Thermodynamic Properties of Small Systems*

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We investigate the dependence of the pressure of a homogeneous system, at a given density ρ and temperature T, on the number of particles N. The particles of the system are assumed to interact via forces of finite range a and are confined to a periodic cube of volume L^3, $\rho\equiv N/L^3$. We find that there are generally two types of N dependencies in the pressure and other intensive properties of the system. There is a simple dependence which goes essentially as a power series in $(1/N)$ and may be computed explicitly in terms of the grand-ensemble averages of these properties where it is absent. The other, more complex, dependence comes from the volume dependence of those cluster integrals which are large enough to wind at least once around the periodic torus. These do not appear in a virial expansion for terms $k\leq(N/\rho a^3)^{\frac{1}{3}}$. They play however a dominant role in the N dependence observed by Alder and Wainwright in their machine computations on a hard-sphere gas. While the explicit calculation of these terms is very difficult and has been carried through only in a few special cases, they may be related, approximately at least, to the radial distribution function in an infinite system. We also find an expression for the correlation between the particles of an ideal gas represented by a microcanonical ensemble.

1. INTRODUCTION

THE purpose of this paper is to consider some properties of systems with a small number of particles. More specifically, we are interested in the dependence of the pressure on the number of particles N in a periodic box of volume $L^3=N/\rho$ for a given density ρ. For a system of macroscopic size, the dependence on N of the intensive variables and distribution functions is of interest only in very special cases which we have investigated previously.[1] The recent machine calculations of Alder and Wainwright and Wood[2] of the pressure of a collection of hard spheres, at various densities, varying in number between 4 and 500 do however supply "experimental" results for a system of small N. The results do not seem to yield any simple pattern for the dependence of the pressure on N and seem to be unrelated to the N dependence of the first two virial coefficients given explicitly by Mazur and Oppenheim.[3]

Our interest in this problem arose from the fact that we had recently derived a simple expression for the coefficient of the $1/N$ term of the low-order distribution functions in the asymptotic region (large separation between groups of particles). One method of proof we used indicated that for a system with periodic boundary conditions our result should give the N dependence of the whole radial distribution function and of the thermodynamic quantities whenever the virial expansion converges. The expression we obtained for the dependence of the pressure on N was indeed in agreement, when expanded in powers of the density, with that of Mazur and Oppenheim, but in complete disagreement with the published results of Alder and Wainwright, for the medium to high density region. This led us to investigate the problem more carefully.

We discovered that the discrepancy arises from the existence of two types of N dependence, one of which does not appear at all in the virial expansion at large N, but is important in the range considered by Alder and Wainwright. The explicit calculations necessary for comparison with their result, which would also indicate the general reliability of their method, turned out to be too complicated however and were carried through only in the relatively low-density region. We found further that there is a relationship between the cluster integrals involved in these volume corrections and the coefficients of the density expansion in the radial distribution function $g(r)$ in an infinite system.

The general formulation of the problem is given in Sec. 2, where we express the pressure $p(N,V)=p(N,\rho,\{b'\})$ as the ratio of two polynomials in ρ, of order N. The coefficients of ρ^k are given explicitly as polynomials in N with coefficients which are themselves functions of the cluster integrals b_l', $l\leq k+1$. For a periodic rectangular box, b_l' will have an implicit dependence on V for $l>L/a$, a being the range of the intermolecular forces. and L the length of the smallest side. For a given V this is largest for a cube $L^3=V$, which is the only shape we shall consider explicitly since the extension to other shapes is obvious. Alder and Wainwright use rectangular boxes for 8 and 16 molecules, and thus the volume dependence of the b_l' begins at the same density for these N as for $N=4$.

In Sec. 3, we expand $p(N,\rho,\{b'\})$ as a power series in ρ and show that the coefficient of ρ^k is a polynomial of order $k-1$ in $1/N$. The coefficient of $(1/N)^j$ is a function of the b_l', $l\leq k$, and also depends implicitly on

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[1] J. L. Lebowitz and J. K. Percus, Phys. Rev. **122**, 1675 (1961).
[2] B. J. Alder and T. E. Wainwright, J. Chem. Phys. **33**, 1439 (1960). W. W. Wood, R. R. Parker, and J. D. Jacobson, Nuovo cimento **9**, 133S (1958).
[3] I. Oppenheim and P. Mazur, Physica **23**, 197 (1957).

N for $k>N$. Considering only the low virial coefficients (i.e., the volume-independent ones) Oppenheim and Mazur had found a recurrence relation for these coefficients α_k^j (as well as for the $1/N$ terms in the distribution functions) in terms of α_k^0 which was shown to equal the usual volume-independent virial coefficient of Mayer's theory. As indicated before, this is true only for $k\leq L/a=(N/\rho a^3)^{\frac{1}{3}}$, which for small N is very small; thus for $N=8$ and $\rho a^3=\frac{1}{2}$ it holds only for the first two virial coefficients. It is however still true that α_k^0, the value of the N-independent coefficient of ρ^k is the same as that of $\bar{\rho}^k$ in the expansion of $\bar{p}$, where $\bar{p}$ is the average value of the pressure for a system of average density $\bar{\rho}$ in a volume V represented by a grand canonical ensemble. The values of α_k^0 for $k>N$ are also given.

We then present an alternative, more direct, proof of the above result and also find explicit expressions for the $1/N$ dependence of the pressure $p(N,\rho,\{b'\})$ in terms of $\bar{p}(\rho,\{b'\})$. This yields the corrections to p as a power series in $1/N$, the first term of which is $p(N,\rho,\{b'\})=\bar{p}(\rho,\{b'\})-(\rho^2/2N)d\ln(d\bar{p}/d\rho)/d\rho$. This expansion is correct for all virial coefficients up to $k=N$, while for $k>N$ there are other corrections due to the essentially discrete nature of N. The extra correction terms are of lower order in $1/N$, so that the $1/N$ term should also hold for dense systems.

We see from the above that the complete N dependence of the pressure consists of two parts: the explicit terms in $1/N$ and the implicit volume (N) dependence of $\bar{p}$ through the b_l'. The explicit $1/N$ dependence would always lead to an increase in p with N for a hard-sphere gas. As indicated earlier, however, the implicit volume (N) dependence of $\bar{p}$ enters very early in the virial expansion when N is small: $k\geq(N\rho a^3)^{\frac{1}{3}}$. It is the nature and initial form of this dependence (which appears the dominant one in the Alder-Wainwright results) which we consider in Secs. 4 and 5.

