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Statistical Mechanics of Small Systems

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Using the determinental form of the *N-V-T* and *N-P-T* partition functions, we derive explicit expressions for the *N*-dependent virial coefficients occurring in the expansions of the equations of state in the *N-V-T* and *N-P-T* ensembles. The results are presented in a matrix algebra formalism. The equation of state of *N* hard spheres in an *N-P-T* ensemble of systems is analyzed by the method of Padé Approximants.

I. INTRODUCTION

In recent years the development of computer-simulated physical systems has created a need for theories to relate the machine-determined properties of these finite systems to the properties of similar infinite systems [1, 2]. The equation of state for a classical fluid whose molecules interact with pairwise additive forces has been analyzed by Oppenheim and Mazur [3] and also by Lebowitz and Percus [4]. In the latter paper the pressure $P(N, V)$ exerted on the walls of a periodic box of volume V by N particles was expressed as a power series in the number density $\rho = N/V$ and the coefficient of ρ^l was found to be a complicated function of N and V which could be explicitly determined only in a relatively low density region. The general result was that the coefficient of ρ^l ($l \leqslant N$) could be expressed as a polynomial of order $(l - 1)$ in $1/N$, the coefficient of N^{-j} ($j \leqslant l - 1$) being a function of the connected cluster integrals b_k' ($k \leqslant l$). For a periodic parallelepiped or rectangular box b_l' was an implicit function of V for $l > L/a$, a being the range of the intermolecular forces and L the length of the smallest edge of the box.

In this paper we are mainly concerned with the b_l' for $l < L/a$ so that the connected cluster integrals become the volume independent integrals b_l. A matrix algorithm is developed for generating the N dependent virial coefficients occurring in the density expansion of the canonical pressure. A similar analysis is performed on the *N-P-T* equation of state, $\overline{V}/N$ being the dependent variable and P/k_BT the independent variable, where k_B is Boltzmann's constant and T is the absolute temperature. The N-dependent virial coefficients have a particularly simple form in the N-P-T formalism, that of a polynomial of order 1 in $1/N$ for the lth coefficient, $l \leqslant N + 1$. In other words, the coefficients are of the form $a_l + d_l/N$, $l \leqslant N + 1$, where a_l, d_l are functions of the connected cluster integrals b_l.

We compare the condition $l \leqslant N$ to that necessary in the N-V-T ensemble for volume-independent virial coefficients, that in the expansion [5]

$$P/k_BT = \sum_{l=1}^{N} B_l'(N, V)\, \rho^l \tag{I.1}$$

the B_l' are not functions of V for $l \leqslant L/a$, or assuming the box to be cubical, $l \leqslant (N/\rho a^3)^{1/3}$. The two conditions $l \leqslant N$ (N-P-T) and $l \leqslant (N/\rho a^3)^{1/3}$ (N-V-T) are qualitatively different because the independent variable P/k_BT does not appear in the former inequality while the independent variable ρ does appear in the latter inequality.

Thus if we consider a fluid under high compression in a periodic box with small N we would expect the P/k_BT expansion in the N-P-T ensemble to be easier to formulate than the ρ expansion in the N-V-T ensemble. With this in mind we analyze the N-P-T equation of state for hard spheres using the method of Padé Approximants. The purpose of this analysis is to provide some quantitative information about the properties of finite N-P-T systems with the hope that it may be useful in interpreting computer experiments performed in the N-P-T ensemble.

II. A Matrix Formula for the N-V-T Virial Coefficients

We start with the product representation of $Q(N, V, T)$, the canonical partition function, in terms of the connected cluster integrals b_l', with l between 1 and N [6].

$$Q(N, V, T) = \frac{1}{\Lambda^{3N}} \sum_{\{m_l\}}{}' \prod_{l=1} \frac{(Vb_l')^{m_l}}{m_l!},$$

$$\Lambda = (h^2/2\pi m k_BT)^{1/2}. \tag{II.1}$$

The summation in Eq. (II.1) is carried out over all sets of nonnegative integers $\{m_l\} = \{m_1, m_2, ..., m_l\}$ which satisfy the restrictions

$$\sum l m_l = N. \tag{II.2}$$

A decomposition similar to Eq. (II.1) can be obtained for the quantum mechanical case and also for many body forces [7], but from here on we shall concern ourselves only with classical statistics and pairwise additive forces. This simplification enables us to define unambiguously the condition

$$b_l' = b_l \qquad \text{if} \quad l < L/a, \tag{II.3}$$

when the system is enclosed by a periodic box. We shall assume that Eq. (II.3) holds throughout the remainder of this section.

