

# High dimensionality as an organizing device for classical fluids

H. L. Frisch<sup>1</sup> and J. K. Percus<sup>2</sup>

<sup>1</sup>*Chemistry Department, State University of New York at Albany, Albany, New York 12222*

<sup>2</sup>*Courant Institute and Physics Department, New York University, New York, New York 10012*

(Received 16 March 1999)

The Mayer diagrammatic expansion for a classical pair-interacting fluid in thermal equilibrium is cast in a form particularly appropriate to high-dimensional space. At asymptotically high dimensionality, the series, when it converges, is dominated by a single term. Focusing upon repulsive interactions, the dominant term belongs to a ring diagram and can have either sign, but when negative, the series must diverge. The nature of the divergence is found explicitly for hard core interactions, and analytic extension in density obtained by summing up the dominant ring contributions. The result is that a second virial truncation remains valid at densities much higher than that at which the series diverges. Corrections first appear in the vicinity of a particle volume-scaled density of  $\frac{1}{2}(e/2)^{1/2}$  per dimension, and produce a spinodal in the equation of state. Suggestions are made as to elucidating the resulting phase transition. [S1063-651X(99)01509-3]

PACS number(s): 05.20.Gg

## I. INTRODUCTION

The virial series, or MacLaurin expansion in density, is a standard and powerful technique for analyzing the thermodynamic properties of low density classical fluids. However, it is of questionable utility for examining thermodynamics, and thermodynamic singularities, arising at higher density. If one imagines density measured in units of interaction range, limiting high density situations often have special properties which simplify their treatment. Soft long-range repulsive interactions give rise to a crystal lattice with simple normal mode deviations [1]. For Coulomb forces, of effectively infinite range, the virial coefficients diverge, requiring resummation of the density series [2], not to a MacLaurin expansion, dominated by the initially most divergent terms. Another limiting situation which has been considered on a number of occasions [3–6] is that of high spatial dimensionality which, as we will see, does correspond to high density in the above sense. Here, fluctuations are reduced by high effective coordination number, so, e.g., interfaces tend to be even sharper, and one generally expects clean caricatures of any thermodynamic phenomenology that indeed extends to higher dimensionality. This is the domain that is the subject of the present investigation which, it must be emphasized, is of a heuristic nature, with suggested rather than proven conclusions.

In summary, after briefly reviewing the relevant Mayer expansion [7] for uniform pair-interacting classical fluids, we express the diagrammatic contributions in a form in which dimensionality enters as a parameter, and then carry out a tentative scaling to permit a stable representation as dimensionality increases. Restricting attention to repulsive interactions, we see that ring diagrams dominate at each order and that, if their sum converges, a single order dominates at a given density. Since ring contributions, e.g., to pressure, are negative at even orders greater than 2, convergence cannot hold beyond some characteristic density. To examine this point in detail, we restrict attention to a fluid of hard spheres and show that in fact there are two density regimes: low, for which the second virial coefficient dominates, and high, for

which the ring series diverges. We then sum the ring series explicitly and find that the second virial form extends far into the high density regime, eventually shifting to an infinite compressibility spinodal. A preliminary assessment of the new phase appearing beyond the spinodal is carried out, as well as an indication of how the next order in the high-dimensional expansion can be expected to contribute.

## II. VIRIAL EXPANSION

In order to study the effect of high spatial dimensionality in the simplest context, we will restrict our attention to a uniform isotropic simple classical fluid in volume  $V$ , with pair interaction  $\phi(r_{ij})$ ;  $r_{ij}$  is the  $D$ -dimensional interparticle vector, and only its magnitude enters into  $\phi$ . For such a system, we have the familiar Mayer diagrammatic expansion [7], prototypically that of the Helmholtz free energy

$$\beta F = \int (n \ln n - n) dr - \sum_{s=2}^{\infty} \frac{n^s}{s!} \sum_{G_s} \int \prod_{\alpha \in G_s} f_{\alpha} dr^s. \quad (2.1)$$

Here,  $\beta$  is the reciprocal temperature,  $n$  the particle density, and  $\alpha = (ij)$  denotes an unordered particle pair, with  $f_{ij} = f(r_{ij}) = e^{-\beta\phi(r_{ij})} - 1$  the interaction Mayer function. The  $G_s$  stand for distinguishable labeled graphs of Mayer functions connecting  $s$  vertices, with the restriction that at most one  $f_{ij}$  bond appears between  $i$  and  $j$ , and  $G_s$  is both connected and free of articulation vertices, those whose removal would destroy the simple connectivity. We are concerned with the thermodynamic limit, in which the system volume becomes infinite. In this limit, the intensive or per particle energies are defined; we will want to have available those related to specific free energy, chemical potential, compressibility factor, and inverse compressibility. With the notation  $dr^{s-1}$  meant to imply that  $r_s$  is fixed at the origin, these are

$$\beta f = \frac{1}{n} \frac{\beta F}{V} = \ln n - 1 - \sum_{s=2}^{\infty} \frac{n^{s-1}}{s!} \sum_{G_s} \int \prod_{\alpha \in G_s} f_{\alpha} dr^{s-1},$$