2. GENERAL EXPRESSION FOR THE CANONICAL PRESSURE

We consider a system of N particles, interacting via two-particle forces, in a periodic cube of volume $V=L^3$. The pressure of this system at a given temperature T will be obtained from the canonical ensemble. For a hard-sphere gas, the potential energy over the allowed configuration space vanishes and the canonical pressure should conicide (assuming ergodicity in configuration space) with the virial pressure of a single system of total energy $3NkT/2$. It is the latter pressure which is computed by Alder and Wainwright.

The partition function of a general system of the above type may be written as[4]

$$Z=\frac{V^N}{N!}\left(\frac{2\pi m}{\beta h^2}\right)^{3N/2}Z_c, \tag{2.1}$$

$$Z_c=\sum_{k=0}^{N-1}A_k\rho^k,\quad (\rho=N/V) \tag{2.2}$$

$$A_k=\sum_{\{m_l\}}\left\{[N!/(N-k-\sum_{l=2}^{\infty}m_l)!]\frac{1}{N^k}\prod_{l=2}^{\infty}\frac{(b_l')^{m_l}}{m_l!}\right\}, \tag{2.3}$$

where the $\{m_l\}$ satisfy

$$\sum_{l=2}^{\infty}(l-1)m_l=k,$$

and

$$b_l'=\frac{1}{l!V}\int\cdots\int\sum_{\text{connected}}\prod_{i<j\epsilon 1,\cdots l}(e^{-\beta\phi(r_{ij})}-1)dt_1\cdots dt_l. \tag{2.4}$$

$\beta=1/kT$ enters as a constant parameter throughout, and we shall henceforth set it equal to unity. Since ratios of factorials can be expanded in terms of the Stirling numbers of the first kind,[5]

$$x(x-1)\cdots(x-s+1)=\sum_{j=1}^{s}S_s^jx^j, \tag{2.5}$$

(2.3) may be further developed in a Laurent series in N. We have

$$Z_c=\sum_{k=0}^{N-1}\rho^kN^kC_k\{N,\{b'\}\}, \tag{2.6}$$

$$C_k(N,\{b'\})=\sum_{j=0}^{2k-1}C_k^j\{b'\}\left(\frac{1}{N}\right)^j, \tag{2.7}$$

$$C_k^j\{b'\}=\sum S_\nu^{2k-j}\prod_{l=2}^{\infty}\frac{(b_l')^{m_l}}{m_l!}, \tag{2.8}$$

where $\nu=k-\sum_2^\infty m_l$ and the range of $\{m_l\}$ is the same as that given in Eq. (2.3).

The $C_k^j\{b'\}$ of (2.7) are seen to be polynomials in the connected cluster integrals b_l' for $l\leq k+1$. In a periodic system, the b_l' will be independent of the container volume $V=L^3$ whenever $l\leq L/a$, or

$$l\leq(N/\rho a^3)^{\frac{1}{3}}, \tag{2.9}$$

where a is the range of the interatomic potential, assumed finite. (The volume-independent cluster integrals will be denoted by b_l.) Thus, from (2.1) and (2.6), the pressure $p=\partial\ln Z/\partial V$ becomes

$$p(N,V)=\rho-[1+\sum_{k=1}^{N-1}N^kC_k(N,\{b'\})\rho^k]^{-1}\times\sum_{k=1}^{N-1}N^{k-1}[kC_k(N,\{b'\})-\dot{C}_k(N,\{b'\})]\rho^{k+1}, \tag{2.10}$$

[4] T. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956).

[5] C. Jordan, *Calculus of Finite Differences* (Chelsea Publishing Company, New York, 1947), p. 142.

where

$$\dot{C}_k(N,\{b'\})=V\frac{\partial}{\partial V}C_k(N,\{b'\}) \quad [=0 \quad \text{for} \quad k\leq(N/\rho a^3)^{\frac{1}{3}}]. \quad (2.11)$$

In particular, for $N<(N/\rho a^3)^{\frac{1}{3}}$, or $V>(Na)^3$, the only dependence of $p(N,V)$ on V is in the explicit form of the ratio of two polynomials in $\rho=N/V$. Hence for a given N, there will always be some volume $V(N)$ such that for $V>V(N)$, $p(N,V)$ is an analytic function of $1/V$ and may therefore be expanded in a Taylor series in ρ for some range of ρ. For a two-dimensional system, the condition is $V>(Na)^2$, and in one dimension $V>Na$. For a hard-sphere system, the condition is always satisfied in one dimension.

3. VIRIAL EXPANSION

Suppose then that $V>V(N)$, so that $b_l'=b_l$. The second term of (2.10) drops out, and we may write

$$p(N,V)=\sum_{k=1}^{\infty}\alpha_k(N,b)\rho^k, \qquad V>V(N) \quad (3.1)$$

$$\ln Z_c=N\sum_{k=1}^{\infty}\frac{1}{k}\alpha_{k+1}\rho^k,$$

where

$$\alpha_k(N,\{b\})=\begin{cases}\sum_{j=0}^{k-1}\alpha_k{}^j(b_2,\cdots,b_k)\left(\frac{1}{N}\right)^j, & k\leq N\\ \sum_{j=0}^{k-1}\alpha_k{}^j(N,b_2,\cdots,b_N)\left(\frac{1}{N}\right)^j, & k>N.\end{cases} \quad (3.2)$$

Here $\alpha_k{}^j(N,\{b\})$ is gotten from $\alpha_k{}^j\{b\}$ by setting all b_l equal to zero for $l>N$. The limit $j=k-1$ in (3.2) stems from the fact that the coefficient of V^{-k} in (2.2) is a polynomial in N with constant term missing; the coefficient of V^{-k} in $p=(\partial Z/\partial V)/Z$ of (3.1) must also have this property. The limit $j=0$, as opposed to $j<0$, is implied by the requirement that the virial coefficients remain finite as $N\rightarrow\infty$. This can also be established directly. We can extend (3.1) and (3.2) to arbitrary volume V. When V is not necessarily greater than $V(N)$, we have generally

$$p(N,V)=\rho+\sum_{k=2}^{\infty}\left[\alpha_k(N,\{b'\})-\frac{1}{k-1}\dot{\alpha}_k(N,\{b'\})\right]\rho^k, \quad (3.3)$$

where

$$\dot{\alpha}_k\equiv V\frac{\partial}{\partial V}\alpha_k$$

and

$$\alpha_k(N,\{b'\})=\alpha_k(N,\{b\}), \quad \dot{\alpha}_k=0 \quad \text{for} \quad k<L/a. \quad (3.4)$$