Equation (II.1) can be expressed as a determinant [8]:

$$Q(N, V, T) = \frac{1}{\Lambda^{3N}N!}\begin{vmatrix} Vb_1 & -1 & 0 & 0 & \cdots & 0 \\ 2Vb_2 & Vb_1 & -2 & 0 & \cdots & 0 \\ 3Vb_3 & 2Vb_2 & Vb_1 & -3 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & & \vdots \\ NVb_N & (N-1)Vb_{N-1} & (N-2)Vb_{N-2} & (N-3)Vb_{N-3} & \cdots & Vb_1 \end{vmatrix}_N, \tag{II.4}$$

which is a new result.

Expressing Eq. (II.4) in terms of the number density ρ, we have

$$Q(N, V, T) = \frac{(\rho^{-1}N)^N}{\Lambda^{3N}N!} \det \mathbf{M}_N,$$

$$\mathbf{M}_N = \begin{Bmatrix} b_1 & -\rho N^{-1} & 0 & 0 & \cdots & 0 \\ 2b_2 & b_1 & -2\rho N^{-1} & 0 & \cdots & 0 \\ 3b_3 & 2b_2 & b_1 & -3\rho N^{-1} & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & & \vdots \\ Nb_N & (N-1)b_{N-1} & (N-2)b_{N-2} & (N-3)b_{N-3} & \cdots & b_1 \end{Bmatrix}_N. \tag{II.5}$$

The equation of state may be written as

$$\begin{aligned} \frac{P}{k_B T} &= -\frac{\rho^2}{N}\left(\frac{\partial \ln Q(N, V, T)}{\partial \rho}\right)_{T,N} \\ &= \rho - \frac{\rho^2}{N}\left(\frac{\partial \ln \Delta_N}{\partial \rho}\right)_{T,N} \end{aligned} \tag{II.6}$$

where Δ_N represents $\det \mathbf{M}_N$.

From matrix algebra, we have

$$\left(\frac{\partial \ln \Delta_N}{\partial \rho}\right)_{T,N} = \text{Trace}\left[\mathbf{M}_N^{-1} \cdot \left(\frac{\partial \mathbf{M}_N}{\partial \rho}\right)_{T,N}\right], \tag{II.7}$$

where $\mathbf{M}_N^{-1}$ is the inverse of the matrix $\mathbf{M}_N$ [9]. Since the b_l are independent of ρ, we may write

$$\left(\frac{\partial \mathbf{M}_N}{\partial \rho}\right)_{T,N} = \mathbf{T}_N = -\frac{1}{N}\begin{Bmatrix} 0 & 1 & 0 & 0 & \cdots & 0 \\ 0 & 0 & 2 & 0 & \cdots & 0 \\ 0 & 0 & 0 & 3 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & & \vdots \\ 0 & 0 & 0 & 0 & \cdots & 0 \end{Bmatrix}_N. \tag{II.8}$$

The virial coefficients are obtained by expanding Eq. (II.7) in powers of ρ (assuming ρ to be small), the result being

$$\frac{P}{k_B T} = \sum_{l=1}^{N} B_l(N)\rho^l = \rho + \sum_{l=2}^{N} \frac{(-1)}{N(l-2)!}\frac{\partial^{l-2}}{\partial \rho^{l-2}}(\mathrm{Tr}\,\mathbf{M}_N^{-1}\cdot\mathbf{T}_N)\Big|_{\rho=0}\rho^l$$

$$= \rho + \sum_{l=2}^{N} \frac{(-1)}{N(l-2)!}\,\mathrm{Tr}\left[\left(\frac{\partial^{l-2}\mathbf{M}_N^{-1}}{\partial \rho^{l-2}}\right)_{\rho=0}\cdot\mathbf{T}_N\right]\rho^l. \tag{II.9}$$