$$\beta\mu = \frac{\partial}{\partial n} (n\beta f) = \ln n - \sum_{s=2}^{\infty} \frac{n^{s-1}}{s-1!} \sum_{G_s} \int \prod_{\alpha \in G_s} f_{\alpha} dr^{s-1}, \quad (2.2)$$

$$\beta p/n = n \frac{\partial}{\partial n} \beta f = 1 - \sum_{s=2}^{\infty} \frac{s-1}{s!} n^{s-1} \sum_{G_s} \int \prod_{\alpha \in G_s} f_{\alpha} dr^{s-1},$$

$$\partial \beta p / \partial n = \frac{\partial}{\partial n} (n \beta p / n) = 1 - \sum_{s=2}^{\infty} \frac{n^{s-1}}{s-2!} \sum_{G_s} \int \prod_{\alpha \in G_s} f_{\alpha} dr^{s-1}.$$

For meaningful comparative results at arbitrarily high dimensionality, suitable scaling must be adopted, which, however, will depend upon our focus at the moment. To start with, we choose the following, emanating from two sources. First, we recall the readily verified observation [8] that, indicating dimensionality of the vector  $r^{(D)}$  by its parenthesized superscript and particle number designation by index,

$$\begin{aligned} & \int f(\cdots \mathbf{r}_i^{(D)} \cdot \mathbf{r}_j^{(D)} \cdots) dr_1^{(D)} \cdots dr_{s-1}^{(D)} \\ &= \prod_{j=1}^{s-1} \left( \frac{S_{D-s+1+j}}{S_j} \right) \int f(\cdots \mathbf{r}_i^{(s-1)} \cdot \mathbf{r}_j^{(s-1)} \cdots) \\ & \times |\det(r_1^{(s-1)}, \dots, r_{s-1}^{(s-1)})|^{D+1-s} dr_1^{(s-1)} \cdots dr_{s-1}^{(s-1)}, \end{aligned} \quad (2.3)$$

where  $S_D$  is the surface area of a  $D$ -dimensional unit sphere,  $V$  its volume:

$$\frac{1}{D} S_D = V_D = \pi^{D/2} / (D/2)!. \quad (2.4)$$

where

$$B_s = - \sum_{G_s} \int \operatorname{sgn} \left( \prod_{\alpha \in G_s} f_{\alpha} \right) \left( \prod_{\alpha \in G_s} \hat{f}_{\alpha} \right)^D |r_{1,1} \cdots r_{s-1,s-1}|^{D+1-s} dr_1 \cdots dr_{s-1} / a^{(s-1)D}. \quad (2.8)$$

Note that, again by Stirling's approximation,

$$n^{1/D} a = (D/2\pi e)^{1/2} \rho. \quad (2.9)$$

Hence for  $\rho$  of order 1, we are indeed dealing with a very high density [ $\rho$  is related to the more usual volume-normalized density by  $\eta = (\rho/2)^D$ ].

### III. CONVERGENCE OF THE VIRIAL SERIES

As an entree into the pathology of the expansion (2.8), let us specialize to the case in which all interactions are repulsive. Then  $f_{\alpha} \leq 0$ , and the second line of Eq. (2.8) simplifies to

If we then sequentially rotate  $r_j^{(s-1)}$ ,  $j=1,2,\dots,s-1$ , so that only the first  $j$  components of  $r_j^{(s-1)}$  are nonvanishing, this reduces further to

$$\begin{aligned} & \int f(\cdots \mathbf{r}_i^{(D)} \cdot \mathbf{r}_j^{(D)} \cdots) dr_1^{(D)} \cdots dr_{s-1}^{(D)} \\ &= \left( \prod_{j=1}^{s-1} S_{D+1-j} \right) \int f(\cdots \mathbf{r}_i \cdot \mathbf{r}_j \cdots) \\ & \times |r_{1,1} \cdots r_{s-1,s-1}|^{D+1-s} dr_1 \cdots dr_{s-1}, \\ & \text{where } r_{j,k} = 0 \text{ for } k > j. \end{aligned} \quad (2.5)$$

Second, we extend the  $D$ th power of the Jacobian determinant in Eq. (2.3) or Eq. (2.5) by giving the pair interaction an explicit  $D$  dependence, specified by

$$f_{\alpha} = (\hat{f}_{\alpha})^D \operatorname{sgn} f_{\alpha}, \quad \text{where } \hat{f}_{\alpha} \geq 0. \quad (2.6)$$

