Explicit and Implicit Finiteness Corrections of Virial Coefficients

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The equation of state of finite systems deviates from thermodynamic limit. The corresponding finiteness corrections of virial coefficients are studied. Most calculations are based on the canonical ensemble with periodic boundary conditions. *Explicit* and *implicit* finiteness corrections occur. They are displayed up to the eighth virial coefficient. These results are applied to hard spheres in one, two, and three dimensions.

1. INTRODUCTION

In this paper, the pressure P will be considered for gaseous systems in the canonical ensemble. In the thermodynamic limit TDL,

$$P_{\text{TDL}} = k_B T \sum_{i=1}^{\infty} B_i \rho^i, \qquad B_1 = 1 \tag{1}$$

T is the absolute temperature, ρ the number density, k_B Boltzmann's constant. The virial coefficients B_i are functions of temperature. This functional dependence is suppressed in the notation since T is regarded as arbitrary, but fixed parameter throughout the paper.

We are interested in the pressure of a finite one-component system (particle number N, volume V, thus $\rho = N/V$). For simplicity we assume a pairwise additive potential,

$$U(\mathbf{r}_1, \mathbf{r}_2,..., \mathbf{r}_N) = \sum_{1 \leqslant i < j \leqslant N} u_{ij}(r_{ij}) \tag{2}$$

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379

u_{ij} being the spherically symmetrical pair interaction energy. It is convenient to define[1,2]

$$f_{ij} \equiv \exp(-u_{ij}/k_B T) - 1 \qquad (3)$$

The canonical partition function Q and its configurational (spatial) part Q^{conf} will be studied for quasiclassical systems, the tilde in $\tilde{V}$ refers to the shape of the volume which *also* influences the thermodynamic quantities in finite systems (dimension D):

$$Q = (N!)^{-1}(2\pi m k_B T/h^2)^{DN/2} Q^{\text{conf}} \qquad (4a)$$

$$Q^{\text{conf}} \equiv \int_{\tilde{V}} \cdots \int_{\tilde{V}} d\mathbf{r}_1 \cdots d\mathbf{r}_N \exp(-U/k_B T)$$

$$= \int_{\tilde{V}} \cdots \int_{\tilde{V}} d\mathbf{r}_1 \cdots d\mathbf{r}_N \prod_{1 \leqslant i < j \leqslant N} (1 + f_{ij}) \qquad (4b)$$

Pressure P is given by[1,2]

$$P = k_B T(\partial \ln Q/\partial V)|_{N,T,\text{shape}} = k_B T(\partial \ln Q^{\text{conf}}/\partial V)|_{N,T,\text{shape}} \qquad (5)$$

As a first step, the product $\prod(1 + f_{ij})$ occurring in Q^{conf} is expanded in a sum of f products. This results in a virial expansion of Q^{conf}, the first terms being proportional to

$$B_2^+(\tilde{V}) = -\frac{1}{2V} \iint d\mathbf{r}_1 d\mathbf{r}_2 f_{12} \qquad (6a)$$

$$B_3^+(\tilde{V}) = -\frac{1}{3V} \iiint d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 f_{12} f_{13} f_{23} \qquad (6b)$$

$$B^+(\tilde{V}) = \frac{1}{4V} \iiint d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 f_{12} f_{13} \qquad (6c)$$

In homogeneous systems, each point is equivalent. Then, the above expressions are simplified to

$$B_2^+(\tilde{V}) = -\tfrac{1}{2} \int d\mathbf{r}_2 f_{12} \qquad (7a)$$

$$B_3^+(\tilde{V}) = -\tfrac{1}{3} \iint d\mathbf{r}_2 d\mathbf{r}_3 f_{12} f_{13} f_{23} \qquad (7b)$$

$$B^+(\tilde{V}) = [B_2^+(\tilde{V})]^2 \qquad (7c)$$

Homogeneity is valid for periodic and spherical boundary conditions.[3,4] In the thermodynamic limit, the above expressions turn into

$$B_2^+(\tilde{V}) \xrightarrow{\text{TDL}} B_2, \qquad B_3^+(\tilde{V}) \xrightarrow{\text{TDL}} B_3, \qquad B^+(\tilde{V}) \xrightarrow{\text{TDL}} B_2^2 \tag{8}$$

[cf. Eq. (1)]. Now, we turn to the full finiteness dependence. Expanding Q^{conf} yields

$$Q^{\text{conf}}/V^N = 1 - \left\{ \binom{N}{2} 2B_2^+(\tilde{V}) \right\} V^{-1} + \left\{ \binom{N}{3} [12B^+(\tilde{V}) - 3B_3^+(\tilde{V})] \right.$$
$$\left. + 3 \binom{N}{4} [2B_2^+(\tilde{V})]^2 \right\} V^{-2} + O(V^{-3}) \tag{9}$$

$\binom{N}{i}$ being combinatorial factors. Accordingly,

$$\ln Q^{\text{conf}} = N \ln V - \{N(N-1) B_2^+(\tilde{V})\} V^{-1}$$
$$+ \{A - \tfrac{1}{2}N(N-1)(N-2) B_3^+(\tilde{V})\} V^{-2} + O(V^{-3}) \tag{10a}$$

$$A \equiv N(N-1)\{(2N-4) B^+(\tilde{V}) - (2N-3)[B_2^+(\tilde{V})]^2\} \tag{10b}$$

For homogeneous systems,

$$A = -N(N-1)[B_2^+(\tilde{V})]^2 \tag{11}$$

[cf. (7c)]. The virial expansion of pressure follows from (5):

$$P = k_B T(\partial \ln Q^{\text{conf}}/\partial V) = k_B T \sum_{i=1}^{\infty} B_i(N, \tilde{V}) \rho^i \tag{12}$$

with

$$B_1(N, \tilde{V}) = B_1 = 1 \tag{13a}$$

$$B_2(N, \tilde{V}) = (1 - N^{-1}) B_2(\tilde{V}) \tag{13b}$$

$$B_3(N, \tilde{V}) = (1 - N^{-1})(4 - 6N^{-1})B_2^+(\tilde{V}) B_2(\tilde{V}) - (1 - N^{-1})(4 - 8N^{-1})B(\tilde{V})$$
$$+ (1 - N^{-1})(1 - 2N^{-1}) B_3(\tilde{V}) \tag{13c}$$