Equation (II.9) is still in a rather complex form because the inverse of $\mathbf{M}_N$ must be calculated. This problem can be simplified by converting Equation (II.9) to a form that contains the inverse of an $N \times N$ triangular matrix instead of $\mathbf{M}_N$. To do this we make use of an identity that may easily be derived through induction. If $\mathbf{A}_N$ is any $N \times N$ matrix whose elements are differentiable functions of ρ, and if $\mathbf{A}_N^{-1}$ exists, then if $\partial^s\mathbf{A}_N/\partial\rho^s \equiv \mathbf{0}_N$ (the null matrix) for $s > 1$,

$$\frac{\partial^k \mathbf{A}_N^{-1}}{\partial \rho^k} = (-1)^k k!\left[\mathbf{A}_N^{-1}\cdot\frac{\partial \mathbf{A}_N}{\partial \rho}\right]^k \cdot \mathbf{A}_N^{-1}. \tag{II.10}$$

If we identify $\mathbf{A}_N$ with $\mathbf{M}_N$ and set $k = l - 2$, B_l $(l > 1)$ in Eq. (II.9) becomes

$$B_l(N) = \frac{(-1)^{l-1}}{N}\mathrm{Tr}[\mathbf{M}_N^{-1}(0)\cdot\mathbf{T}_N]^{l-1},$$

$$\mathbf{M}_N(0) = \mathbf{M}_N(\rho)\,|_{\rho=0}\,. \tag{II.11}$$

$\mathbf{M}_N(0)$ is a lower triangular matrix and its inverse can be written explicitly. Using $b_1 \equiv 1$, we have, for $\mathbf{M}_N(0)$,

$$\mathbf{M}_N(0) = \begin{Bmatrix} 1 & 0 & 0 & \cdots & 0 \\ 2b_2 & 1 & 0 & \cdots & 0 \\ 3b_3 & 2b_2 & 1 & \cdots & 0 \\ \vdots & \vdots & \vdots & & \vdots \\ Nb_N & (N-1)b_{N-1} & (N-2)b_{N-2} & \cdots & 1 \end{Bmatrix}_N, \tag{II.12}$$

and $\mathbf{M}_N^{-1}(0)$ is given by [10]

$$\mathbf{M}_N^{-1}(0) = \begin{pmatrix} 1 & 0 & 0 & \cdots & 0 \\ \mu_2 & 1 & 0 & \cdots & 0 \\ \mu_3 & \mu_2 & 1 & \cdots & 0 \\ \mu_4 & \mu_3 & \mu_2 & \cdots & 0 \\ \vdots & \vdots & \vdots & & \vdots \\ \mu_N & \mu_{N-1} & \mu_{N-2} & \cdots & 1 \end{pmatrix}_N ,$$

$$\mu_j = (-1)^{j-1} \begin{vmatrix} 2b_2 & 1 & 0 & \cdots & 0 \\ 3b_3 & 2b_2 & 1 & \cdots & 0 \\ 4b_4 & 3b_3 & 2b_2 & \cdots & 0 \\ \vdots & \vdots & \vdots & & \vdots \\ jb_j & (j-1)b_{j-1} & (j-2)b_{j-2} & \cdots & 2b_2 \end{vmatrix}_{j-1} . \quad \text{(II.13)}$$

Thus $\mathbf{M}_N^{-1}(0) \cdot \mathbf{T}_N$ can be written as

$$\mathbf{M}_N^{-1}(0) \cdot \mathbf{T}_N = -\frac{1}{N} \begin{pmatrix} 0 & 1 & 0 & 0 & \cdots & 0 \\ 0 & \mu_2 & 2 & 0 & \cdots & 0 \\ 0 & \mu_3 & 2\mu_2 & 3 & \cdots & 0 \\ 0 & \mu_4 & 2\mu_3 & 3\mu_2 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & & \vdots \\ 0 & \mu_N & 2\mu_{N-1} & 3\mu_{N-2} & \cdots & (N-1)\mu_2 \end{pmatrix}_N . \quad \text{(II.14)}$$

The substitution of Eq. (II.14) into Eq. (II.11) produces a new formula for generating the $B_l(N)$ that is well suited for computer calculations.