It was shown by Oppenheim and Mazur, who considered only the low-order virial coefficients, $k<L/a$, $k<N$ [and thus obtained Eq. (3.1) with $\alpha_k{}^j(\{b\})$ which are independent of N and V] that

$$\alpha_{k+1}{}^0(\{b\})=-\frac{k}{k+1}\beta_k, \quad (3.5)$$

where β_k is the usual irreducible cluster integral. This result is also a consequence of the fact, proven by Lewis,[6] that in the limit of N and V becoming infinite, ρ remaining fixed, the canonical pressure coincides with that obtained from the grand canonical ensemble for a system of average density ρ. The results of Oppenheim and Mazur may be carried over to the case where the cluster integrals are volume dependent, to yield

$$\alpha_{k+1}{}^0(\{b'\})=-\frac{k}{k+1}\beta_k'. \quad (3.5')$$

The β_k' are the volume-dependent irreducible cluster integrals related to the b_l' by the same algebraic relation that relates the β_k to the b_l:[7]

$$k!\beta_k'=-\sum_{m_l\geq 0}(k-1+\sum_{l=2}m_l)!\prod_{l\geq 2}\frac{(-lb_l')^{m_l}}{m_l!}, \quad (3.6)$$

the summation being restricted as in (2.3), or by its inverse:

$$l^2b_l'=\sum_{m_k\geq 0}\prod_k\frac{(l\beta_k')^{m_k}}{m_k!}, \quad \text{where} \quad \sum km_k=l-1. \quad (3.7)$$

The β_k' take on their volume independent values β_k when $k+1<L/a$.

It is recognized from (3.5′) that the $\alpha_k{}^0(\{b'\})$ are the volume-dependent virial coefficients obtained from the grand canonical ensemble for a system with a volume V. In order to gain further insight and obtain in a more transparent form the complete N dependence (explicit and implicit) of the pressure, let us consider the average value of $p(N,V)$ over a grand ensemble. Denoting this average pressure by $\bar{p}$, we have

$$\bar{p}(\lambda,V)=\sum_{N=1}^{\infty}p(N,V)\mathcal{W}(N,\lambda,V), \quad (3.8)$$

where $\mathcal{W}(N,\lambda,V)$, the probability of having N particles in the system, is given by

$$\mathcal{W}(N,\lambda,V)=\lambda^N Z(N,V)/Z_g(\lambda,V), \quad (3.9)$$

$$Z_g(\lambda,V)=\sum\lambda^N Z(N,V)=\exp[V\sum b_l'\lambda^l]. \quad (3.10)$$

Using the definition of $p(N,V)$ in (3.8) readily yields

$$\bar{p}(\lambda,V)=\frac{\partial}{\partial V}\ln Z_g(\lambda,V)=P(\lambda,V)+\dot{P}(\lambda,V), \quad (3.11)$$

$$\dot{P}(\lambda,V)=V\frac{\partial}{\partial V}P(\lambda,V),$$

[6] M. B. Lewis, Phys. Rev. **105**, 348 (1957).
[7] J. Mayer, *Handbuch der Physik* (Springer-Verlag, Berlin, 1958), Vol. 12.

where

$$P(\lambda,V)=\frac{1}{V}\ln Z_g(\lambda,V)=\bar{\rho}-\sum\frac{k}{k+1}\beta_k'\bar{\rho}^{k+1}, \quad (3.12)$$

is the usual grand canonical pressure, with

$$\bar{\rho}(\lambda,\{b'\})=\bar{N}/V=\sum\frac{N}{V}\mathcal{W}(N,\lambda,V)=\sum lb_l'\lambda^l. \quad (3.13)$$

In order to evaluate the second term on the right side of (3.11), we rewrite (3.12) in the form

$$P(\lambda,V)=\bar{\rho}[1-\sum\beta_k'\bar{\rho}^k]+\sum\frac{1}{k+1}\beta_k'\bar{\rho}^{k+1}$$
$$=\bar{\rho}[1-\ln(\bar{\rho}/\lambda)]+\sum\frac{1}{k+1}\beta_k'\bar{\rho}^{k+1}. \quad (3.14)$$

The second equality follows from inverting the series (3.13). We then have

$$\dot{P}(\lambda,V)=\sum\frac{1}{k+1}\dot{\beta}_k'\bar{\rho}^{k+1} \quad (3.15)$$

and

$$\bar{p}(\lambda,V)=\bar{p}(\bar{\rho},\{b'\})=\bar{\rho}-\sum_{k=1}^{\infty}\frac{1}{k+1}(k\beta_k'-\dot{\beta}_k')\bar{\rho}^{k+1}$$
$$=\bar{\rho}+\sum_{k=2}^{\infty}\left[\alpha_k^0(\{b'\})-\frac{1}{k-1}\dot{\alpha}_k^0(\{b'\})\right]\bar{\rho}^k. \quad (3.16)$$

The average pressure $\bar{p}(\bar{\rho},\{b'\})$ thus coincides with the N-independent terms in $p(N,V)=p(N,\rho,\{b'\})$ for all virial terms $k\leq N$, and $\rho=\bar{\rho}$. The form $p(N,\rho,\{b'\})$ separates the explicit N-dependence of p from that contained implicitly in the volume dependence of the b'. It then follows, keeping the b' fixed, that

$$\lim_{N\to\infty}p(N,\rho,\{b'\})=\bar{p}(\rho,\{b'\}). \quad (3.17)$$

The explicit N dependence of $p(N,\rho,\{b'\})$ may now be obtained by expanding $p(N,V)$ in (3.8) about $\bar{N}(\lambda,V)$. This method is not limited to the pressure but may be used to obtain the N dependence of any thermodynamic quantity as well as that of the low-order distribution functions. It was used by us previously[1] to study the asymptotic behavior of the Ursell functions, and we give an entirely different application of it in the appendix. Going back then to the definition (3.8), we write

$$\bar{p}(\lambda,V)=\sum_{N=0}^{\infty}p(\bar{N}(\lambda)+\delta N,\ V)\mathcal{W}(N,\lambda,V)$$
$$=p(\bar{N}(\lambda,V),V)+\sum\frac{1}{k!}(\delta N)^k\frac{\partial^k}{\partial\bar{N}^k}p(\bar{N},V)$$
$$=p(\bar{N},V)+\frac{\bar{\rho}^2}{2\bar{N}}(\bar{\rho}\chi)\frac{\partial^2}{\partial\bar{\rho}^2}\bar{p}(N,\bar{\rho},\{b'\})+O(1/N), \quad (3.18)$$

where $\delta N=N-\bar{N}$. In deriving the last equality, we have made use of the fact that

$$\langle(\delta N)^2\rangle=\lambda\frac{\partial}{\partial\lambda}\bar{N}=N(\partial P/\partial\bar{\rho})^{-1}=\bar{\rho}\chi N, \quad (3.19)$$