The quantities $B_m(\tilde{V})$ and $B(\tilde{V})$ are defined by

$$B_m(\tilde{V}) \equiv B_m^+(\tilde{V}) - (m-1)^{-1} V[\partial B_m^+(\tilde{V})/\partial V], \qquad m \geqslant 2 \tag{14a}$$

$$B(\tilde{V}) \equiv B^+(\tilde{V}) - \tfrac{1}{2}V[\partial B^+(\tilde{V})/\partial V] \tag{14b}$$

For homogeneous systems,

$$B_3(N, \tilde{V}) = 2N^{-1}(1 - N^{-1}) B_2^+(\tilde{V}) B_2(\tilde{V}) + (1 - N^{-1})(1 - 2N^{-1}) B_3(\tilde{V}) \tag{15}$$

Except for Section 4, we restrict ourselves to the homogeneous case. Then quantities like $B^+(\tilde{V})$ need not be considered particularly. The virial coefficients $B_i(N, \tilde{V})$ deviate from B_i in two ways:

(i)   Polynomials in N^{-1} come in which are absent in the TDL; cf. (13). These polynomials come from combinatorial factors, Eq. (9). The resulting finiteness dependence is called *normal, explicit* or *N dependence*.

(ii)   The cluster integrals[2] occurring in $B_m^+(\tilde{V})$ and $B_m(\tilde{V})$ are volume dependent. The corresponding finiteness effect is called *anomalous, implicit* or *V dependence*.

The explicit correction has been known for a long time.[5] It results when the implicit dependence is suppressed:

$$P_{(N)} = k_B T \sum_{i=1}^{\infty} B_i(N) \rho^i \tag{16}$$

with

$$B_1(N) = B_1 = 1 \tag{17a}$$

$$B_2(N) = (1 - N^{-1}) B_2 \tag{17b}$$

$$B_3(N) = 2N^{-1}(1 - N^{-1}) B_2^2 + (1 - N^{-1})(1 - 2N^{-1}) B_3 \tag{17c}$$

In this section, $B_i(N, \tilde{V})$ have only be displayed for $i \leqslant 3$. With increasing i, the problem becomes drastically more complicated. The calculations split up into two parts: First, the explicit finiteness correction has to be evaluated. This will be treated in Section 2. Second, appropriate $B_m^+(\tilde{V})$ and $B_m(\tilde{V})$ have to be substituted for the B_m occurring in $B_i(N)$. This will be done in Section 3. In Sections 4 and 5, the results will be applied to hard spheres in one, two, and three dimensions.

2. EXPLICIT FINITENESS CORRECTION

The explicit finiteness dependence has already been studied in Refs. 5–9 in a formal way. Especially in Refs. 8 and 9 formulas are given which make it possible to calculate $B_i(N)$. However, they use the round-

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[2] Unlike $m = 2$ and 3, Eqs. (6a, b), more than one cluster integral contributes to $B_m^+(\tilde{V})$ for $m > 3$; cf. (4, 6).

about way via cluster integrals, the number of which is quickly increasing with i. Correspondingly, Hubbard[8,9] displays the results only up to $i = 5$. It is the aim of the present paper to obtain $B_i(N)$ up to $i = 8$. Thus, a simpler algorithm is desirable.

First, we use the fact[6,10] that $B_i(N)$ can be expressed as

$$B_i(N) = B_i + \sum_{j=1}^{i-1} \Delta B_{i,j} N^{-j} = \sum_{j=0}^{i-1} \Delta B_{i,j} N^{-j} \tag{18}$$

$\Delta B_{i,j}$ are the coefficients of the polynomial in N^{-1}, $\Delta B_{i,0} \equiv B_i$. $\Delta B_{i,j}$ are functions of $(B_2,..., B_i)$, $i \geqslant 2$. It is not necessary to express the B_m in terms of cluster integrals. In the following, $B_i(N)$ will be needed as functions of V and ρ:

$$B_i(N) = \sum_{j=0}^{i-1} \Delta B_{i,j} V^{-j} \rho^{-j} \tag{19}$$

Thus

$$P_{(N)}/k_B T = \sum_{i=1}^{\infty} \sum_{j=0}^{i-1} \Delta B_{i,j} V^{-j} \rho^{i-j} = \sum_{j=0}^{\infty} V^{-j} \sum_{l=1}^{\infty} \Delta B_{l+j,j} \rho^l \tag{20}$$

l being substituted for $i - j$. Furthermore, we need the series expansion of compressibility,

$$k_B T (\partial P_{\mathrm{TDL}}/\partial \rho)^{-1} = \left[\sum_{t=1}^{\infty} t B_t \rho^{t-1} \right]^{-1} \equiv \sum_{s=1}^{\infty} C_s \rho^{s-1} \tag{21a}$$

$$C_1 = 1, \qquad C_2 = -2B_2, \qquad C_s = C_s(B_2,..., B_s), \qquad s \geqslant 2 \tag{21b}$$

The coefficients C_s have also been considered in Ref. 11. For $s > 2$, the explicit functional form $C_s = C_s(B_2,..., B_s)$ will not be given here.

From Eq. (3.25) of Ref. 6, a relation between $P_{(N)}$ and P_{TDL} can be deduced, pressure being regarded as function of ρ and V:

$$P_{\mathrm{TDL}}(\rho) = \mathcal{O} P_{(N)}(\rho, V) \tag{22a}$$

$$\mathcal{O} = \exp \left\{ \sum_{k=1}^{\infty} V^{-k} [(k+1)!]^{-1} (F^k \rho) \left(\frac{\partial}{\partial \rho} \right)^{k+1} \right\} \tag{22b}$$

$$F^k \rho = \left\{ \left(\sum_{s=1}^{\infty} C_s \rho^s \right) \left(\frac{\partial}{\partial \rho} \right) \right\}^k \rho \tag{22c}$$

When the exponential (22b) is expanded, the corresponding products of $(\partial/\partial\rho)^{k+1}$ are meant to be shifted to the right,[6] thus directly operating on