To complete the explicit parametrization in  $D$  at this stage of the development, we define the scaled density per dimension  $\rho$  by

$$n V_D a^D = \rho^D, \quad (2.7)$$

where  $a$  is the nominal range of interaction, e.g., for short-range forces, the maximum distance at which  $\hat{f}_{\alpha} = 0.1$ . Inserting Eq. (2.5) into Eq. (2.2) and reducing the factors  $\Pi_1^{s-1} (S_{D+1-j})$ ,  $V_D$  by Stirling's approximation:  $V_D = (2\pi e/D)^{D/2} / \sqrt{\pi D}$ ,  $\Pi_i^{s-1} S_{D+1-j} \sim [2e^D (d2\pi/D)^{D-1/2s}]^{1/2(s-1)}$ , we then have, e.g., the large  $D$  result

$$\frac{\partial \beta p}{\partial n} = 1 + \sum_{s=2}^{\infty} \frac{1}{s-2!} \rho^{(s-1)D} D^{(1/4)(s-1)(s+1)} / (2\pi)^{(1/4)(s-1)(s+2)} B_s,$$

$$B_s = \sum_{G_s} (-1)^{1+|G_s|} B(G_s),$$

$$\begin{aligned} \text{where } B(G_s) &= \int \left( \prod_{\alpha \in G_s} |f_{\alpha}| \right)^D |r_{1,1} \cdots r_{s-1,s-1}|^{D+1-s} \\ & \times dr_1 \cdots dr_{s-1} / a^{(s-1)D}. \end{aligned} \quad (3.1)$$

In particular,  $G_2$  and  $G_3$  have only single configurations, so  $|G_2| = |G_3| = 1$  and  $B_2 \geq 0$ ,  $B_3 \geq 0$  (in our notation,  $|G_3|$  is the number of pairs  $\alpha$  in  $G_s$ ). But the signs of  $B_4, B_5, \dots$  depend very much on the nature of  $|f|$  and the value of  $D$ . Typically,  $(\prod_{\alpha \in G_s} |f_{\alpha}|) |r_{1,1} \cdots r_{s-1,s-1}|$  will have a single maximum

$$M(G_2) = \max_{r_1, \dots, r_{s-1}} \left( \prod_{\alpha \in G_s} |f_\alpha| \right) |r_{1,1} \dots r_{s-1,s-1}| / a^{s-1}, \quad (3.2)$$

leading to an arbitrary sharp maximum of the integrand in Eq. (3.1) as  $D \rightarrow \infty$ . If the maximum is in the interior of the allowed domain, a steepest descent evaluation over the  $\binom{s}{2}$  variables  $r_{i,j}$  leads to the asymptotic form

$$B(G_s) = A_D(G_s) D^{-(1/2)\binom{s}{2}} M(G_s)^D, \quad (3.3)$$

where  $A_D(G_s)$  is slowly varying in  $D$ . But for hard particles, the maximum will be on the surface of the allowed region, replacing  $f < \binom{s}{2}$  Gaussian (second order) paths of descent by ones that are exponential (first order), attaching another factor of  $D^{-1/2}$  to Eq. (3.3) for each such relevant variable. Thus Eq. (3.3) is to be replaced by

$$B(G_s) = A_D(G_s) D^{-(1/2)\binom{s}{2}} D^{-(1/2)t} M(G_s)^D. \quad (3.4)$$

Since each additional  $f$  bond decreases Eq. (3.4) by a factor of  $D^{1/2}$  and does not increase  $M(B_s)$ , it is clear that the set of ring diagrams  $R_s$  dominates at each order  $s$ . In any event, incorporating the algebraic  $D$  dependence into a single factor  $\mathcal{A}_D(G_s)$ , Eq. (2.2), say for  $\beta p/n$ , now reads

$$\frac{\beta p}{n} = 1 + \sum_{s=2}^{\infty} \frac{s-1}{s!} \sum_{G_s} (-1)^{1+|G_s|} \mathcal{A}_D(G_s) [\rho^{s-1} M(G_s)]^D. \quad (3.5)$$

If the series (3.5) converges, its qualitative nature at high  $D$  is clear: the single term of maximum  $\rho^{s-1} M(G_s)$  will dominate, and as we have seen, this must be among the ring diagrams at each order  $s$ . Thus, retaining only the potentially dominant terms and observing that there are  $(1/2)(s-1)!$  possible labeled rings of order  $s > 2$ , Eq. (3.5) may be replaced by

$$\frac{\beta p}{n} = 1 + \mathcal{A}_D(12) [\rho M(12)]^D + \sum_{s=3}^{\infty} \frac{1}{2} (-1)^{s+1} \frac{s-1}{s} \mathcal{A}_D(R_s) \times [\rho^{s-1} M(R_s)]^D, \quad (3.6)$$

and hence by the asymptotic

$$(\beta p/n)^{1/D} = \max_s (1, \rho M(12), \{\rho^{s-1} M(R_s)\}). \quad (3.7)$$

But the integral of an open chain of  $|f|$  bonds can only be decreased by closing it, so that  $M(R_s) < M(12)^{s-1}$ . We therefore have, subject to convergence, the general result

$$\begin{aligned} |\beta p/n|^{1/D} &= 1 \quad \text{for } \rho < 1/M(12) \\ &= \rho M(12) \quad \text{for } 1/M(12) < \rho < \min_s \left( \frac{M(12)}{M(R_s)} \right)^{1/(s-2)} \\ &\quad \text{with } s = s_1 \text{ as minimizing value} \\ &= \rho^{s_1-1} M(R_{s_1}) \quad \text{for } \left( \frac{M(12)}{M(R_{s_1})} \right)^{1/(s_1-2)} < \rho < \min_s \left( \frac{M(R_s)}{M(R_s)} \right)^{1/(s-s_1)} \\ &\quad \text{with } s = s_2 \text{ as minimizing value,} \\ &\quad \dots, \end{aligned} \quad (3.8)$$

a sequence of analytic breaks in the equation of state. We must examine this point in greater detail.