χ being the isothermal compressibility.

Equation (3.18) may now be inverted to get the N dependence of $p(N,V)$. A somewhat more condensed form of Eq. (3.18), containing an explicit expression for the $\langle(\delta N)^k\rangle$, may be obtained as follows. We consider the average value of the quantity $\exp(a\delta N)$, where a is an arbitrary constant,

$$\langle e^{a\delta N}\rangle=\sum\exp[a(N-\bar{N})]\lambda^N Z(N,V)/\sum\lambda^N Z(N,V)$$
$$=\exp(-a\bar{N})Z_g(\lambda e^a,V)/Z_g(\lambda,V). \quad (3.20)$$

But from (3.13),

$$Z_g(\lambda,V)=\exp\left(\int\bar{N}dz\right),\quad z\equiv\ln\lambda; \quad (3.21)$$

hence

$$\langle e^{a\delta N}\rangle=\exp\left[\int_z^{z+a}\bar{N}dz-a\bar{N}\right]$$
$$=\exp[V\sum_{k=2}^{\infty}(a^k/k!)\partial^{k-1}\bar{\rho}/\partial z^{k-1}]. \quad (3.22)$$

We may equate coefficients of a in (3.22) to obtain

$$\langle(\delta N)^l\rangle$$
$$=l!\sum\left\{\prod_{k=2}^{\infty}\left[\left(\frac{\partial^{k-1}\bar{\rho}}{\partial z^{k-1}}\Big/k!\right)^{n_k}\Big/n_k!\right]V^{\Sigma_2 n_k}\right\}, \quad (3.23)$$

where $\sum_2 kn_k=l$. Observing that $\langle F(\delta N)\rangle=F(\partial/\partial a)\times\langle\exp a\delta N\rangle$ at $a=0$, we have more generally

$$f(\bar{N}+\delta N)=\mathfrak{N}\exp[\sum_{k=2}^{\infty}(V^{1-k}/k!)$$
$$\times(\partial^{k-1}\bar{\rho}/\partial z^{k-1})(\partial/\partial\bar{\rho})^k]f(\bar{\rho}), \quad (3.24)$$

where $\mathfrak{N}$ indicates a normal order in which all $\partial/\partial\bar{\rho}$ go to the right before evaluation.

According to (3.18) and (3.24),

$$\bar{p}(\bar{\rho},\{b'\})=\mathfrak{N}\exp[\sum_{k=2}^{\infty}(V^{1-k}/k!)(\partial^{k-1}\bar{\rho}/\partial z^{k-1})$$
$$\times(\partial/\partial\bar{\rho})^k]p(\bar{\rho},V,\{b'\}). \quad (3.25)$$

One further sees from (3.19) that

$$\frac{\partial}{\partial z}=\bar{\rho}^2(\chi)\frac{\partial}{\partial\bar{\rho}}, \quad (3.26)$$

Inserting (3.26) into (3.25) and inverting the resulting series to find the explicit V dependence of $p(N,V)$, which we have written as a function of ρ, V, and $\{b'\}$,

$$p(\rho,V,\{b'\})=\left[1-\frac{1}{2V}\rho^2\chi\frac{\partial^2}{\partial\rho^2}-\frac{1}{6V^2}\rho^2\chi\right.$$
$$\times\left(\frac{\partial}{\partial\rho}\rho^2\chi\right)\frac{\partial^3}{\partial\rho^3}-\frac{1}{8V^2}(\rho^2\chi)^2\frac{\partial^4}{\partial\rho^4}$$
$$\left.+\frac{1}{4V^2}\rho^2\chi\frac{\partial^2}{\partial\rho^2}\rho^2\chi\frac{\partial^2}{\partial\rho^2}+\cdots\right]\bar{p}(\rho,\{b'\}). \quad (3.27)$$

In terms of N, we thus have

$$p(N,\rho,\{b'\})$$
$$=\left\{1-\frac{1}{2N}\rho^3\chi\frac{\partial^2}{\partial\rho^2}-\frac{1}{N^2}\rho^4\chi\left[\frac{1}{6}\left(\frac{\partial}{\partial\rho}\rho^2\chi\right)\frac{\partial^3}{\partial\rho^3}\right.\right.$$
$$\left.\left.+\frac{1}{8}\rho^2\chi\frac{\partial^4}{\partial\rho^4}-\frac{1}{4}\frac{\partial^2}{\partial\rho^2}\rho^2\chi\frac{\partial^2}{\partial\rho^2}\right]+\cdots\right\}\bar{p}(\rho,\{b'\}). \quad (3.28)$$

Equation (3.28) will result in a virial expansion of the form

$$p(N,\rho,\{b'\})$$
$$=\sum_{k=1}^{\infty}\sum_{j=0}^{k-1}\left[\alpha_k{}^j\{b'\}-\frac{1}{k-1}\dot{\alpha}_k{}^j\{b'\}\right]\left(\frac{1}{N}\right)^j\rho^k, \quad (3.29)$$

i.e., we do not get the correct N dependence of Eq. (3.2) for the $\alpha_k{}^j$ when $k>N$, which is not surprising in view of the fact that we have treated $\bar{N}$ as a continuous variable. Actually, $p(\bar{\rho},V,\{b'\})$ is a discontinuous function of $\bar{\rho}$, the position and size of the discontinuities depending on V, which cannot be included in a power series. This can be taken care of by using an Euler-MacLaurin rather than a Taylor series expansion, or more simply by setting all $b_k'=0$ for $k>N$ in the explicit expansion.