$P_{(N)}$. As to F^k operating on ρ, Eq. (22c), the $k$fold product is interpreted in the usual way, e.g.,

$$F^2\rho = \left[\sum_{s=1}^{\infty} C_s \rho^s \left(\frac{\partial}{\partial \rho} \right) \right] \left[\sum_{t=1}^{\infty} C_t \rho^t \left(\frac{\partial}{\partial \rho} \right) \right] \rho = \sum_{s=1}^{\infty} C_s \rho^s \sum_{t=1}^{\infty} t C_t \rho^{t-1} \qquad (23)$$

Equation (22a) can formally be inverted to yield $P_{(N)}$ as $\mathcal{O}^{-1}P_{\mathrm{TDL}}$ as proposed in Ref. 6. It is preferable, however, to proceed in another way. The solution of (22a) is already known [cf. (20)], only the $\Delta B_{i,j}$ have to be determined explicitly. This can be done by inserting the expansion for $P_{(N)}$ and P_{TDL} in (22a). This yields an identity with indeterminate coefficients $\Delta B_{i,j}$, each power of V^{-1} and ρ yielding a relation which determines a coefficient:

$$-\sum_{n=1}^{\infty} V^{-n} \sum_{s=1}^{\infty} \Delta B_{s+n,n} \rho^s = \sum_{m=1}^{\infty} \frac{1}{m!} \left\{ \sum_{k=1}^{\infty} V^{-k} \frac{1}{(k+1)!} (F^k\rho) \left(\frac{\partial}{\partial \rho} \right)^{k+1} \right\}^m$$

$$\times \left(\sum_{j=0}^{\infty} V^{-j} \sum_{l=1}^{\infty} \Delta B_{l+j,j} \rho^l \right) \qquad (24)$$

To obtain (24), the leading term of the exponential [$m = 0$; cf. (22b)] has been taken into account separately, the result being shifted to the left-hand side. Equation (24) looks rather complicated, but in fact serves as a useful tool to determine $\Delta B_{..}$ iteratively. Concentrating on the powers of V^{-1}, we notice that $n > j$. Thus, unknown $\Delta B_{.,n}$ can be traced back to $\Delta B_{.,j}$ with $n > j$. The recursion ends at $j = 0$, $\Delta B_{i,0}$ being the virial coefficients B_i themselves.

The case $n = 1$ will be treated explicitly. This induces $m = k = 1$ and $j = 0$ on the right-hand side of (24). Thus, the identity (for terms proportional to V^{-1}) reads

$$-\sum_{s=1}^{\infty} \Delta B_{s+1,1} \rho^s = \frac{1}{2} \sum_{t=1}^{\infty} C_t \rho^t \sum_{l=1}^{\infty} l(l-1) B_l \rho^{l-2} \qquad (25)$$

The first nonvanishing term of the last sum occurs for $l = 2$. With $r \equiv l - 2$,

$$-\sum_{s=1}^{\infty} \Delta B_{s+1,1} \rho^s = \sum_{t=1}^{\infty} C_t \rho^t \sum_{r=0}^{\infty} \binom{r+2}{2} B_{r+2} \rho^r \qquad (26)$$

Now the powers of ρ have to be identified. $s = 1$ induces $t = 1$ and $r = 0$. Thus,

$$-\Delta B_{2,1} = C_1 B_2 = B_2 \qquad (27)$$

which confirms (17b). $s = 2$ corresponds to $(t = 2, r = 0)$ or $(t = 1, r = 1)$. Thus,

$$-\Delta B_{3,1} = C_2 B_2 + 3C_1 B_3 = -2B_2^2 + 3B_3 \tag{28}$$

cf. (21b). The result is consistent with Eq. (17c). Determining $\Delta B_{i,1}$ for increasing i gets more complicated, but we calculated all cases up to $i = 10$ without too much trouble. In this paper, the results will be given for $i \leqslant 8$.

Now we return to (24). If $n = 2$, this induces three possible cases on the right-hand side: $(m = k = j = 1)$, $(m = 1, k = 2, j = 0)$ and $(m = 2, k = 1, j = 0)$. The first case, however, is analogous to $n = 1$, only $j = 1$ instead of 0. Generally, part of the calculations necessary for n have in fact already been done in the case $n - 1$. Thus, the complexity is not growing too fast with n. $\Delta B_{i,n}$ up to $i = 8$ ($n < i$) have been calculated explicitly. The results for $i \leqslant 5$ are just a check since they are already known,[8,9] the results for $i = 6$ to 8 are new.

It has already been mentioned that $\Delta B_{i,n}$ are functions of $(B_2, ..., B_i)$. This can be made more concrete. For combinatorial reasons, the general form of the solution is

$$B_i(N) = \sum_{n=0}^{i-1} N^{-n} \Delta B_{i,n} = \sum_{n=0}^{i-1} N^{-n} \sum_{k=1}^{K(i)} a_{i,n,k} \prod_{l=1}^{L(k)} B_{I_{ik}(l)}, \qquad i \geqslant 2 \tag{29}$$

where $l \to I_{ik}(l)$ is the kth decomposition of $(i - 1)$ satisfying[4]

$$\sum_{l=1}^{L(k)} [I_{ik}(l) - 1] = i - 1, \qquad I_{ik}(l) \geqslant 2 \tag{30}$$

Thus, calculating the explicit finiteness correction means evaluating the numbers $a_{i,n,k}$. Again, (29) looks more complicated than it is in practice. First we turn to the products occurring in (29). For $i = 2$, Eq. (30) has only one solution. Thus, $K(2) = 1$ and $L(1) = 1$. The "product" is just B_2 itself. For $i = 3$, the products $B_2 B_2 = B_2^2$ and B_3 fulfil (30). Arbitrarily, $B_2 B_2$ is called the first product ($k = 1$), B_3 the second one ($k = 2$). Then, $L(1) = 2$ and $L(2) = 1$ [cf. (29)]. Two products occur for $i = 3$, thus $K(3) = 2$. The solution for $i = 2$ and $i = 3$ is

$$a_{2,0,1} = 1, \qquad a_{2,1,1} = -1, \qquad a_{3,0,1} = 0, \qquad a_{3,0,2} = 1$$
$$a_{3,1,1} = 2, \qquad a_{3,1,2} = -3, \qquad a_{3,2,1} = -2, \qquad a_{3,2,2} = 2 \tag{31}$$

which is just another representation of Eqs. (17b, c). The results for $4 \leqslant i \leqslant 8$ are displayed in Tables I–V. Instead of the formal number k, the kth product $\prod B_m$ is explicitly stated in any case. m is just an abbreviation

