

Reply to “Comment on ‘Critical exponent for glassy packing of rigid spheres and disks’ ”

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The weak algebraic divergence of the pressure at random close packing in a classical system of hard spheres or hard disks does not rely on the behavior of the equilibrium canonical partition function at such packing, as suggested by M. Alexanian [Phys. Rev. A 37, 4527 (1988)], but rather is a result numerically suggested by the series analysis reported earlier.

The nature of the pressure divergence in a continuous classical system of hard disks or hard spheres, as the random-close-packed (RCP) density is approached, was recently investigated.¹ The principal thrust of that paper was a seven-virial-coefficient “derivative-logarithm” series analysis.² Studies such as this one were carried out earlier in more traditional critical-exponent series-analysis work³ for spin systems where series with 20 or more coefficients are encountered. Our analysis was applied to the low-density pressure- P series

$$P/kT = \rho + B_2\rho^2 + B_3\rho^3 + \dots, \tag{1}$$

via Padé approximants, to generate a *nonequilibrium* pressure branch that ultimately diverges at RCP.

This procedure is expressly condoned in the preceding Comment⁴ [middle of paragraph above Eq. (3)]. Nevertheless, disagreement is therein expressed over a conjectural, heuristic attempt reported in our paper, to extract, formally, the nonequilibrium RCP pressure state from the *equilibrium* canonical partition function. We agree that this attempt must be abandoned, but emphasize that the subsequent numerical conclusions reported in our paper are independent of this picture, since we worked directly with the pressure virial series itself.

Our conjecture was inspired in part by the model problem, attributed to Ford,⁵ of a particular grand partition function that is volume- and activity- (but not temperature-) dependent. The model is exactly soluble and yields an explicit pressure-density equation of state. The pressure has a striking resemblance to the general features displayed by the hard-sphere system as revealed by both laboratory⁶ and computer⁷ experiments. Ford proposed the grand partition function

$$\Xi(V,z) = (1+z)^V \frac{1-z^V}{1-z} = \sum_{i=0}^V \sum_{j=0}^{V-1} \binom{V}{i} z^{i+j}, \tag{2}$$

where V is the volume in units of some length cubed so that, for large V , it can be taken as an integer, and z is the fugacity $e^{\mu/kT}$ with μ the chemical potential. The *pressure* in the thermodynamic limit is then obtained with the first Mayer equation⁸

$$P(z)/kT = \lim_{V \rightarrow \infty} V^{-1} \ln[\Xi(V,z)] = \begin{cases} \ln(1+z), & z < 1 \\ \ln[z(1+z)], & z > 1. \end{cases} \tag{3}$$

The density $\rho(z)$ is introduced through the second Mayer equation

$$\rho(z) = z \frac{\partial P(z)/kT}{\partial z}. \tag{4}$$

Eliminating z between Eqs. (3) and (4) yields the equation of state $P(\rho)$. This function can, furthermore, be identified with the *canonical* pressure via a theorem by van Hove as reenunciated by Huang.⁹ Thence

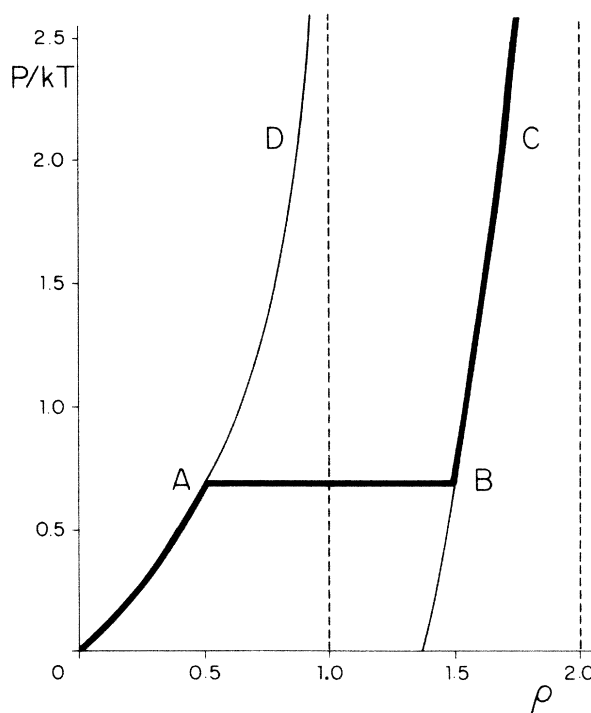


FIG. 1. Pressure-vs-density equation of state as given by Eq. (5), in arbitrary units.

$$P/kT = \begin{cases} \ln \left[\frac{1}{1-\rho} \right], & 0 \leq \rho < \frac{1}{2} \\ \ln 2, & \frac{1}{2} \leq \rho \leq \frac{3}{2} \\ \ln \left[\frac{\rho-1}{(2-\rho)^2} \right], & \frac{3}{2} < \rho < 2. \end{cases} \quad (5a)$$

$$(5b)$$

$$(5c)$$

This is graphed in Fig. 1 (thick curve) and represents the equilibrium (or stable) branches of the system. The *thin* curves in the figure correspond to the two nonequilibrium (or metastable) portions which are analytical extensions of Eqs. (5a) and (5c). The two poles, at $\rho=1$ and $\rho=2$, are reminiscent of the random and regular (primitive-hexagonal) close-packing divergences, respectively, known to occur in the classical hard-sphere system. As one might expect, a series analysis of (5a) does indeed¹⁰ point to the first (weak) divergence at $\rho=1$.