III. A Matrix Formula for the *N-P-T-* Virial Coefficients

We begin with Eq. (II.1), collecting all factors of the volume V:

$$Q(N, V, T) = \frac{1}{\Lambda^{3N}} \sum_{\{m_l\}}' V^m \prod_{l=1}^{N} \frac{(b_l')^{m_l}}{m_l!} ,$$

$$\Sigma l m_l = N,$$

$$\Sigma m_l = m. \quad \text{(III.1)}$$

We can write

$$Q(N, V, T) = \tilde{Q}(N, V, T) + \Delta Q(N, V, T), \quad \text{(III.2)}$$

where $\tilde{Q}(N, V, T)$ is formed from the volume independent integrals b_l and $\Delta Q(N, V, T)$ contains both the b_l and b_l'. From Eq. (II.3), we see that

$$\Delta Q(N, V, T) = 0 \quad \text{for} \quad L \geqslant L_N = aN \quad \text{or} \quad V \geqslant V_N . \tag{III.3}$$

The *N-P-T* partition function may be written as

$$Q(N, P, T) = z \int_0^\infty dVe^{-zV}Q(N, V, T) + z \int_0^{V_N} dVe^{-zV}\, \Delta Q(N, V, T)$$
$$= \frac{1}{\Lambda^{3N}} \left[\frac{1}{z^N} \sum_{\{m_l\}}' m! z^{N-m} \prod_{l=1}^{N} \frac{(b_l)^{m_l}}{m_l!} + z \int_0^{V_N} dVe^{-zV} \sum_{\{m_l\}}' V^m F_n(\{b_l'\}, \{b_l\})\right], \tag{III.4}$$

the primed summations indicating that the two restrictions in Eq. (III.1) are imposed [11]. F_N is some algebraic function of the b_l' and the b_l and z represents the independent variable P/k_BT. The exponential function in the last term can be expanded to give

$$\Delta Q(N, P, T) = \frac{1}{\Lambda^{3N}} \left[\frac{1}{z^N} \sum_{j=0}^{\infty} \frac{(-z)^{N+j+1}}{j!} \int_0^{V_N} dV \sum_{\{m_l\}}' V^{m+j} F_N(\{b_l'\}, \{b_l\})\right]. \tag{III.5}$$

If we factor out the term z^{-N} from Eqs. (III.4) and (III.5) we see that the lowest power of z occurring in Eq. (III.5) is z^{N+1} while the highest power of z occurring in the first term of Eq. (III.4) is z^{N-1} since the minimum value of m is 1. It is not difficult to show that if, in the virial expansion

$$\frac{\bar{V}}{N} = -\frac{1}{N}\left(\frac{\partial \ln Q(N, P, T)}{\partial z}\right)_{N,T} = \sum_{l=1}^{\infty} C_l(N)\, z^{l-2}, \tag{III.6}$$

we limit ourselves to the consideration of terms up to order z^{N-1}, we avoid the complication of the higher order terms due to Eq. (III.5) [12]. Thus the first term in Eq. (III.4) gives the correct virial expansion for terms up to order z^{N-1}. In the rest of this section we restrict our attention to these terms.

A new formula for $Q(N, P, T)$ can then be written in the form [8]

$$Q(N, P, T) = \frac{1}{\Lambda^{3N} z^N} \det \mathbf{P}_N$$

$$\mathbf{P}_N = \begin{Bmatrix} b_1 & -z & 0 & 0 & \cdots & 0 \\ b_2 & b_1 & -z & 0 & \cdots & 0 \\ b_3 & b_2 & b_1 & -z & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & & \vdots \\ b_N & b_{N-1} & b_{N-2} & b_{N-3} & \cdots & b_1 \end{Bmatrix}_N . \tag{III.7}$$

Following the procedure in Section II, the equation of state may be written as

$$\frac{\bar{V}}{N}=\frac{1}{z}-\frac{1}{N}\left(\frac{\partial \ln \Gamma_N}{\partial z}\right)_{N,T}=\frac{1}{z}-\frac{1}{N}\operatorname{Tr}\left[\mathbf{P}_N^{-1}\cdot\left(\frac{\partial \mathbf{P}_N}{\partial z}\right)_{N,T}\right]$$

$$\Gamma_N=\det \mathbf{P}_N, \tag{III.8}$$

where

$$\left(\frac{\partial \mathbf{P}_N}{\partial z}\right)_{N,T}=\mathbf{W}_N=-\begin{Bmatrix}0&1&0&0&\cdots&0\\0&0&1&0&\cdots&0\\0&0&0&1&\cdots&0\\\vdots&\vdots&\vdots&\vdots&&\vdots\\0&0&0&0&\cdots&0\end{Bmatrix}_N. \tag{III.9}$$