<table>
<tr><td colspan="4">Table I. $B_4(N)$, Expressed
in Terms of $a_{4,n,k}$
Compare Eq. (29)</td></tr>
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n	B_2^3	$B_2 B_3$	B_4
0			1
1	−4	9	−6
2	16	−27	11
3	−12	18	6

Table II. $B_5(N)$, Expressed in Terms of $a_{5,n,k}$

n	B_2^4	$B_2^2 B_3$	$B_2 B_4$	B_3^2	B_5
0					1
1	8	−24	16	9	−10
2	−80	192	−96	−51	35
3	192	−408	176	90	−50
4	−120	240	−96	−48	24

of $I_{ik}(l)$. The $a_{i,n,k}$ turn out to be integers. Furthermore, the tables reveal several *sum rules* for the $a_{i,n,k}$. For instance, the sum of all columns is zero. The sum of the first row is 1, of the second row is -1. The sum of the further rows vanishes. One may conjecture that these sum rules are generally valid. This is in fact true. For instance, we look on the first row, i.e., $n = 0$,

$$B_i = \lim_{N \to \infty} B_i(N) = \sum_k a_{i,0,k} \prod_l B_{I_{ik(l)}} \tag{32}$$

which induces that $a_{i,0,k}$ connected with $\prod B_m = B_i$ is 1, all others are zero. Thus, the sum of the first row is 1. As to the other rows, see Section 4. Now we study the columns. The sum of the kth column is

$$\sum_{n=0}^{i-1} a_{i,n,k} = \sum_{n=0}^{i-1} 1^{-n} a_{i,n,k} \tag{33}$$

This is the total contribution of the kth product $\prod B_m$ to $B_i(N)$ if $N = 1$. If all these sums are zero, this means that no product contributes to $B_i(N = 1)$, $i \geqslant 2$. Thus,

$$P_{(N=1)} = k_B T(1 + 0) = k_B T \tag{34}$$

Table III. $B_6(N)$, Expressed in Terms of $a_{6,n,k}$

n	B_2^5	$B_2^3 B_3$	$B_2^2 B_4$	$B_2 B_3^2$	$B_2 B_5$	$B_3 B_4$	B_6
0							1
1	−16	60	−40	−45	25	30	−15
2	320	−1 000	540	585	−250	−280	85
3	−1 680	4 680	−2 240	−2 340	875	930	−225
4	3 056	−7 940	3 540	3 600	−1 250	−1 280	274
5	−1 680	4 200	−1 800	−1 800	600	600	−120

Table IV. $B_7(N)$, Expressed in Terms of $a_{7,n,k}$

n	B_2^6	$B_2^4 B_3$	$B_2^3 B_4$	$B_2^2 B_3^2$	$B_2^2 B_5$	$B_2 B_3 B_4$	$B_2 B_6$	B_3^3	$B_3 B_5$	B_4^2	B_7
0											1
1	32	−144	96	162	−60	−144	36	−27	45	24	−21
2	−1 120	4 320	−2 432	−3 996	1 230	2 808	−540	513	−630	−328	175
3	10 752	−37 296	18 912	30 132	−8 400	−18 288	3 060	−3 240	3 375	1 728	−735
4	−40 000	129 168	−61 312	−95 094	25 050	52 488	−8 100	9 054	−8 550	−4 328	1 624
5	60 576	−186 768	85 056	129 276	−32 940	−67 104	9 864	−11 340	10 080	5 064	−1 764
6	−30 240	90 720	−40 320	−60 480	15 120	30 240	−4 320	5 040	−4 320	−2 160	720

Table V. $B_8(N)$, Expressed in Terms of $a_{8,n,k}$

n	B_2^7	$B_2^5 B_3$	$B_2^4 B_4$	$B_2^3 B_3^2$	$B_2^3 B_5$	$B_2^2 B_3 B_4$	$B_2^2 B_6$
1	−64	336	−224	−504	140	504	−84
2	3 584	−16 464	9 520	21 000	−5 040	−17 472	2 436
3	−56 448	235 200	−124 124	−266 112	58 940	196 623	−24 780
4	365 120	−1 417 920	704 312	1 469 580	−310 800	−1 002 246	118 860
5	−1 084 608	4 008 144	−1 912 148	−3 900 708	802 760	2 518 677	−287 616
6	1 437 696	−5 137 776	2 387 112	4 787 496	−969 360	−2 979 774	332 304
7	−665 280	2 328 480	−1 064 448	−2 110 752	423 360	1 283 688	−141 120

n	$B_2 B_3^3$	$B_2 B_3 B_5$	$B_2 B_4^2$	$B_2 B_7$	$B_3^2 B_4$	$B_3 B_6$	$B_4 B_5$	B_8
0								1
1	189	−210	−112	49	−126	63	70	−28
2	−6 426	5 775	3 024	−1 029	3 339	−1 239	−1 330	322
3	69 741	−55 860	−28 847	8 575	−30 933	9 765	10 220	−1 960
4	−343 035	256 725	131 334	−36 015	136 731	−39 165	−40 250	6 769
5	836 325	−600 390	−305 277	79 576	−309 645	83 412	84 630	−13 132
6	−966 546	676 200	342 510	−86 436	340 242	−88 116	−88 620	13 068
7	409 752	−282 240	−142 632	35 280	−139 608	35 280	35 280	−5 040

This corresponds to the ideal gas law. This law is really valid for any interaction potential as long as only one particle is present since no interaction takes place then.

Much more can be said about the $a_{i,n,k}$. When expanding Q^{conf}, the cluster integrals with s integration variables [cf. Eqs. (6)] are multiplied by a combinatorial factor which contains $N(N-1)\cdots(N-s+1)$. This may be checked when comparing (4b) with (9). When taking the logarithm $\ln Q^{\text{conf}}$ and differentiating with respect to V, Eq. (5), this property essentially survives. The correct formulation for the $B_i(N)$ is as follows: Any product $\prod B_m$ contributing to $B_i(N)$ is connected with a factor that contains $\prod [1 - (j/N)]$, $1 \leqslant j \leqslant m_{\max} - 1$, $m_{\max} = \max(m)$ of the product considered.