#### IV. HARD SPHERE FLUID

Let us concentrate on the case of a fluid of hard spheres of diameter  $a$ , which is thereby the interaction range. Here  $\hat{f}(r, r') = \theta(a - |r - r'|)$ , and according to Eq. (2.8),  $M(R_s)/(s-1)!$  is  $1/a^{s-1}$  times the maximum  $s-1$  space volume of an  $s$ -link ring with links of length  $a$ , i.e., the maximum with unit links. One readily finds

$$\begin{aligned} M(12) &= 1, \quad M(R_3) = (\frac{3}{4})^{1/2} = 0.8660, \\ M(R_4) &= 4/(27)^{1/2} = 0.7698, \\ M(R_5) &= (5)^{3/2}/16 = 0.6988, \end{aligned} \quad (4.1)$$

$$M(R_6) = 36/(5)^{3/2} = 0.6440$$

and so, using only this information, Eq. (3.8) would tell us that

$$|\beta p/n|^{1/D} = \begin{cases} 1 & \text{for } \rho < 1 \\ \rho & \text{for } 1 < \rho < 1.1163 \quad (\text{at } s_1 = 6) \\ 0.6440\rho^5 & \text{for } \rho > 1.1163, \dots \end{cases} \quad (4.2)$$

But the sign of the  $R_6$  term is negative, so the third line of Eq. (4.2) would correspond to negative pressure; in fact, if Eq. (4.1) were terminated at  $R_5$ , one would have  $s_1 = 5$  at  $\rho = 1.1264$  and a positive pressure, if at  $R_4$ ,  $s_1 = 4$  at  $\rho = 1.1398$  and a negative pressure, etc. Hence we expect that we will find either that  $s_1$  is an odd integer or that  $s_1 \rightarrow \infty$ , the signature of a nonconvergent series.

In order to check whether there is indeed a finite value for the crossover index  $s_1$ , we would want to extend our evaluation past that of  $B(R_6)$ . But the geometry of maximal volume rings in  $s-1$  space is daunting, and a more direct Fourier evaluation is suggested. Now for an  $s$ -link ring,

$$\begin{aligned} & \left( \prod_1^{s-1} S_{D+1-j} \right) B(R_s) \\ &= \int \theta(1-r_1) \theta(1-r_{12}) \cdots \theta(1-r_{s-2,s-1}) \theta(1-r_{s-1}) \\ & \quad \times dr_1^{(D)} \cdots dr_{s-1}^{(D)} = (2\pi)^{-D} \int \tilde{\theta}(k)^s dk^{(D)}, \end{aligned} \quad (4.3)$$

where

$$\begin{aligned} \tilde{\theta}(k) &= \int_{|r| \leq 1} e^{ikr} dr^{(D)} = \int_{|r| \leq 1} e^{ikr \cos \theta} dr^{(D)} \\ &= (2\pi/k)^{D/2} J_{D/2}(k). \end{aligned} \quad (4.4)$$

For assessing the series, we then evaluate

$$\begin{aligned} B(R_s) &= \left( S_D^{1/D} / \prod_1^{s-1} S_{D+1-j}^{1/D} \right) \\ & \quad \times (2\pi)^{(1/2)s-1} \left( \int J_{D/2}(k)^s dk^{(D)} / k^{sD/2} S_D \right)^{1/D} \\ &= (D/e)^{s/2-1} \left( \int J_{D/2}(k)^s k^{D-1-sD/2} dk \right)^{1/D} \end{aligned} \quad (4.5)$$

for large  $D$ , so that, knowing that the integral is positive,

$$\begin{aligned} M(R_s) &= B(R_s)^{1/D} \\ &= (D/e)^{s/2-1} [\max_k J_{D/2}(k)^2 k^{-(1/2)(s-2)D}]^{1/D}. \end{aligned} \quad (4.6)$$

The maximum in Eq. (4.6) will occur somewhere before the transition to oscillation of  $J_{D/2}$ . But in this region, we have the familiar asymptotic result [9] (large  $\nu$  at fixed  $\alpha$ )

$$J_\nu(\nu \operatorname{sech} \alpha) \sim e^{\nu(\tanh \alpha - 2)} / (2\pi \nu \tanh \alpha)^{1/2}. \quad (4.7)$$