The virial expansion becomes

$$\frac{\bar{V}}{N}=\sum_{l=1}^{N+1}C_l(N)\,z^{l-2}=\frac{1}{z}+\sum_{l=2}^{N+1}\frac{(-1)}{N(l-2)!}\frac{\partial^{l-2}}{\partial z^{l-2}}(\operatorname{Tr}\mathbf{P}_N^{-1}\cdot\mathbf{W}_N)\Big|_{z=0}z^{l-2}$$

$$=\frac{1}{z}+\sum_{l=2}^{N+1}\frac{(-1)}{N(l-2)!}\operatorname{Tr}\left[\left(\frac{\partial^{l-2}\mathbf{P}_N^{-1}}{\partial z^{l-2}}\right)_{z=0}\cdot\mathbf{W}_N\right]z^{l-2}. \tag{III.10}$$

We use Eq. (II.10) to simplify Eq. (III.10) so that C_l $(l>1)$ in Eq. (III.10) becomes

$$C_l(N)=\frac{(-1)^{l-1}}{N}\operatorname{Tr}[\mathbf{P}_N^{-1}(0)\cdot\mathbf{W}_N]^{l-1},$$

$$\mathbf{P}_N(0)=\mathbf{P}_N(z)\,|_{z=0}, \tag{III.11}$$

which closely resembles Eq. (II.11). Again taking $b_1\equiv 1$, we have for $\mathbf{P}_N(0)$

$$\mathbf{P}_N(0)=\begin{Bmatrix}1&0&0&\cdots&0\\b_2&1&0&\cdots&0\\b_3&b_2&1&\cdots&0\\\vdots&\vdots&\vdots&&\vdots\\b_N&b_{N-1}&b_{N-2}&\cdots&1\end{Bmatrix}_N, \tag{III.12}$$

and $\mathbf{P}_N^{-1}(0)$ is given by

$$\mathbf{P}_N^{-1}(0) = \begin{pmatrix} 1 & 0 & 0 & \cdots & 0 \\ t_2 & 1 & 0 & \cdots & 0 \\ t_3 & t_2 & 1 & \cdots & 0 \\ t_4 & t_3 & t_2 & \cdots & 0 \\ \vdots & \vdots & \vdots & & \vdots \\ t_N & t_{N-1} & t_{N-2} & \cdots & 1 \end{pmatrix}_N ,$$

$$t_j = (-1)^{j-1} \begin{vmatrix} b_2 & 1 & 0 & \cdots & 0 \\ b_3 & b_2 & 1 & \cdots & 0 \\ b_4 & b_3 & b_2 & \cdots & 0 \\ \vdots & \vdots & \vdots & & \vdots \\ b_j & b_{j-1} & b_{j-2} & \cdots & b_2 \end{vmatrix}_{j-1} . \tag{III.13}$$

Thus $\mathbf{P}_N^{-1}(0) \cdot \mathbf{W}_N$ can be written as

$$\mathbf{P}_N^{-1}(0) \cdot \mathbf{W}_N = - \begin{pmatrix} 0 & 1 & 0 & 0 & \cdots & 0 \\ 0 & t_2 & 1 & 0 & \cdots & 0 \\ 0 & t_3 & t_2 & 1 & \cdots & 0 \\ 0 & t_4 & t_3 & t_2 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & & \vdots \\ 0 & t_N & t_{N-1} & t_{N-2} & \cdots & t_2 \end{pmatrix}_N . \tag{III.14}$$

The substitution of Eq. (III.14) into Eq. (III.11) gives us a matrix algorithm for generating the $C_l(N)$. This is also a new result.