Example 1. B_2^2 and B_3 contribute to $B_3(N)$. Equation (17c) confirms that $(1 - N^{-1})$ is contained in the contribution of B_2^2, $(1 - N^{-1})(1 - 2N^{-1})$ of B_3. Since $B_3(N \to \infty) = B_3$, $(1 - N^{-1})(1 - 2N^{-1})$ is the whole factor of B_3, and the factor of B_2^2 must additionally contain N^{-1} (already mentioned properties "of the first row"). Apart from the factor 2 occurring in the contribution of B_2^2, all other factors can thus be predicted just on reflection.

Example 2. If we look at Table II, the contribution of $B_2 B_4$ can be written as $(16N^{-1} - 96N^{-2} + 176N^{-3} - 96N^{-4}) B_2 B_4$. In fact, this contains $(1 - N^{-1})(1 - 2N^{-1})(1 - 3N^{-1})$:

$$16N^{-1} - 96N^{-2} + 176N^{-3} - 96N^{-4}$$
$$= 16N^{-1}(1 - N^{-1})(1 - 2N^{-1})(1 - 3N^{-1}) \tag{35}$$

Since $m_{\max} \geqslant 2$, the contribution of *any* product is at least proportional to $(1 - N^{-1})$, which induces the sum rule for the columns [cf. (33)].

The above regularities of $a_{i,n,k}$ have considerable physical consequences: If virial coefficients $B_i(N)$ are considered with $i > N$, then $m_{\max} > N$ in at least one product contributing. Thus, integrals over $m_{\max}$ points ("particles") occur even when not so many particles are physically present. However, owing to the combinatorial factor, the contribution of the corresponding products vanishes. Thus, one need not worry about any contradiction between mathematical and physical clusters.

3. FULL FINITENESS CORRECTION

Incorporating the implicit finiteness correction is not so difficult as it seems to be. In fact, this problem has already been solved formally.[4] In the present paper, the solution will be displayed in a more intuitive way.

We start with the explicit correction. $B_i(N)$ is a virial coefficient of $P_{(N)}$ [cf. (16)]. Equation (29) shows the expansion of $B_i(N)$ in terms of N^{-1} and products $\prod B_m$. In the following, we concentrate on these products, the other quantities are not changed when incorporating the implicit correction. In a first step, all B_m are substituted by $B_m^+(\tilde{V})$. The corresponding virial coefficients will be termed $B_i^+(N, \tilde{V})$:

$$P^+ = k_B T \sum_{i=1}^{\infty} B_i^+(N, \tilde{V}) \rho^i, \qquad B_1^+(N, \tilde{V}) = 1 \tag{36}$$

P^+ is not yet the true pressure P defined in Eq. (5). To obtain $B_i(N, \tilde{V})$ and thus P, a second step is necessary, i.e., the substitution

$$\prod_{l=1}^{L(k)} B_{I_{ik(l)}}^+(\tilde{V}) \rightarrow \sum_{l=1}^{L(k)} \left[\frac{I_{ik(l)} - 1}{i - 1} \right] B_{I_{ik(l)}}(\tilde{V}) \prod_{j \neq l} B_{I_{ik(j)}}^+(\tilde{V}) \tag{37}$$

[cf. (29)]. The product of $L(k)$ coefficients $B_m^+(\tilde{V})$ splits up into $L(k)$ products with one $B_m(\tilde{V})$, Eq. (14a), and $L(k) - 1$ coefficients $B_m^+(\tilde{V})$. If $i = 4$, the products $B_2 B_2 B_2$, $B_2 B_3$, and B_4 occur (cf. Table I). Then, the two steps mentioned are

$$B_2 B_2 B_2 \rightarrow B_2^+(\tilde{V}) B_2^+(\tilde{V}) B_2^+(\tilde{V}) \rightarrow B_2(\tilde{V}) B_2^+(\tilde{V}) B_2^+(\tilde{V}) \tag{38a}$$

$$B_2 B_3 \rightarrow B_2^+(\tilde{V}) B_3^+(\tilde{V}) \qquad \rightarrow \tfrac{1}{3} B_2(\tilde{V}) B_3^+(\tilde{V}) + \tfrac{2}{3} B_2^+(\tilde{V}) B_3(\tilde{V}) \tag{38b}$$

$$B_4 \rightarrow B_4^+(\tilde{V}) \qquad \rightarrow B_4(\tilde{V}) \tag{38c}$$

Thus, the full finiteness correction can be constructed on the basis of the explicit correction alone. Accordingly, Tables I–V can also be used for the full correction, the designation of the columns has only to be changed using the two steps; see (38) for Table I. In this sense, N and V dependences occur separately. Especially, all sum rules treated in Section 2 remain valid. Therefore, coefficients $B_m^+(\tilde{V})$ or $B_m(\tilde{V})$ formally contributing to $B_i(N, \tilde{V})$ do *not really* contribute if $m > N$. The combinatorial factor is zero then. This has been overlooked in Ref. 6. Thus, one need not distinguish between $k \leqslant N$ and $k > N$ in Eq. (3.2) of that reference, and the comments after (3.29) are also not valid. In fact, the method proposed in (3.25) is correct and yields the true finiteness corrections.

Up to now, P_{TDL}, $P_{(N)}$, P^+, and P have been considered. In $P_{(N)}$, the implicit correction is suppressed. On the other hand, suppressing the explicit correction in P^+ and P, i.e., taking the limit $N \rightarrow \infty$, yields $P_{(V)}^+$ and $P_{(V)}$, respectively:

$$P_{(V)}^+ = k_B T \sum_{i=1}^{\infty} B_i^+(\tilde{V}) \rho^i, \qquad B_1^+(\tilde{V}) = 1 \tag{39a}$$

$$P_{(V)} = k_B T \sum_{i=1}^{\infty} B_i(\tilde{V}) \rho^i, \qquad B_1(\tilde{V}) = 1 \tag{39b}$$

This follows from the properties "of the first row." To obtain this consistent formulation, the notation $B_i^+(\tilde{V})$ and $B_i(\tilde{V})$ has been introduced when defining volume-dependent virial coefficients in Section 1.