Choosing  $\nu = D/2$ ,  $k = D/2 \operatorname{sech} \alpha$ , then

$$\begin{aligned} M(R_s) &= (D/e)^{s/2-1} \max_\alpha e^{(3/2)(\tanh \alpha - \alpha)} \cosh \alpha^{(1/2)(s-2)} \\ & \quad \times (D/2)^{-(1/2)(s-2)} \\ &= (2/e)^{(1/2)(s-2)} \max_\alpha (e^{s(\tanh \alpha - \alpha)} \cosh \alpha^{s-2})^{1/2}. \end{aligned} \quad (4.8)$$

The maximum is achieved at  $e^{2\alpha} = s-1$ , and so we find

$$M(R_s) = [s^{s-2}/(s-1)^{s-1}]^{1/2}. \quad (4.9)$$

Arguing as we did after Eq. (3.7), the crossover for  $\rho < 1$  will occur at a value of  $\rho$  given by the minimum over  $s$  of  $[(s-1)^{s-1}/s^{s-2}]^{1/2(s-1)} \sim \exp(1/2s)(\ln s-1)$ . Hence, as soon as  $\rho > 1$  then dominant terms move to  $s = \infty$ , so indeed the series ceases to converge.

The fact that an alternating series does not converge says little about the function it is supposed to represent. If we can sum up the series of dominant ring terms, we will instead obtain the analytic continuation that constitutes the true leading order for  $\rho > 1$ . This is not hard to do.

## V. EFFECT OF RESUMMATION

Let us proceed directly from the original expression (2.2), now restricted to ring diagrams  $R_s$ , of which there are 1 for  $s=2$ ,  $\frac{1}{2}(s-1)!$  for  $s > 2$ . This of course coincides with the primitive resummation of Montroll and Mayer [10], without the renormalization introduced by Green [11]. Focusing upon the expression for the chemical potential  $\mu$  this time, we have, since  $\int f dr^D = -V_D a^D$ ,

$$\beta\mu = \ln n + \rho^D - \frac{1}{2} \sum_{s=3}^{\infty} n^{s-1} f^{(s)*}(0), \quad (5.1)$$

where  $f^{(s)*}$  denotes the iterated convolution of  $s$  factors  $f$ . Noting that  $f^{(2)*}(0) = V_D a^D$  as well, we therefore have

$$\begin{aligned} \beta\mu &= \ln n + \frac{3}{2} \rho^D - \frac{1}{2} \frac{1}{(2\pi)^D} \int n \tilde{f}(k)^2 / [1 - n \tilde{f}(k)] dk^D \\ &= \ln n + \frac{3}{2} \rho^D - \frac{1}{2} \frac{S_D}{(2\pi)^D} \int_0^\infty \frac{n \tilde{f}(k)^2}{1 - n \tilde{f}(k)} k^{D-1} dk. \end{aligned} \quad (5.2)$$

But  $\tilde{f}(k) = -\tilde{\theta}(ka) a^D = -(2\pi a/k)^{D/2} J_{D/2}(ka)$ , so that Eq. (5.2) becomes

$$\beta\mu = \ln n + \frac{3}{2} \rho^D - \frac{D}{2} \rho^D \int_0^\infty \frac{J_{D/2}(k)^2}{1 + (\rho^D/V_D)(2\pi/k) J_{D/2}(k)} \frac{dk}{k}. \quad (5.3)$$

We are interested in the domain  $\rho > 1$ . We note first that  $(2\pi)^{D/2}(\rho^D/V_D)k^{-D/2}J_{D/2}(k)$  has its maximum of  $\rho^D$  at  $k=0$ , so that, as expected, the reciprocal cannot be expanded in  $\rho$  when  $\rho > 1$ . However, we also note that  $(2\pi)^{D/2}/V_D k^{-D/2} J_{D/2}(k)$  has its (negative) absolute minimum at  $k_0 J'_{D/2}(k_0) = (D/2) J_{D/2}(k_0)$ , or  $J_{D/2+1}(k_0) = 0$ , yielding asymptotically  $k_0 = D/2 + z_0(D/2)^{1/3} + 1 + O(1/D)$ , with  $z_0 = 1.8558$ , and that the minimum is then given by  $-m_D$ , where

$$m_D = 1.148(2/e)^{D/2} D^{-1/6} e^{-1.473D^{1/3}}. \quad (5.4)$$

This tells us not to expect any singular behavior until  $\rho^D m_D \sim 1$  or  $\rho \sim \rho_0$  where

$$\rho_0 = m_d^{-1/d} \sim \left( \frac{e}{2} \right)^{1/2}. \quad (5.5)$$

To find the behavior of Eq. (5.3) in detail, we need control over high index Bessel functions, and the uniform leading asymptotic forms [12] (Ai is the Airy function)

$$J_\nu(v \operatorname{sech} \alpha) = \left( \frac{12}{v^2} \frac{\alpha - \tanh \alpha}{\tanh^3 \alpha} \right)^{1/6} \operatorname{Ai} \left( \left[ \frac{3v}{2} (\alpha - \tanh \alpha) \right]^{2/3} \right),$$