Since most of the numerical results on virial coefficients are presented in terms of the irreducible cluster integrals β_k (for an infinite system), we express b_j in terms of the β_k [6]:

$$b_j = \frac{1}{j^2} \sum_{\{n_k\}}{}' \prod_{k=1}^{j-1} \frac{(j\beta_k)^{n_k}}{n_k!} ,$$

$$\sum_{k=1}^{j-1} k n_k = j - 1, \tag{III.15}$$

or in determinental form [8]:

$$b_j = \frac{1}{j^2(j-1)!} \begin{vmatrix} j\beta_1 & -1 & 0 & \cdots & 0 \\ 2jb_2 & j\beta_1 & -2 & \cdots & 0 \\ 3j\beta_3 & 2j\beta_2 & j\beta_1 & \cdots & 0 \\ 4j\beta_4 & 3j\beta_3 & 2j\beta_2 & \cdots & 0 \\ \vdots & \vdots & \vdots & & \vdots \\ (j-1)j\beta_{j-1} & (j-2)j\beta_{j-2} & (j-3)j\beta_{j-3} & \cdots & j\beta_1 \end{vmatrix}_{j-1} . \tag{III.16}$$

The β_k are defined by [6]

$$\beta_k = \frac{1}{k!V} \int \underset{V}{\cdots} \int S_{1,2,\cdots,k+1}\, d\mathbf{r}_1 \cdots d\mathbf{r}_{k+1}\,, \tag{III.17}$$

where $S_{1,2,\ldots,k+1}$ is defined as the sum over all products of Mayer f-functions such that for a particular product the f-bonds between the labeled points form a labeled graph on $k+1$ points distinct from any other labeled graph on $k+1$ points and which has at least two independent paths along f-bonds which do not cross at any point for each pair of labeled points in the labeled graph. We define the f-function by

$$f_{ij} = \exp(-\varphi_{ij}/k_B T) - 1, \tag{III.18}$$

where φ_{ij} is a pair potential.

The density-virial coefficients for an infinite system, $B_l(\infty)$ (see Eq. (II.9)), are related to the β_k by

$$B_l(\infty) = -\frac{l-1}{l}\beta_{l-1}\,. \tag{III.19}$$

IV. Algebraic Expressions for the Virial Coefficients $B_l(N)$ and $C_l(N)$

We now recall Wood's result for $B_l(N)$, $1 \leqslant l \leqslant 5$, described by Eq. (II.9) and Eq. (II.11) in terms of the $B_l(\infty)$ (or simply B_l) [1]:

$$\begin{aligned}
B_1(N) &= 1,\\
B_2(N) &= B_2 - B_2 N^{-1},\\
B_3(N) &= B_3 + (2B_2^2 - 3B_3)\, N^{-1} + (-2B_2^2 + 2B_3)\, N^{-2},\\
B_4(N) &= B_4 + (-4B_2^3 + 9B_2B_3 - 6B_4)\, N^{-1} + (16B_2^3 - 27B_2B_3 + 11B_4)\, N^{-2}\\
&\quad + (-12B_2^3 + 18B_2B_3 - 6B_4)\, N^{-3},\\
B_5(N) &= B_5 + (-24B_2^2B_3 + 9B_3^2 + 16B_2B_4 - 10B_5 + 8B_2^4)\, N^{-1}\\
&\quad + (192B_2^2B_3 - 51B_3^2 - 96B_2B_4 + 35B_5 - 80B_2^4)\, N^{-2}\\
&\quad + (-408B_2^2B_3 + 90B_3^2 + 176B_2B_4 - 50B_5 + 192B_2^4)\, N^{-3}\\
&\quad + (240B_2^2B_3 - 48B_3^2 - 96B_2B_4 + 24B_5 - 120B_2^4)\, N^{-4}.
\end{aligned} \tag{IV.1}$$