4. ANOMALOUS VOLUME DEPENDENCE

For virial expansion terms with $k<L/a$, there is no volume dependence in the $\alpha_k{}^j$ of (3.29), so that these terms in the expansion of $\bar{p}(\rho,\{b'\})$ and $P(\rho,\{b'\})$ are the same. Since $\partial P/\partial\rho=1/\rho\chi$, (3.28) then becomes

$$p(N,\rho,\{b\})$$
$$=P(\rho)+\frac{1}{2}\rho^2\frac{\partial}{\partial\rho}\ln(\rho\chi)\frac{1}{N}-\left\{\rho^5\chi\left[\frac{1}{8}\frac{\partial^3}{\partial\rho^3}\ln\rho\chi\right.\right.$$
$$+\frac{5}{24}\frac{\partial^2}{\partial\rho^2}\ln\rho\chi\frac{\partial}{\partial\rho}\ln\rho\chi+\frac{1}{24}\left(\frac{\partial}{\partial\rho}\ln\rho\chi\right)^3$$
$$\left.\left.+\frac{1}{6}\left(\frac{\partial}{\partial\rho}\ln\rho\chi\right)^2\right]+\rho^4\chi\frac{1}{3}\frac{\partial^2}{\partial\rho^2}\ln\rho\chi\right\}\frac{1}{N^2}+\cdots, \quad (4.1)$$

for terms in the virial expansion with $k\leq L/a$. When the last equation is expanded in ρ, defining

$$P(\rho)=\rho+B\rho^2+C\rho^3+\cdots$$

and thus

$$\chi=\beta[\rho^{-1}-2B+(4B^2-3C)\rho+\cdots], \quad (4.2)$$

we obtain

$$p(N,\rho,\{b'\})=\rho+\left(1-\frac{1}{N}\right)B\rho^2+\left[C+\frac{1}{N}(2B^2-3C)\right.$$
$$\left.+\frac{2}{N^2}(C-B^2)\right]\rho^3+\cdots. \quad (4.3)$$

This N dependence of the virial coefficients has previously been obtained by means of a recurrence relation by Oppenheim and Mazur. As we have seen, however, it is only valid through the kth virial coefficient, where $k=L/a=(N/\rho a^3)^{\frac{1}{3}}$. In particular, for a hard-sphere gas, with maximum density $\rho_c=\sqrt{2}/a^3$, the above relations for the N dependence of the pressure hold for

$$k\leq(\rho_c/\rho)^{\frac{1}{3}}(N/\sqrt{2})^{\frac{1}{3}} \quad (\text{and } k\leq N). \quad (4.4)$$

Thus for $N=8$, they will not be valid even for the third virial coefficient unless $\rho/\rho_c<8/(27\sqrt{2})\sim\frac{1}{4}$, and hence are not relevant at the densities considered by Alder and Wainwright.

When (4.4) is violated for virial coefficients which are not negligible for the equation of state in the region of interest, the volume dependence of the pressure at given density may be strongly affected by the volume dependence of the b_l'. A little thought shows that in a periodically bounded system, this volume dependence arises only from those terms in a cluster which would vanish if V is increased sufficiently. This means that the cluster must be at least doubly connected, and in fact must have at least one loop which touches diametrically opposite boundaries, i.e., it winds at least once around the "periodic" doughnut. If we think of this doughnut as made out of rubber which can be inflated, then the volume dependent clusters are those which would burst as the doughnut gets larger. The first contribution will come from the ring clusters, and they can be evaluated explicitly. For example, in a four-particle system, the first volume dependence will appear when a four-particle ring can touch opposite walls, that is, when

$$\rho/\rho_c\geq 4/(\sqrt{2}\times 4^3); \quad (4.5)$$

this will be the only contribution to volume dependence until a 3-particle ring can do the same,

$$\rho/\rho_c=4/(\sqrt{2}\times 3^3), \quad (4.6)$$

at approximately double the above density.

Let us compare the usual residual N dependence of the pressure with the "anomalous" dependence engendered by the variation of cluster coefficients with volume. According to (4.1), the leading term in the former is given by

$$p(N,\rho,\{b\})=p(N,\rho)=P(\rho)-\frac{1}{2N}\rho^2\frac{\partial}{\partial\rho}\ln(1/\rho\chi), \quad (4.1')$$

which for repulsive forces (or more accurately, for $\partial^2\bar{p}/\partial\rho^2>0$), necessarily increases as N increases at fixed density. On the other hand, if the volume dependence adds a term ΔZ_c to the coordinate partition function, then $p'=\rho+(\partial/\partial V)\ln(Z_c+\Delta Z_c)$ compared to an uncorrected $p=\rho+(\partial/\partial V)\ln Z_c$. Hence to first order

$$p'=p+\frac{\partial}{\partial V}\frac{\Delta Z_c}{Z_c}, \quad (4.7)$$

whose N dependence may be expected to be governed principally by the rate of growth of ΔZ_c.

Suppose that the largest relevant cluster coefficient for a given system at density ρ is b_l. For an N-body system the coefficient b_l, but not b_{l-1}, shows an anomalous volume dependence when $N/(l-1)^3\geq\rho a^3\geq N/l^3$. According to (2.3), the "threshold" behavior of Z_c is then

$$\Delta Z_c=\frac{N!}{(N-l)!N^{l-1}}\rho^{l-1}\Delta b_l. \quad (4.8)$$

It is clear that, counting the three possible ways of stretching from wall to wall, and calling $\hat{z}$ a unit vector in the z direction,

$$\Delta b_l=\left(\frac{3(l-1)!}{(l!V)}\right)V\int\cdots\int f(\mathbf{r}_1)f(\mathbf{r}_{12})f(\mathbf{r}_{23})\cdots \times f(\mathbf{r}_{l-2,l-1})f(\hat{z}L-\mathbf{r}_{l-1})d\tau^{l-1}$$

$$=\frac{3}{l}\int\cdots\int f(\mathbf{r}_1)\cdots f(\mathbf{r}_l)\delta(\textstyle\sum\mathbf{r}_j-L\hat{z})d\tau^l$$

$$=\frac{3}{8\pi^3 l}\int\cdots\int f(\mathbf{r}_1)\cdots f(\mathbf{r}_l)\times\exp[i\mathbf{s}\cdot(\textstyle\sum\mathbf{r}_j-L\hat{z})]d\tau^l d\mathbf{s}$$

$$=\frac{3}{8\pi^3 l}\int(f_s)^l\exp(-iLs_z)d\mathbf{s}$$

$$=(3/2\pi^2 lL)\int_0^\infty(f_s)^l\sin(sL)sds.$$

Hence

$$\Delta b_l=\frac{3i}{4\pi^2 lL}\int_{-\infty}^{\infty}(f_s)^l e^{-isL}sds, \quad (4.9)$$

where

$$f(r)=(e^{-\phi(r)}-1),\quad\text{and}\quad f_s=\int f(r)e^{i\mathbf{r}\cdot\mathbf{s}}d\mathbf{s}.$$