$$J_v(v \sec \alpha) = \left( \frac{12}{v^2} \frac{\tan \alpha - \alpha}{\tan^3 \alpha} \right)^{1/6} \text{Ai} \left( - \left[ \frac{3v}{2} (\tan \alpha - \alpha) \right]^{2/3} \right) \quad (5.6)$$

certainly suffice. For most purposes, the reductions to low argument, transition region, and large argument,

$$J_v(v \operatorname{sech} \alpha) \sim e^{v(\tanh \alpha - \alpha)/(2\pi v \tanh \alpha)^{1/2}}, \quad (5.7a)$$

$$J_v(v+z v^{1/3}) \sim (2/v)^{1/3} \text{Ai}(-2^{1/3}z), \quad (5.7b)$$

$$J_v(v \operatorname{sech} \alpha) \sim 2 \cos \left( v(\tan \alpha - \alpha) - \frac{\pi}{4} \right) / (2\pi \tan \alpha)^{1/2}, \quad (5.7c)$$

are good enough.

To start, one has, using Eq. (5.7a)—identical with Eq. (4.7)—

$$\begin{aligned} I_- &= \frac{D}{2} \int_0^{D/2} \frac{J_{D/2}(k)^2}{1 + (\rho^D/V_D)(2\pi/k)^{D/2} J_{D/2}(k)} \frac{dk}{k} \\ &< \frac{D}{2} \int_0^{D/2} J_{D/2}(k)^2 dk/k \\ &\sim \frac{1}{2\pi} \int_0^\infty e^{D(\alpha - \tanh \alpha)} d\alpha = O(D^{-1/3}), \end{aligned} \quad (5.8)$$

so that  $I_-$  can be dropped. To continue, we need

$$\begin{aligned} I_+ &= \frac{D}{2} \int_{D/2}^\infty \frac{J_{D/2}(k)^2}{1 + (\rho^D/V_D)(2\pi/k)^{D/2} J_{D/2}(k)} \frac{dk}{k} \\ &= \frac{D}{2} \int_{D/2}^\infty J_{D/2}(k)^2 dk/k \\ &\quad - \frac{D}{2} \frac{\rho^D}{V_D} (2\pi)^{D/2} \int_{D/2}^\infty \frac{J_{D/2}(k)^3}{1 + (\rho^D/V_D)(2\pi/k)^{D/2} J_{D/2}(k)} \\ &\quad \times \frac{dk}{k^{1+D/2}}. \end{aligned} \quad (5.9)$$

But, using Eq. (5.7c),

$$\begin{aligned} I_0 &= \frac{D}{2} \int_{D/2}^\infty J_{D/2}(k)^2 dk/k \\ &\sim \frac{2}{\pi} \int_0^{\pi/2} \cos^2 \left( \frac{D}{2} (\tan \alpha - \alpha) - \frac{\pi}{4} \right) d\alpha \\ &= \frac{1}{\pi} \int_0^{\pi/2} [1 + \sin D(\tan \alpha - \alpha)] d\alpha \\ &= \frac{1}{2} + O(D^{-1/3}). \end{aligned} \quad (5.10)$$

Hence, to  $O(D^{-1/3}\rho^D)$ ,

$$\begin{aligned} \beta \mu &= \ln n + \rho^D + \rho^D I \\ \text{where } I &= \frac{D}{2} \frac{(2\pi)^{D/2}}{V_D} \rho^D \\ &\times \int_{D/2}^\infty \frac{J_{D/2}(k)^3}{1 + (\rho^D/V_D)(2\pi/k)^{D/2} J_{D/2}(k)} \frac{dk}{k^{1+D/2}}. \end{aligned} \quad (5.11)$$

Clearly,

$$\begin{aligned} |I| &\leq [(2\pi)^{D/2}/V_D]/(1 - m_D \rho^D) \int_{D/2}^\infty |J_{D/2}(k)|^3 dk^{D/2} \\ &\leq (4\pi/D)^{D/2} \frac{\rho^D}{V_D} \max |J_{D/2}(k)|^3 / (1 - m_D \rho^D), \end{aligned}$$

but from the second of Eqs. (5.6), together with  $|\text{Ai}(-x)| < (\frac{1}{4})^{1/3}$  for  $x > 0$ , we see that  $J_v(v \operatorname{sech} \alpha) < (1/2v)^{1/3}$ . Hence, evaluating  $V_D$  in Stirling approximation, we find

$$|I| \leq \sqrt{\pi/D} 0.871 D^{1/6} e^{1.473 D^{1/3}} (\rho/\rho_0)^D \left/ \left[ 1 - \left( \frac{\rho}{\rho_0} \right)^D \right] \right. \quad (5.12)$$

In other words, the second virial truncation of Eq. (5.11) remains valid for  $1 < \rho < (1 - \epsilon)(e/2)^{1/2}$ , an enormously enhanced range of density.