The $C_l(N)$ (see Eqs. (III.10) and (III.11)) for $1 \leqslant l \leqslant 7$, expressed in terms of the $C_l(\infty)$ (or simply C_l) are given by

$$\begin{aligned}
C_1(N) &= 1, \\
C_2(N) &= C_2 - C_2 N^{-1}, \\
C_3(N) &= C_3 + (C_2^2 - 2C_3)\, N^{-1}, \\
C_4(N) &= C_4 + (-C_2^3 + 3C_2C_3 - 3C_4)\, N^{-1}, \\
C_5(N) &= C_4 + (C_2^4 + 4C_3C_4 - 4C_3C_2^2 + 2C_3^2 - 4C_5)\, N^{-1}, \\
C_6(N) &= C_6 + (-C_2^5 + 5C_3C_2^3 - 5C_3^2C_2 - 5C_4C_2^2 \\
&\qquad + 5C_3C_4 + 5C_2C_5 - 5C_6)\, N^{-1}, \\
C_7(N) &= C_7 + (C_2^6 - 2C_3^3 + 9C_2^2C_3^2 - 6C_2^4C_3 + 6C_2^3C_4 - 12C_2C_3C_4 \\
&\qquad + 3C_4^2 - 6C_5C_2^2 + 6C_2C_6 + 6C_3C_5 - 6C_7)\, N^{-1}.
\end{aligned} \tag{IV.2}$$

The $C_l(\infty)$ may be expressed in terms of the more familiar $B_l(\infty)$, the relationship being [13]

$$\begin{aligned}
C_2 &= B_2, \\
C_3 &= B_3 - B_2^2, \\
C_4 &= B_4 - 3B_2B_3 + 2B_2^3, \\
C_5 &= B_5 - 4B_2B_4 + 10B_2^2B_3 - 2B_3^2 - 5B_2^4, \\
C_6 &= B_6 - 5B_2B_5 - 5B_3B_4 + 15B_2B_3^2 + 15B_2^2B_4 - 35B_2^3B_3 + 14B_2^5, \\
C_7 &= B_7 - 6B_2B_6 - 6B_3B_5 - 3B_4^2 + 7B_3^2 + 42B_2B_3B_4 + 21B_2^2B_5 - 84B_2^2B_3^2 \\
&\qquad - 56B_2^3B_4 + 126B_2^4B_3 - 42B_2^6.
\end{aligned} \tag{IV.3}$$

For hard spheres of diameter σ,

$$\begin{aligned}
B_2 &= \frac{2\pi}{3}\sigma^3, \\
B_2/B_2 &= 1, \\
B_3/B_2^2 &= 0.62500, \\
B_4/B_2^3 &= 0.28695, \\
B_5/B_2^4 &= 0.1103 \pm .0003, \\
B_6/B_2^5 &= 0.0386 \pm .0004, \\
B_7/B_2^6 &= 0.0138 \pm .0004 \quad [14],
\end{aligned} \tag{IV.4}$$

so that

$$C_2(N)/B_2 = 1 - N^{-1},$$

$$C_3(N)/B_2^2 = -0.3750 + 1.7500\, N^{-1},$$

$$C_4(N)/B_2^3 = 0.41195 - 3.3609\, N^{-1},$$

$$C_5(N)/B_2^4 = (-.56875 \pm .0003) + (6.7041 \pm .0012)\, N^{-1},$$

$$C_6(N)/B_2^5 = (0.8790 \pm .0019) + (-13.6490 \pm .0110)\, N^{-1},$$

$$C_7(N)/B_2^6 = (-1.4524 \pm .0102) + (28.1363 \pm .0751)\, N^{-1}, \tag{IV.5}$$

V. The Padé Approximation to the *N-P-T* Equation of State for Hard Spheres

Equation (III.10) may be written in the form

$$\frac{P\bar{V}}{Nk_BT} = 1 + z'[C_2/B_2 + (C_3/B_2^2)(z')^2 + \cdots] + \frac{z'}{N}[C_2^{(N)}/B_2 + (C_3^{(N)}/B_2^2)(z')^2 + \cdots], \tag{V.1}$$

where $z' = B_2 z$, the C_l are the *N-P-T* virial coefficients for the infinite system and $C_l^{(N)}$ is the coefficient of N^{-1} in $C_l(N)$ ($C_l(N) = C_l + C_l^{(N)} N^{-1}$).