In general, for a repulsive potential, $f(\mathbf{r})$ is negative and Δb_l, directly from its coordinate integral expression, has the sign $(-1)^l$. In particular, for hard spheres of diameter a, a more detailed result may be given. We have

$$f_s=-(4\pi/s^3)(\sin as-as\cos as)$$
$$=-(2\pi i/s^3)[(1+ias)e^{-ias}-(1-ias)e^{ias}], \quad (4.10)$$

so that

$$\Delta b_l=(-1)^l(3i/4\pi^2 lL)(2\pi i)^l\int\left\{s^{1-3l}\sum\binom{l}{j}\times(1+ias)^j(-1)^{l-j}(1-ias)^{l-j}\times\exp[is((l-2j)a-L)]\right\}ds.$$

For a contour passing below the origin, if $la>L>(l-2)a$, only the $j=0$ term contributes, so

$$\Delta b_l=\left(\frac{3i}{4\pi^2 lL}\right)(2\pi i)^{l+1}\left(\frac{d}{ds}\right)^{3l-2}\times(1-ias)^l e^{i(la-L)s}/(3l-2)!\bigg|_{s=0}$$

$$=(-1)^l\frac{3}{lL}(2\pi)^{l-1}\frac{1}{(3l-2)!}(la-L)^{3l-2}\times\left(\frac{d}{dt}\right)^{3l-2}\left(1+\frac{a}{la-L}t\right)^l e^{-t}\bigg|_{t=0}$$

$$=(-1)^l\frac{3}{lL}(2\pi)^{l-1}\frac{1}{(3l-2)!}(la-L)^{2l-2}\times a^l\left(\frac{d}{du}\right)^{3l-2}e^{(la-L)/a}u^l e^{-u}\bigg|_{u=-(la-L)/a},$$

or

$$\Delta b_l=(-1)^l\left(\frac{3}{lL}\right)\frac{(2\pi)^{l-1}}{(2l-2)!}(la-L)^{2l-2}\times a^l\phi(-l,2l-1;l-L/a), \quad (4.11)$$

where ϕ is the confluent hypergeometric funciton ${}_1F_1$. For large A and B, small x, one has

$$\ln\phi(A,B;x)=\frac{A}{B}x+\frac{A}{B}\frac{B-A}{B(B+1)}\frac{x^2}{2}+\frac{(B-A)(B-2A)}{B^2(B+1)(B+2)}\frac{x^3}{3}+\cdots. \quad (4.12)$$

In the present case, $x\lesssim 1$, and hence we have from (4.8), (4.11), and (4.12),

$$\Delta Z_c\simeq\frac{(-1)^l}{l}\frac{3a/L}{(2l-2)!}\frac{N!}{(N-l)!N^{l-1}}(2\pi\rho a^3)^{l-1}\times\left(l-\frac{L}{a}\right)^{2l-2}\exp\left[\frac{-l}{2l-1}\left(l-\frac{L}{a}\right)\right]. \quad (4.13)$$

Since the b_{l+1} ring contribution to ΔZ_c is roughly $-(2\pi\rho a^3)[(l+1-L/a)^{2l}/(l-L/a)^{2l-2}]4l^2$ times that due to b_l, the large l asymptotic b_l contribution of the rings in fact going as

$$\Delta Z_c \sim (-1)^l (6Na/L)\exp(-3L/2a)(\tfrac{1}{2}\pi e^2\rho a^3)^{l-1}/l^{\frac{3}{2}},$$

the expression (4.13) is dominant among clusters l and higher only for quite small ρ, say $\rho a^3 < \frac{1}{10}$, or for the threshold l little smaller than N. Let us investigate numerically the situation for a somewhat higher density, $\rho a^3 = \frac{1}{4}$. We will be interested in the pressure deviation, which according to (4.2) and (4.13) is given by

$$\Delta p = -\frac{\Delta Z_c}{Z_c}\left\{p - \left(1 + \frac{1}{N}\frac{l}{2l-1}\frac{L}{3a}\right)\rho + \frac{1}{3N}\left[3l-2+(2l-2)\frac{L/a}{l-(L/a)}\right]\rho\right\}. \tag{4.14}$$

For hard spheres, the virial coefficients are

$$B = \tfrac{2}{3}\pi a^3, \quad C = \tfrac{5}{8}B^2, \quad D = 0.2869B^3, \quad E = 0.115B^4, \cdots, \tag{4.15}$$

the irreducible cluster coefficients

$$\beta_1 = -2B, \quad \beta_2 = -\tfrac{3}{2}C, \quad \beta_3 = -\tfrac{4}{3}D, \cdots, \tag{4.16}$$

yielding connected cluster coefficients

$$\begin{aligned} b_2 &= \tfrac{1}{2}\beta_1 = -B \\ b_3 &= \tfrac{1}{2}\beta_1^2 + \tfrac{1}{3}\beta_2 = (27/16)B^2 \\ b_4 &= \tfrac{2}{3}\beta_1^3 + \beta_1\beta_2 + \tfrac{1}{4}\beta_3 = 3.554B^3. \end{aligned} \tag{4.17}$$