## VI. INCEPTION OF PHASE TRANSITION

Finally, we must attend to the behavior of the hard sphere fluid as  $\rho$  approaches  $\rho_0$ . As we have seen, it is only when  $\rho_0 - \rho = O(1/D)$  that a deviation from the second virial result can appear. To evaluate  $I$  of Eq. (5.11), let us first reverse the procedure from Eq. (5.9) to Eq. (5.11) and write

$$\begin{aligned} I &= \frac{-D}{2} \int_{D/2}^\infty J_{D/2}(k)^2 \left\{ \left[ 1 + \frac{\rho^D}{V_D} \left( \frac{2\pi}{k} \right)^{D/2} \right. \right. \\ &\quad \times J_{D/2}(k) \left. \right]^{-1} - 1 \left. \right\} dk/k. \end{aligned} \quad (6.1)$$

Then, set  $k = (D/2) \sec \alpha$ , so that Eq. (5.7c) can be used:

$$\begin{aligned} I &= -\frac{2}{\pi} \int_0^{\pi/2} d\alpha \cos^2 \left( \frac{D}{2} (\tan \alpha - \alpha) - \frac{\pi}{4} \right) \\ &\quad \times \left\{ \left[ 1 + \frac{2}{\sqrt{\pi D}} \frac{\rho^D}{V_D} \left( \frac{4\pi}{D} \cos \alpha \right)^{-D/2} \cot^{1/2} \alpha \right. \right. \\ &\quad \times \cos \left( \frac{D}{2} (\tan \alpha - \alpha) - \frac{\pi}{4} \right) \left. \right]^{-1} - 1 \left. \right\}. \end{aligned} \quad (6.2)$$

Since  $\cos[(D/2)(\tan \alpha - \alpha) - \pi/4] \sim \cos[(D/6)\alpha^3 - \pi/4]$  first goes negative when  $\alpha^3 > 9\pi/2D$ , this produces a small concentrated negative maximum due to the rapid falloff of

$\cos^{D/2} \alpha \sim \exp -(D/4) \alpha^2$ , and the next maximum has a negligible contribution for the same reason. The only contribution to  $I$  comes from the  $\alpha \sim D^{-1/3}$  region, and so we can rewrite Eq. (6.2) as

$$I = \frac{-2}{\pi} \int_0^{\pi/2} \cos^2 \left( \frac{D}{6} \alpha^3 - \frac{\pi}{4} \right) \left\{ \left[ 1 + \frac{2}{\alpha^{1/2}} \left( \frac{2}{e} \right)^{D/2} \times \rho^D e^{-(D/4)\alpha^2} \cos \left( \frac{D}{6} \alpha^3 - \frac{\pi}{4} \right) \right]^{-1} - 1 \right\} d\alpha. \quad (6.3)$$

The region around  $D^{-1/3}$  only contributes when the denominator is very small. Expanding,  $\alpha = \alpha_0 + \epsilon$ , about  $\alpha_0 = (9\pi/2D)^{1/3}$  we can write

$$I = \frac{-2}{\pi} \int \left( \frac{D}{2} \alpha_0^2 \right)^2 \times \epsilon^2 \left\{ \left[ 1 - D \alpha_0^{3/2} \left( \frac{2}{e} \right)^{D/2} \times \rho^D e^{-(D/4)\alpha_0^2} \epsilon e^{(D/2)\alpha_0\epsilon} \right]^{-1} - 1 \right\} d\epsilon, \quad (6.4)$$

and further expanding,  $\epsilon = \epsilon_0 + \eta$ , about  $\epsilon_0 = 2/D\alpha_0$ ,

$$I = \frac{-2\alpha_0^2}{\pi} \int \left\{ \left[ 1 - \left( \frac{\rho}{\rho'_0} \right)^D e^{-(1/8)D^2\alpha_0^2\eta^2} \right]^{-1} - 1 \right\} d\eta$$

$$\text{where } \alpha_0 = (9\pi/2D)^{1/3}, \quad (\rho'_0)^D = \left( \frac{e}{2} \right)^{D/2} \frac{e}{2\alpha_0^{1/2}} e^{-(D/4)\alpha_0^2}. \quad (6.5)$$

Thus,  $I = (4\sqrt{2}\alpha_0/\pi D)(\rho/\rho'_0)^D \int_0^\infty x^{-1/2} dx / [e^x - (\rho/\rho'_0)^D]$ , integrating for  $\rho/\rho'_0 \sim 1$  to

$$I \sim -(4\sqrt{2}\alpha_0/D)(\rho/\rho'_0)^D / [1 - (\rho/\rho'_0)^D]^{1/2}, \quad (6.6)$$

which supplies the evaluation of Eq. (5.11). The parameter  $\rho'_0$  is of course an approximation to  $\rho_0$  of Eqs. (5.4) and (5.5).