There is an interesting connection between $P_{(V)}$ and the pressure P_g in the grand canonical ensemble.[6] The partition function $\Xi = \Xi(\mu, \tilde{V}, T)$ in this ensemble is given by

$$\Xi(\mu, \tilde{V}, T) = \sum_{N=0}^{\infty} \exp(\mu N / k_B T)\, Q(N, \tilde{V}, T) \qquad (40)$$

μ being the chemical potential. As to $Q = Q(N, \tilde{V}, T)$; see Eqs. (4). Unlike the canonical ensemble, N and thus ρ is fluctuating now. The mean value shall be denoted by ρ_g. The connection between pressure and partition function is

$$P_g^+ = k_B T V^{-1} \ln \Xi \qquad (41a)$$

$$P_g = k_B T (\partial \ln \Xi / \partial V)\big|_{\mu, T, \text{shape}} \qquad (41b)$$

P_g is the *correct* pressure in the finite system, P_g^+ is the *usual* pressure considered,[6] which is equal to P_g only in the thermodynamic limit, but is more directly related to Ξ. If the grand canonical ensemble is characterized by $(\rho_g, \tilde{V}_g, T_g)$ and the canonical ensemble by $(\rho, \tilde{V}, T)$, the following relations hold:

$$(\rho_g, \tilde{V}_g, T_g) = (\rho, \tilde{V}, T): \qquad P_g^+ = P_{(V)}^+, \qquad P_g = P_{(V)} \qquad (42)$$

Thus the two ensembles are characterized by the same implicit finiteness correction, the explicit correction being absent in the grand canonical ensemble. By the way, P_g is identical to the average of the canonical P over the grand canonical ensemble.[6]

Now, we turn to the deviations from thermodynamic limit (in the canonical ensemble):

$$\Delta P_{(N)} \equiv P_{(N)} - P_{\text{TDL}} \qquad (43a)$$

$$\Delta P_{(V)}^+ \equiv P_{(V)}^+ - P_{\text{TDL}} \qquad (43b)$$

$$\Delta P_{(V)} \equiv P_{(V)} - P_{\text{TDL}} \qquad (43c)$$

Usually, these deviations are small compared with P_{TDL}. Then, their influence on the whole finiteness correction will be additive:

$$P^+ = P_{\text{TDL}} + \Delta P_{(N)} + \Delta P_{(V)}^+ + \Delta P_{(NV)}^+ \approx P_{\text{TDL}} + \Delta P_{(N)} + \Delta P_{(V)}^+ \quad (44a)$$

$$P = P_{\text{TDL}} + \Delta P_{(N)} + \Delta P_{(V)} + \Delta P_{(NV)} \approx P_{\text{TDL}} + \Delta P_{(N)} + \Delta P_{(V)} \quad (44b)$$

the small cross-terms $\Delta P_{(NV)}^+$ and $\Delta P_{(NV)}$ being negligible. This has already been used in Refs. 10 and 12 for hard disks with periodic boundary conditions. Hard-core potentials are especially appropriate for neglect of $\Delta P_{(NV)}$ since for *periodic boundary conditions*[6]

$$B_m^+(\tilde{V}) = B_m(\tilde{V}) = B_m \qquad \text{if} \quad m \leqslant [L_{\min}/a] \tag{45}$$

where $[L_{\min}/a]$ means integral part of $L_{\min}/a$. a is the range of the inter-molecular potential, $L_{\min}$ the length of the smallest side of the periodic cell (considered to be rectangular). For hard-core potential, $a = \sigma$ is especially small, so that the first few $B_m^+(\tilde{V})$ and $B_m(\tilde{V})$ are identical to B_m if N is not too small. On the other hand, the main contribution of the explicit finiteness correction comes from the first few virial coefficients.[12] Thus there is almost no "mixing" of finiteness effects for hard disks and spheres, $\Delta P_{(NV)} \approx 0$. In the one-dimensional case (hard rods), the situation is especially simple:

$$N \leqslant [L_{\min}/a] = [V/\sigma] \tag{46}$$

Thus, no implicit finiteness correction occurs at all. Up to $m = [V/\sigma]$, Eq. (45) can be imployed. If $m > [V/\sigma]$, $m > N$ due to (46). In this case, the $B_m^+(\tilde{V})$ and $B_m(\tilde{V})$ do not contribute to $B_i(N, \tilde{V})$ according to the combinatorial reason discussed above.

4. HARD RODS IN THE CANONICAL ENSEMBLE

For hard rods of length σ, the thermodynamics is well known.[13] Nevertheless, studying this system will give more insight in the formalism proposed. For periodic boundary conditions PBC,

$$\text{PBC:} \qquad P/(\rho k_B T) = 1(1 - N^{-1}) \sigma\rho(1 - \sigma\rho)^{-1} \tag{47}$$

with the thermodynamic limit

$$P_{\text{TDL}}/(\rho k_B T) = 1 + \sigma\rho(1 - \sigma\rho)^{-1} = (1 - \sigma\rho)^{-1} \tag{48}$$

In the molecular dynamics ensemble MD, it follows from the formula[13]

$$P_{\text{MD}}/(\rho k_B T) = 1 + [P/(\rho k_B T) - 1]/[1 - N^{-1}] \tag{49}$$

that

$$P_{\text{MD}} = P_{\text{TDL}} \tag{50}$$

for hard rods with periodic boundary conditions. The virial coefficients B_i are just σ^{i-1} [cf. (48)]. Furthermore, there is no implicit finiteness effect as shown in Section 3. Thus,

$$P = P_{(N)}, \qquad B_i(N, \tilde{V}) = B_i(N) \tag{51}$$

From Eq. (47) it follows that

$$B_i(N) = (1 - N^{-1}) \sigma^{i-1}, \qquad i \geqslant 2 \tag{52}$$

This can be used to prove the "sum rules for the rows," Section 3. Since $B_i = \sigma^{i-1}$ now, all products $\prod B_m$ occurring in (29) have the same value σ^{i-1} [cf. (30)]. Thus,

$$B_i(N) = \left\{ \sum_{n=0}^{i-1} N^{-n} \sum_{k=1}^{K(i)} a_{i,n,k} \right\} \sigma^{i-1}, \qquad i \geqslant 2. \tag{53}$$

Comparing (52) with (53) yields for $i \geqslant 2$

$$n = 0: \qquad \sum_k a_{i,n,k} = 1 \tag{54a}$$

$$n = 1: \qquad \sum_k a_{i,n,k} = -1 \tag{54b}$$

$$n \geqslant 2: \qquad \sum_k a_{i,n,k} = 0 \tag{54c}$$

which are the sum rules mentioned.