The coordinate partition function for a system of N particles may be written out explicitly from Eqs. (2.2), (2.3) as

$$\begin{aligned} Z_c = 1 + (N-1)b_2'\rho &+ \left[\frac{(N-1)(N-2)(N-3)}{2N}(b_2')^2 + \frac{(N-1)(N-2)}{N}b_3'\right]\rho^2 \\ &+ \left[\frac{(N-1)(N-2)(N-3)(N-4)(N-5)}{6N^2}(b_2')^3 + \frac{(N-1)(N-2)(N-3)(N-4)}{N^2}b_2'b_3' \right. \\ &\left. + \frac{(N-1)(N-2)(N-3)}{N^2}b_4'\right]\rho^3 + \cdots \end{aligned} \tag{4.18}$$

$$= \left\{1 + b_2'\rho + \frac{N-2}{N}(b_3' - \tfrac{3}{2}b_2'^2)\rho^2 + \frac{N-2}{N^2}(N-3)b_4' - (5N-12)b_2'b_3' + \left[\frac{29}{6}(N-10)b_2'^3\right]\cdots\right\}^{N-1}. \tag{4.19}$$

Neglecting the difference between b' and b, and inserting Eq. (4.17), we obtain the "free boundary" partition function

$$Z_c = \left[1 - B\rho + \frac{3}{16}\frac{N-2}{N}B^2\rho^2 + \frac{N-2}{N}(7.16N - 20.9)B^3\rho^3\cdots\right]^{N-1}. \tag{4.20}$$

At $\rho a^3 = \frac{1}{4}$, we find from (4.15) the $N = \infty$ limit $p/\rho = 1.75$. The expansion, Eq. (4.3), in powers of $1/N$ goes as

$$\Delta(p/\rho) = -\frac{1}{N}(\tfrac{2}{3}\pi a^3\rho) + \frac{1}{N}\tfrac{1}{16}(\tfrac{2}{3}\pi a^3\rho)^2 - \frac{1}{N^2}\tfrac{3}{4}(\tfrac{2}{3}\pi a^3\rho)^2 + \cdots. \tag{4.21}$$

This may be compared with the results obtained from Eq. (4.18) when b' is set equal to b but the N dependence is kept exact, and is tabulated in Table I.

TABLE I. Explicit N dependence of the pressure.

N	p/ρ Eq. (4.21)	p/ρ Eq. (4.18)
2	1.45	1.55
3	1.56	1.55
4	1.61	1.64
8	1.68	···
∞	1.75	1.75

The lowest size anomalous cluster which exists for a volume $V = L^3 = N/\rho = Na^3/\rho a^3$ is in general given by $N \geq l > L/a = (N/\rho a^3)^{\frac{1}{3}}$. The anomalous corrections to Z_c and p, as computed from Eqs. (4.13), (4.14), are given in Table II in which the $N = 8$ result may be a considerable overestimate, since all contributions for $l > 4$ have been neglected.

TABLE II. Contribution of anomalous ring clusters.

N	Z_c	l	ΔZ_c	$\Delta p/\rho$
2				0.000
3	0.260	3	−0.0035	0.040
4	0.135	3, 4	−0.0024, +0.0034	−0.053
8	0.0316	4, ···	1.42×10^{-4}	−0.077, ···

5. RELATION BETWEEN ANOMALOUS VOLUME DEPENDENCE AND 2-BODY DISTRIBUTION

The above computation involves a configuration space integral with endpoints separated by a fixed distance L, and hence suggests a relation to the two-body distribution function. Thus for example the l-particle anomalous ring cluster considered in the previous section is clearly equivalent, except for a volume factor, to a cluster of $l+1$ particles connected in series, the two end particles being kept fixed at a separation L. The value of this cluster integral therefore corresponds to the value of the coefficient of ρ^{-1} in the virial expansion of the radial distribution function $g(r)$ at $r=L$ in an infinite system, providing that $(l-1)a<L<la$, and except for a combinatorial factor.

A more general approximate relation of this type, not restricted to the ring clusters, may also be derived. We have

$$\lim_{N\to\infty}\frac{\ln Z_c(N,\rho,\{b'\})}{N}=\sum\frac{\beta'_k}{k+1}\rho^k, \tag{5.1}$$

where the β_k', defined in Eqs. (3.6), (3.7), are (because of the translation invariance of the periodic box) the irreducible *volume-dependent* cluster integrals. Looking now at the two-particle distribution function $n_2(\mathbf{x}_1-\mathbf{x}_2)$, it was shown in reference 1 that

$$\frac{\delta \ln Z_c}{\delta f(\mathbf{x})}=\tfrac{1}{2}Ve^{\phi(\mathbf{x})}n_2(\mathbf{x})=N\sum_{k=1}^{\infty}\frac{\rho_k}{k+1}\frac{\delta\beta_k'}{\delta f(\mathbf{x})}. \tag{5.2}$$

We observe that any cluster in β_k' which winds once around the periodic doughnut, and which as the result of a single cut is no longer anomalous emanates (in three different ways) from a similar cluster in β_{k+1} with two particles separated by L. Conversely, if one performs the operation $\delta/\delta f(L)$ on $(k+1)!V\beta_{k+1}$, two types of terms result: those in which the pair separated by L has two connections to another particle, and these vanish for $L\geq 2a$; the remainder, which become legitimate anomalous elements of $k!V\beta_k$ when the pair is identified as a single particle. Dividing by $(k+1)(k+2)/2$ is equivalent to differentiating with respect to a single specified link and hence to considering those diagrams in which a specified particle say 1 appears with its periodic image. Ring clusters are counted correctly by this procedure but all others are underestimated. With this proviso, we have

$$\Delta(k!V\beta_k)=\frac{2}{(k+1)(k+2)}3\frac{\delta}{\delta f(L)}(k+1!V\beta_{k+1}), \tag{5.3}$$

or

$$\Delta\beta_k=\frac{6}{k+2}\frac{\delta}{\delta f(L)}\beta_{k+1},\quad k\geq 1. \tag{5.3}$$

Hence

$$\begin{aligned}\Delta\ln Z_c&=N\sum_{k=1}^{\infty}\frac{\rho^k}{k+1}\frac{6}{k+2}\frac{\delta\beta_{k+1}}{\delta f(L)}\\&=6\int_0^N\sum_{1}^{\infty}\frac{\rho^k}{k+2}\frac{\delta\beta_{k+1}}{\delta f(L)}dN\\&=3\int_0^N\frac{1}{\rho^2}[n_2(L)-\rho^2]dN.\end{aligned} \tag{5.4}$$

As a check, suppose that $L>2a$; then in the Nijboer-Van Hove[8] notation, $n_2(L)=\rho^2[1+\rho^2g_2(L)+\rho^3g_3(L)+\cdots]$, $\Delta\ln Z_c=2N[\frac{1}{3}\rho^2g_2(L)+\frac{1}{4}\rho^3g_3(L)+\cdots]$. In the special case of hard spheres with $\rho a^3=\frac{1}{4}$, $N=3$, $L/a=2.29$, so that $\Delta\ln Z_c=\frac{3}{16}(-0.114)=-0.021$, which coincides with the result of Table II if $(Z_c)^{1/N}$ is given its infinite-particle limiting value.