The result (5.11), (6.6) is striking. Despite the (oscillatory) divergence of the density expansion, the second virial truncation remains valid until  $\rho$  is very close to  $\rho_0$ . This is of course not restricted to hard core repulsive interactions. The crucial point is that although the series expansion of  $1/[(1 - n\tilde{f}(k))]$  in Eq. (5.2) for repulsive forces diverges as soon as  $n > 1/|\tilde{f}(0)| = 1/\int (1 - e^{-\beta\phi(r)}) dr$ , the resulting contribution in excess of the second virial becomes very small due to the smallness of  $\tilde{f}(k)^2$  over the rest of  $k$  space, until  $n$  approaches  $\min[1/\tilde{f}(k)]$ , at which point a branch point typically occurs. The resulting singularity, signaling a phase transition, was previously suggested, on the basis of stability arguments, by indirect means some years ago, but now we have a direct explicit verification.

Past the first spinodal, care must be exercised. One may ignore the infinite negative value of  $I$  at  $\rho = \rho_0$  as occurring in the inaccessible van der Waals loop region, regularize the subsequent two-point vanishing of the denominator of Eq.

(5.11) by performing a principal part integration, and then continue to the second spinodal. Or, it is certainly possible, but not trivial, to sum the next order,  $D^{-1/2}$  lower in magnitude, of diagrams with a single path across a ring, and indeed it appears that this would reverse the sign of the ultimate pressure singularity, producing a van der Waals loop in the process. This may be justified as an effective analytic continuation in density but is not fully satisfactory since it could not change the location of the infinite pressure singularity, which in reality should not occur until close packing. An alternative systematic approach addressing this issue would "simply" resum the dominant terms contributing to the divergence at  $\rho = \rho_0$ , and we plan to report on this strategy in future.

## VII. CONCLUDING REMARKS

We have investigated the Mayer expansion mainly for uniform pair-interacting repulsive interactions subject to a dimensionality-dependent scaling. As the dimensionality becomes large, we have established (if not proven) at least for repulsive interactions that ring diagrams dominate at each order. If their sum converges, a single order dominates at each density. Since even ring contributions, of order greater than 2, to the pressure are negative, there must be a density beyond which the sum can no longer converge.

To investigate this behavior in greater detail, we have restricted ourselves to a fluid of hard spheres, for which explicit calculations are easier. One finds here that the equation of state reduces asymptotically to two regimes. At low density, the ideal gas equation of state is augmented by the dominating second virial coefficient. At higher densities, the ring series diverges, but one can sum the series explicitly and evaluate it by steepest descent. The second virial form of the equation of state then extends significantly far into the high density region, until an infinite compressibility spinodal is found.

The next contribution, ring diagrams with one cross-path, is of opposite sign and suggests an upturning in the plot of reduced pressure versus scaled density reminiscent of a true first order transition to the high-dimensional solid. While we have not carried out the considerable labor to evaluate this next contribution explicitly for large but finite  $D$ , our calculations suggest that at a density less than that of the Kirkwood transition (see, e.g., Ref. [4]), a first order transition intervenes. Only in the limit as  $D \rightarrow \infty$  does the continuous Kirkwood transition dominate. An interesting special case for investigation is the Gaussian potential fluid for large  $D$ , which has already been investigated to some extent by Stillinger [13].

The scaling introduced in Eqs. (2.1)–(2.4) should also allow us to obtain similar asymptotic results for attractive potentials. In any case, it is of interest to speculate that for large but finite  $D$ , there are, universally, first order transitions of uniform classical fluids.

## ACKNOWLEDGMENTS

This work was supported in part by NSF Grant Nos. DMR 962 8224 and CHE 970 8562, and the Donors of the Petroleum Fund of the American Chemical Society.

- [1] A. A. Maradudin, E. W. Montroll, and G. H. Weiss, *Theory of Lattice Dynamics* (Academic, New York, 1963).
- [2] E. E. Salpeter, Ann. Phys. (N.Y.) **5**, 183 (1958).
- [3] H. L. Frisch, N. Rivier, and D. Wyler, Phys. Rev. Lett. **54**, 2061 (1985).
- [4] H. L. Frisch and J. K. Percus, Phys. Rev. A **35**, 4696 (1987).
- [5] H.-O. Carmesin, H. L. Frisch, and J. K. Percus, Phys. Rev. B **40**, 9416 (1989).
- [6] H.-O. Carmesin, H. L. Frisch, and J. K. Percus, J. Stat. Phys. **63**, 791 (1991).
- [7] J. Mayer, J. Chem. Phys. **5**, 67 (1937).
- [8] J. K. Percus, Commun. Pure Appl. Math. **XI**, 449 (1987).
- [9] See, e.g., W. Magnus and F. O. Oberhettinger, *Functions of Mathematical Physics* (Chelsea, New York, 1954), p. 23.
- [10] E. W. Montroll and J. E. Mayer, J. Chem. Phys. **9**, 626 (1941).
- [11] H. S. Green, *Molecular Theory of Fluids* (North-Holland, Amsterdam, 1952).
- [12] See, e.g., *Handbook of Mathematical Functions*, edited by M. A. Abramowitz and I. A. Stegun (Dover, New York, 1965), Chap. 9.
- [13] F. H. Stillinger, J. Chem. Phys. **70**, 4067 (1979).