In the simple case of hard rods, it is worthwhile to study *rigid* boundary conditions RBC which induce inhomogeneity [cf. Section 1]. The particles are confined in a volume V^*, V^* being the distance between the "hard walls," which are just points in the one-dimensional case. Now we assume that the left wall remains fixed, but the rods shrink to points. Their position and that of the right wall are shifted to the left in such a way that the distances of adjacent ends turn into distances of the points. Then,

$$V^* \to V^* - N\sigma \tag{55}$$

The thermodynamical situation (P, T) is not changed. For the points, however, the ideal gas law must be valid. Thus

$$\text{RBC:} \qquad P(V^* - N\sigma)/(Nk_B T) = 1 \tag{56}$$

If N/V^* is interpreted as ρ, $P = P_{\text{TDL}}$ would result [cf. (48)]. However, this is not true. For rigid boundary conditions, one must think about the mean-

ing of volume. If V^* is the distance between the walls, only $V^* - \sigma$ is accessible to the centers of the rods. (For *periodic* boundary conditions, there is no such difference.) We have to go back to the foundations of statistical physics. Strictly speaking, the potential energy of a configuration also depends on the interaction with the wall:

$$U^{\text{tot}}(\mathbf{r}_1, \mathbf{r}_2,..., \mathbf{r}_N) = \sum_{i=1}^{N} u_i^{\text{wall}}(\mathbf{r}_i) + U(\mathbf{r}_1, \mathbf{r}_2,..., \mathbf{r}_N) \tag{57}$$

[cf. (2)]. Equation (4b) changes to

$$Q^{\text{conf}} = \int d\mathbf{r}_1 f_1 \int d\mathbf{r}_2 f_2 \cdots \int d\mathbf{r}_N f_N \prod (1 + f_{ij}) \tag{58}$$

the limitation of the integration region being hidden in $f_i \equiv \exp(-u_i^{\text{wall}}/k_B T)$. The leading term of Q^{conf} when expanding $\prod(1 + f_{ij})$ is $(\int d\mathbf{r}_1 f_1)^N$. This corresponds to the ideal gas term known as V^N. Thus

$$V = \int d\mathbf{r}_1 \exp(-u_1^{\text{wall}}/k_B T) \tag{59}$$

Strictly speaking, the value of the volume depends on the particle-wall interaction. For the hard-core interaction, V reduces to the volume which is accessible to the *centers* of the particles. Then Eq. (4b) remains strictly valid even for rigid boundary conditions.

In the case of hard rods, we have to identify V with $V^* - \sigma$. Then Eq. (56) turns into

$$\text{RBC:} \quad P = k_B T \rho [1 - (1 - N^{-1}) \sigma \rho]^{-1} = k_B T \sum_{i=1}^{\infty} [(1 - N^{-1}) \sigma]^{i-1} \rho^i \tag{60}$$

The corresponding pressure is neither P_{TDL} [Eq. (48)] not the pressure for periodic boundary conditions [Eq. (47)]. The latter equation represents the explicit finiteness correction alone [cf. (52)]. In (60), the implicit correction for RBC is additionally present. Strangely enough, V does not occur in (60). To get further insight, we calculate the first few virial coefficients directly [cf. (6) and (14)]:

$$\left. \begin{array}{l} B_2^+(\tilde{V})/\sigma = 1 - \frac{1}{2}\sigma/V \\[4pt] B_2(\tilde{V})/\sigma = 1 - \sigma/V \\[4pt] B_3^+(\tilde{V})/\sigma^2 = 1 - \frac{2}{3}\sigma/V \\[4pt] B_3(\tilde{V})/\sigma^2 = 1 - \sigma/V \end{array} \right\} V \geqslant \sigma \tag{61a}$$

$$B^+(\tilde{V})/\sigma^2 = 1 - \tfrac{5}{6}\sigma/V \left.\vphantom{\begin{matrix}a\\b\end{matrix}}\right\} \quad V \geqslant 2\sigma \tag{61b}$$
$$B(\tilde{V})/\sigma^2 = 1 - \tfrac{5}{4}\sigma/V$$

Owing to inhomogeneity, in fact $B^+(\tilde{V}) \neq B_2^+(\tilde{V})^2$ [cf. (7c)]. If $V < \sigma$ or $V < 2\sigma$, the corresponding virial coefficients displayed in (61a, b) have another functional form. However, this does not affect the equation of state since $N < 2$ and $N < 3$ follow from $V < \sigma$ and $V < 2\sigma$, respectively. This is just the condition that the corresponding virial coefficients do *not* contribute to the pressure; see Section 3.

From (61), virial coefficients $B_2(N, \tilde{V})$ and $B_3(N, \tilde{V})$ result:

$$B_2(N, \tilde{V}) = (1 - N^{-1}) \sigma(1 - \sigma/V) \tag{62a}$$

$$B_3(N, \tilde{V}) = (1 - N^{-1}) \sigma^2[1 - 2(\sigma/V) + N^{-1}(\sigma/V) + 2(\sigma/V)^2 - 3N^{-1}(\sigma/V)^2] \tag{62b}$$

[cf. (13b, c)]. At first sight, this seems in contradiction to Eq. (60). However, it is possible to express (σ/V) as $N^{-1}\sigma\rho$:

$$B_2(N, \tilde{V}) = (1 - N^{-1}) \sigma(1 - N^{-1}\sigma\rho) \tag{63a}$$

$$B_3(N, \tilde{V}) = (1 - N^{-1}) \sigma^2(1 - 2N^{-1}\sigma\rho + N^{-2}\sigma\rho + 2N^{-2}\sigma^2\rho^2 - 3N^{-3}\sigma^3\rho^3) \tag{63b}$$

Thus, the sum $\sum B_i(N, \tilde{V}) \rho^i$ may be rearranged so that the powers of ρ in the representation (63) are collected. In fact, this yields $(1 - N^{-1}) \sigma$ for the coefficient proportional to ρ and $[(1 - N^{-1}) \sigma]^2$ for that proportional to ρ^2. Since the leading term of $B_4(N, \tilde{V})$ is $(1 - N^{-1}) \sigma^3$, even the subsequent coefficient can be calculated from (63b) and turns out to be $[(1 - N^{-1}) \sigma]^3$. Now, consistency with (60) is achieved.