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APPENDIX I. CORRELATIONS IN A MICROCANONICAL ENSEMBLE

We present here, mainly for the purpose of illustration of our method, a simple derivation of a formula derived rigorously, and incidentally quite laboriously, by Khinchin.[9] Consider a system of N independent particles represented by a microcanonical ensemble of fixed energy E. This fixing of the total energy is the source, the only one, of correlations between the particles. It is the form of the correlations, which are intuitively of order $1/N$, which we seek. To apply our method, we compare the value of a function in a system with energy E (i.e. average over a microcanonical ensemble) with its average value over a canonical ensemble of temperature T. This temperature is chosen so that the average energy $\bar{E}$ is equal to E.

We then have, in complete analogy with Eq. (3.18), for a function $a(E)$ (with $\beta=1/kT$),

$$\bar{a}(\beta,(\bar{E}))=a(\bar{E})+\sum_{k=2}^{\infty}\frac{1}{k!}\langle(\delta E)^k\rangle\frac{\partial^k}{\partial\bar{E}^k}a(\bar{E}), \tag{I.1}$$

and keeping only terms to order $1/N$, we have as a consequence

$$a(\bar{\epsilon})=\bar{a}(\beta(\bar{\epsilon}))-\tfrac{1}{2}kT^2(C_V/N^2)\partial^2\bar{a}(\beta(\bar{\epsilon}))/\partial\bar{\epsilon}^2, \tag{I.2}$$

where C_V is the specific heat of the whole system at constant volume [which is of order $O(N)$], $\bar{\epsilon}=\bar{E}/N$, and we have used the fact that

$$\langle(\delta E)^2\rangle=-\partial\bar{E}/\partial\beta=\partial^2\ln Z/\partial\beta^2=kT^2C_V. \tag{I.3}$$

[8] B. R. A. Nijboer and L. van Hove, Phys. Rev. **85**, 777 (1952).
[9] A. Khinchin, *Statistical Mechanics* (Dover Publications, New York, 1949).

Here, Z is the classical partition function,

$$Z(\beta)=\int\cdots\int \exp[-\beta \sum_{i=1}^{N} h_i(x_i)]dx_1\cdots dx_N = \prod_{i=1}^{N} z_i(\beta), \quad (I.4)$$

in which x_i denotes the set of canonical variables of a single particle and $h_i(x_i)$ is the Hamiltonian of that particle.

Let $\phi(x_1)$, $\psi(x_2)$ be some functions of the phase spaces of particles one and two respectively. Then we define

$$\phi(E)\equiv\langle\phi(x_1)\rangle_E = \frac{\int \phi(x_1)\delta[\sum h_i(x_i)-E]dx_1\cdots dx_N}{\int \delta[\sum h_i(x_i)-E]dx_1\cdots dx_N}, \quad (I.5)$$

$$\bar{\phi}(\beta)=\int \phi(x_1)e^{-\beta h_1(x_1)}dx_1/z_1=\langle\phi\rangle, \quad (I.6)$$

with corresponding expressions for $\psi(E)$, $\langle\psi\rangle$, and for $\langle\phi(x_1)\psi(x_2)\rangle$. This latter quantity has the obvious property

$$\langle\phi\psi\rangle=\langle\phi\rangle\langle\psi\rangle. \quad (I.7)$$

When use is made of Eq. (I.6) for each of the quantities $\phi(E)$, $\psi(E)$ and $\langle\phi(x_1)\psi(x_2)\rangle$, we find

$$\langle[\phi(x_1)-\phi(\bar{\epsilon})][\psi(x_2)-\psi(\bar{\epsilon})]\rangle_E=\frac{1}{N}\frac{\partial\bar{\epsilon}}{\partial\beta}\left[\frac{\partial\bar{\phi}}{\partial\bar{\epsilon}}\frac{\partial\bar{\psi}}{\partial\bar{\epsilon}}\right]. \quad (I.8)$$

The quantity $\partial\bar{\phi}/\partial\bar{\epsilon}$ may be evaluated directly from (I.8) by changing $\psi=h_2$:

$$\frac{\partial\bar{\phi}}{\partial\bar{\epsilon}}=\frac{\partial\beta}{\partial\bar{\epsilon}}\frac{\partial\bar{\phi}}{\partial\beta}=\frac{\partial\beta}{\partial\bar{\epsilon}}\langle[\phi(x_1)-\bar{\phi}][h_2(x_2)-h_2(\bar{\epsilon})]\rangle. \quad (I.9)$$

If we neglect terms lower than first order in the coefficient of $1/N$ on the right side of (I.8), which is correct to the order we are working with, we may write

$$\frac{\partial\bar{\phi}}{\partial\bar{\epsilon}}=\frac{\partial\beta}{\partial\bar{\epsilon}}\langle[\phi(x_1)-\phi(\bar{\epsilon})][h_2(x_2)-h_2(\bar{\epsilon})]\rangle_E. \quad (I.10)$$

Combining Eqs. (I.10), (I.9), and (I.3) finally yields

$$R(\phi,\psi)=-\left(\frac{\partial^2 \ln z_1}{\partial\beta^2}\right)^{\frac{1}{2}}\left(\frac{\partial^2 \ln z_2}{\partial\beta^2}\right)^{\frac{1}{2}}\Big/\left(\frac{\partial^2 \ln Z}{\partial\beta^2}\right) \times R(\phi,h_1)R(\psi,h_2), \quad (I.11)$$

where

$$R(\phi,\psi)=\langle[\phi(x_1)-\phi(\bar{\epsilon})][\psi(x_2)-\psi(\bar{\epsilon})]\rangle_{\bar{E}} /\{\langle[\phi-\phi(\bar{\epsilon})]^2\rangle_{\bar{E}}\langle[\psi-\psi(\bar{\epsilon})]^2\rangle_{\bar{E}}\}. \quad (I.12)$$

Eq. (I.11) is identical with Eq. (91) of Khinchin.