsilon_5 \equiv 0.091\,186, \quad \epsilon_6 \equiv 0.405\,129, \tag{1}$$

where P and V are pressure and volume, N the number of particles, k Boltzmann's constant, T the absolute temperature, $\rho \equiv N/V$ the particle density, and $x \equiv \rho/\rho_0$, where $\rho_0 \equiv \sqrt{2}/c^3$ is the regular (fcc or hcp) close-packing density, with c the hard sphere diameter.

The $[L/M](x)$, $L+M \leq 6$ approximants to Eq. (1) is defined such that it differs by terms of $0(x^7)$ from the power series (1). It is given by

$$[L/M](x) \equiv \frac{1 + p_1 x + p_2 x^2 + \cdots + p_L x^L}{1 + q_1 x + q_2 x^2 + \cdots + q_M x^M} , \tag{2}$$

where the coefficients p_i and q_i are determined[4] according to the definition stated. Table I gives the values x_0 closest to the Scott–Kilgour value of 0.8597 for which the various approximants (2) diverge, and Table II lists the values of p_i and q_i for the [3/3], [2/4], and [2/3] approximants, assuming $\epsilon_5 = \epsilon_6 = 0$ in Eq. (1). Figure 1 shows the *inverse* of Eq. (1) as represented by these three Padé approximants. MD data points (circles) for $N = 108$ spheres as well as MC data (squares) for $N = 32$ spheres are also shown. All three approximants virtually coincide at low density. At higher densities the [3/3] and [2/4] approximants are virtually the same, whereas the [2/3] (which contains all but the last known virial coefficient) differs slightly from these.

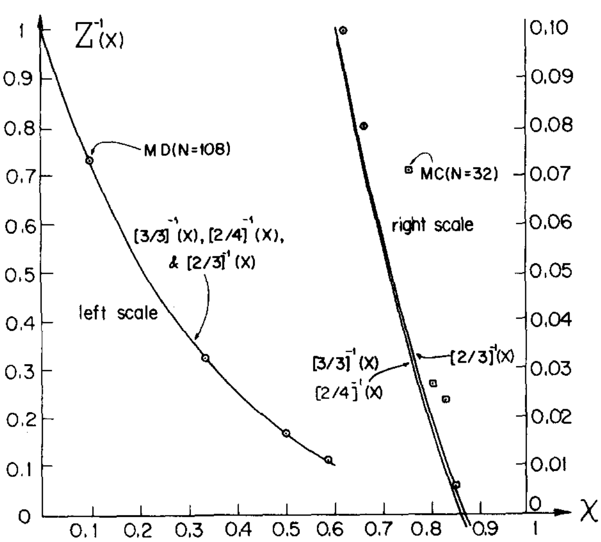

FIG. 1. Inverse of Eq. (1), as function of density x in units of the regular (fcc or hcp) close-packing density of $\rho_0 \equiv \sqrt{2}/c^3$, as represented by the three best Padé approximants (2) to the virial series (1). Open circles are MD data points (Ref. 3) for 108 hard spheres and open squares MC data points (Ref. 5) for 32 hard spheres.

The empirical value of the random close-packing density for hard disks is much less certain. A crude experiment by Stillinger *et al.*[15] gives the value of 0.89 times the regular (triangular) close-packing density of $\rho_0 \equiv 2/\sqrt{3}c^2$. Computer-generated values[16] range from

TABLE III. Same as Table I but for hard disks. Note that here $\rho_0 \equiv 2/\sqrt{3}\,c^2$. The empirical value (Refs. 15, 16) is between 0.89 and 0.92.

L, M	2, 3	4, 1	2, 3	2, 1
x_0	0.88	0.92	0.96	0.81

)0 to 0.92 for this quantity. Our "best" (i.e., with)ole closest to ~ 0.9) Padé results, based on Kratky's[17] cial coefficients, appear in Table III. Both the [3/3] d [4/2] Padé's have denominators with real roots but r $x > 1$, i.e., beyond regular close packing, while the /4] denominator has four complex roots. We have ırthermore looked at the poles of Padé approximants ased on the fifth-order polynomial factorized from the $_1x$ term of Eq. (1) as well as for the fourth-order ne factorized from the A_2x^2 term of Eq. (1). These ave pole locations *distinct* from the (regular) approxi-nants of Table III. For the fifth-order polynomial-ɔased Padé's we found no poles for $0 \leq x \leq 1$, while for he fourth-order cases [0/2], [0/3], and [0/4] we found $x_0 = 0.89$, 0.94, and 0.98, respectively.

In spite of the confused situation for two dimensions, the three dimensional case is clear at least insofar as more than one Padé approximant is consistent with the empirical close-packing density. The more ambitious prospect of extracting, with Padé or similar techniques, the *crystallization density* of the hard sphere fluid suggests itself and is under study at present.

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Lightning rod effect in surface enhanced Raman scattering

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Several models have been proposed to explain the observations of surface enhanced Raman scattering.[1,2] One of the most successful theories has been an electromagnetic model,[1–3] in which plasmon resonances of microscopic bumps or particles on the surface act to increase the local field at an adsorbed molecule and to amplify the reradiated Raman field. Although more than one mechanism may be responsible for the total enhancement, the particle plasmon model has correctly predicted enhancement beyond the first layer of molecules,[4] the need for surface roughness,[5] and that silver surfaces should give the largest enhancement. Detailed predictions of the model with regard to its resonance character have been verified with lithographically prepared surfaces.[6] In addition, good correlation of anomalous low frequency Raman scattering with the particle plasmon model has been observed.[7]

Gersten and Nitzan[1] have recently discussed the electromagnetic model in some detail. They consider the problem of Raman scattering from a metallic ellipsoid with a molecule adsorbed at the tip, and express the enhancement in terms of Legendre polynomials of the first and second kind. Three sources of enhancement were noted: the image dipole effect (which we shall neglect), the increase in local field by "lightning rod" effect, and the resonant particle plasmon effect. It is our purpose here to expand the discussion of the lightning rod effect. We find we can rewrite the Gersten and Nitzan result as the product of two simple factors. One factor gives the enhancement due to dipolar fields of the particle plasmon resonance while the second is a purely geometric factor which we identify as the lightning rod factor. This definition of the effect is somewhat different from that of Gersten and Nitzan. Also, rather than express results in terms of Legendre polynomials, we use the formulation of depolarization factors which are well known in calculations of local fields around dielectric or magnetic particles.[8] If the major (a) and minor (b) axis dimensions of an ellipsoid of revolution are such that $a, b \ll \lambda$ the electrostatic approximation[1] can be used. A uniform applied laser