We form the Padé approximation to Eq. (V.1) by introducing

$$\frac{P\bar{V}}{Nk_BT} = 1 + z'P^{(\infty)}(n, m) + \frac{z'}{N} P^{(N)}(n, m), \tag{V.2}$$

where the $P(n, m)$ are defined by [15]

$$P(n, m) = \frac{\sum_{i=1}^{n} \alpha_i (z')^i}{1 + \sum_{i=1}^{m} \gamma_i (z')^i}. \tag{V.3}$$

The α's and γ's are constants determined by the substitution of Eq. (V.3) into Eq. (V.1). For hard spheres, the $C_l(N)$ for $2 \leqslant l \leqslant 7$ are given by Eq. (IV.5) so for this system the α's and γ's are uniquely determined for $n + m \leqslant 7$.

Since we are dealing with a hard core system, it is convenient to introduce the close packed volume V_0 into Eqs. (V.2) and (V.3), where

$$V_0 = N\sigma^3/\sqrt{2} \tag{V.4}$$

for hard spheres of diameter σ. The variable z' may then be expressed as

$$z' = \frac{2\sqrt{2}\,\pi}{3}\varphi,$$
$$\varphi = PV_0/Nk_BT. \tag{V.5}$$

If we express Eq. (V.2) in terms of φ and define the dependent variable

$$\tau = \bar{V}/V_0, \tag{V.6}$$

Eq. (V.2) becomes

$$\tau\varphi = \varphi\tau^{(\infty)}(n, m) + \frac{\varphi}{N}\tau^{(N)}(n, m), \tag{V.7}$$

where

$$\tau^{(\infty)}(n, m) = \varphi^{-1} + \frac{2\sqrt{2}\,\pi}{3} P^{(\infty)}(n, m),$$
$$\tau^{(N)}(n, m) = \frac{2\sqrt{2}\,\pi}{3} P^{(N)}(n, m) \quad [16]. \tag{V.8}$$

TABLE I

The Padé Approximants $\tau^{(\infty)}(n, m)$ and $\tau^{(N)}(n, m)$ as a function of $\varphi = PV_0/Nk_BT$ for hard spheres in an N-P-T ensemble[a]

φ	$\tau^{(\infty)}(4, 3)$	$\tau^{(\infty)}(3, 4)$	$\tau^{(\infty)}(3, 3)$	$\tau^{(N)}(4, 3)$	$\tau^{(N)}(3, 4)$	$\tau^{(N)}(3, 3)$
.50	4.25	4.25	4.27	−.894	−.898	−.904
.75	3.43	3.44	3.47	−.669	−.679	−.692
1.00	2.99	2.99	3.05	−.529	−.549	−.567
1.25	2.68	2.70	2.79	−.429	−.461	−.485
1.50	2.45	2.48	2.61	−.352	−.398	−.426
2.00	2.12	2.19	2.37	−.235	−.313	−.349
3.00	1.67	1.82	2.13	−.070	−.220	−.266

[a] V_0 is the close packed volume, P is the pressure, N the number of spheres, k_B Boltzmann's constant and T is the absolute temperature.

Table I gives the $\tau^{(\infty)}$ and $\tau^{(N)}$ as a function of φ for various n and m. We restrict our attention to the cases $n = m \pm 1$ and $n = m$, since these produce the most consistent results. The stability of the Padé approximation is remarkable considering the fact that the C_l and $C_l^{(N)}$ in Eq. (IV.5) alternate in sign and increase in absolute value as l increases. The largest deviation from the arithmetic mean of $\tau^{(\infty)}$ at $\varphi = 2$ is 6.3 % of the mean.

A comparison between Table I and the molecular dynamics studies of Alder and Wainwright [2] can be made in the region where N is so large that finite N effects can be neglected and $\tau^{(\infty)}(4, 3)$, $\tau^{(\infty)}(3, 4)$ and $\tau^{(\infty)}(3, 3)$ can be taken as constant for a given φ. For $\varphi = 1.00$, Table I gives $P\bar{V}/Nk_BT \approx 3.01$ while Alder and Wainwright give $PV/Nk_BT \approx 3.05$.

For larger values of φ ($\varphi > 2$) agreement with the molecular dynamics results seems to be rather poor when compared with the agreement Ree and Hoover oqtained with a Padé treatment of the 6 and 7 term virial series in an N-V-T formalism [14]. However, the main test of the usefulness of the N-P-T formalism will be the comparison of Eqs. (V.7) and (V.8) with the results of computer experiments performed directly in the N-P-T ensemble.

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