I stress again, however, that these considerations are merely heuristic and did not influence in any way the numerical outcome of the derivative-logarithm analysis in

Ref. 1 of the pressure virial series (1).

Although entirely missed during several decades of "integral-equation" studies¹¹ such as the Percus-Yevick, hypernetted-chain, scaled-particle theory, etc., bifurcations such as those appearing in Fig. 1 at point *A* (as density is raised) or point *B* (as density is lowered), have recently shown up within density-functional theories¹² applied to the hard-sphere fluid. In some cases,¹³ these bifurcations are very close to the empirical⁶ RCP density value. The integral-equation schemes of Ref. 11 are basically "third-virial-coefficient approximations" in the sense that, upon expansion about zero density, they reproduce exactly the coefficients in (1) up to B_3 . Extensions¹⁴ that reproduce also up to B_4 have proved both extremely difficult and expensive to solve in terms of computer time. The series analyses reported in Ref. 1 incorporate virial coefficients up to B_7 , although it should be mentioned that in a recent new version of the third-virial-coefficient approximation, Gonchar and Rudyk¹⁵ also found both bifurcation followed by two divergences in the pressure of the hard-sphere system.

¹S. Jasty, M. Al-Naghy, and M. de Llano, *Phys. Rev. A* **35**, 1376 (1987).

²G. A. Baker, Jr. and P. Graves-Morris, in *Encyclopedia of Mathematics and its Applications*, edited by G.-C. Rota (Addison-Wesley, New York, 1981), Vol. 13, p. 55 ff.; Vol. 14, p. 33 ff.

³D. S. Gaunt and A. J. Guttmann, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1974), Vol. 3.

⁴M. Alexanian, preceding paper, *Phys. Rev. A* **37**, 4527 (1988).

⁵G. E. Uhlenbeck and G. W. Ford, *Lectures in Statistical Mechanics* (American Mathematical Society, Providence, 1963).

⁶G. D. Scott and D. M. Kilgour, *J. Phys. D* **2**, 863 (1969); J. L. Finney, *Proc. R. Soc. London, Ser. A* **319**, 479 (1970); *J. Phys. (Paris) Colloq.* **C2**, 1 (1975).

⁷W. G. Hoover and F. H. Ree, *J. Chem. Phys.* **49**, 3609 (1968).

⁸J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, 2nd ed. (Wiley, New York, 1977).

⁹K. Huang, *Statistical Mechanics* (Wiley, New York, 1963), p. 321.

¹⁰V. C. Aguilera-Navarro, M. Fortes, M. de Llano, and O. Rojo, *J. Chem. Phys.* **81**, 1450 (1984).

¹¹J. K. Percus and G. J. Yevick, *Phys. Rev.* **1**, 110 (1958); T. Morita, *Prog. Theor. Phys.* **20**, 920 (1958); H. R. Reiss, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.* **31**, 369 (1959); H. R. Reiss, in *Statistical Mechanics and Statistical Methods in Theory and Applications*, edited by U. Landman (Plenum, New York, 1977).

¹²J. D. Weeks, S. A. Rice, and J. J. Kozak, *J. Chem. Phys.* **52**, 2416 (1970); J. J. Kozak, S. A. Rice, and J. D. Weeks, *Physica* **54**, 573 (1971); H. J. Raveche and C. A. Stuart, *J. Chem. Phys.* **65**, 2305 (1976); W. Klein and N. Grewe, *ibid.* **72**, 5456 (1980); L. Feijoo and A. Rahman, *ibid.* **77**, 5687 (1982).

¹³B. Bagchi, C. Cerjan, and S. A. Rice, *J. Chem. Phys.* **79**, 5595 (1983).

¹⁴G. Stell, *Physica* **29**, 517 (1963); S. A. Rice and J. Lekner, *J. Chem. Phys.* **42**, 3559 (1965); Y. T. Lee, F. H. Ree, and T. Ree, *ibid.* **48**, 3506 (1968); **55**, 234 (1971); Y. Uehara, T. Ree, and F. H. Ree, *ibid.* **70**, 1876 (1979).

¹⁵N. S. Gonchar and A. B. Rudyk, *Phys. Lett. A* **124**, 392 (1987); **124**, 399 (1987).