5. HARD DISKS AND SPHERES

We return to periodic boundary conditions and consider the finiteness corrections for hard disks and spheres in the canonical ensemble. In Ref. 10, the computer experimental pressure of the *hard-disk fluid* was compared with theory; see Eq. (44b). No final decision could be made if the neglect of $\Delta P_{(NV)}$ was responsible for the discrepancy occurring. Approximations[14] in the expression for $\Delta P_{(V)}$ or extrapolation errors in $\Delta P_{(N)}$ have also to be taken into account as possible reasons for the discrepancy. In the following, we concentrate on the last possibility. The results of the present paper make it feasible to determine $\Delta P_{(N)}$ more accurately. Table VI shows the hard-disk values of $\Delta B_{i,n}$, $i \leqslant 7$, which have

Table VI. $\Delta B_{i,n}$ up to $i=7$ for Hard Disks

i	$B_i = \Delta B_{i,0}$	$\Delta B_{i,1}$	$\Delta B_{i,2}$	$\Delta B_{i,3}$	$\Delta B_{i,4}$	$\Delta B_{i,5}$	$\Delta B_{i,6}$
1	1.						
2	1.	−1.					
3	0.78200444	−0.3460	−0.4360	−1.1173			
4	0.53223181	−0.1554	0.7404	4.9750	−4.761		
5	0.33355604(1)[a]	−0.0842	−0.4630	−9.203(2)	37.285(3)	−28.356(1)	
6	0.19883(1)	−0.0452(2)	0.1197(9)	9.5(4)	−124.2(8)	331.4(9)	−216.8(4)
7	0.1148(5)	−0.022(11)	−0.02(9)				

[a] The number in brackets denotes the uncertainty of the last digit.

been calculated using (31) and Tables I–IV. The virial coefficients B_i, $i \leqslant 7$, have been taken from Ref. 12. They are also included in Table VI (in units of B_2). For easier comparison with literature, we consider the compressibility factor $Z = P/(\rho k_B T)$ instead of P in the following:

$$Z_{(N)} = \sum_{i=1}^{\infty} B_i(N) \rho^{i-1} = \sum_{i=1}^{\infty} [B_i(N)/B_2^{i-1}](B_2\rho)^{i-1} \qquad (64)$$

[cf. (16, 17)]. Thus, measuring virial coefficients in units of B_2 is equivalent to measuring density in terms of $(B_2\rho)$. Equations (18) and (43a) suggest definition of quantities $\Delta Z_{(N)}^n$,

$$Z_{(N)} = Z_{\text{TDL}} + \Delta Z_{(N)} = \sum_{n=0}^{\infty} \Delta Z_{(N)}^n N^{-n} \qquad (65a)$$

$$\Delta Z_{(N)}^n \equiv \sum_{i=n+1}^{\infty} (\Delta B_{i,n}/B_2^{i-1})(B_2\rho)^{i-1} \qquad (65b)$$

Now Table VI may easily be interpreted. The first column (after the numbering i) yields successive contributions to $\Delta Z_{(N)}^0 \equiv Z_{\text{TDL}}$, the $(n+1)$th column to $\Delta Z_{(N)}^n$. It is remarkable that all B_i displayed are positive, all $\Delta B_{i,1}$ negative, whereas the $\Delta B_{i,n}$ for higher n have alternating sign. The last property together with the factor N^{-n} [Eq. (65a)] suggests that $\Delta Z_{(N)}^n$, $n > 1$, is negligible for hard disks if N is not too small. This has already been conjectured in Ref. 10 from the results for $i \leqslant 5$. In that paper, $N = 48$ and the high fluid density $(B_2\rho) = 1.2956$ have been investigated. For these values, summing up all terms up to $i = 7$ yields because of Table VI

$$Z_{(N)}[\text{up to } i=7] \equiv \sum_{i=1}^{7} B_i(N) \rho^{i-1} = 6.974(2) - 0.57(1) - 0.0000(2)$$

$$+ 0.0002(0) - 0.0001(0) + 0.0000(0) - 0.0000(0) \qquad (66)$$

The successive terms $N^{-n} \Delta Z_{(N)}^n [\text{up to } i=7]$, $0 \leqslant n \leqslant 6$, are displayed [cf. (65)]. The numbers in parentheses are the uncertainties of the last digits. In fact, the contributions from $n > 1$ are very small. Accordingly, one need not worry about extrapolation to higher i. As to $n = 0$ and 1, extrapolation is necessary. $n = 0$ means Z_{TDL} which is known very well for hard disks.[12] The case $n = 1$ has been treated in Refs. 10 and 12, reasonable extrapolations yielding

$$\Delta Z_{(N)}^1/N = -0.059 \text{ (Ref. 12)}, \qquad \Delta Z_{(N)}^1/N = -0.061 \text{ (Ref. 10)} \qquad (67)$$

[cf. (66)]. However, $\Delta Z_{(N)}^1/N = -0.133$ would be necessary in order to remove the above-mentioned discrepancy theory–experiment in Ref. 10. In

the meantime, Eq. (67) has been confirmed by a Padé approximant analysis.[15] Thus $\Delta Z_{(N)}$ as proposed in Ref. 10 is correct and errors in $\Delta Z_{(V)}$ or $\Delta Z_{(NV)}$ must be responsible for the discrepancy occurring.

Now we turn to *hard spheres*. Table VII shows the corresponding $\Delta B_{i,n}$, $i \leqslant 7$. The virial coefficients have been taken from Refs. 16 and 17. The uncertainties of B_6 and B_7 displayed in Table VII are rough estimates.[15]

It is interesting to compare the $\Delta B_{i,n}$ values for *hard spheres* with those for *disks* (Table VI) and *rods*. For the latter,

$$\Delta B_{i,0}/B_2^{i-1} = 1 \tag{68a}$$

$$\Delta B_{i,1}/B_2^{i-1} = -1 \tag{68b}$$

$$\Delta B_{i,n}/B_2^{i-1} = 0, \qquad n > 1 \tag{68c}$$

[cf. (52)]. As far as the coefficients are known, all $B_i = \Delta B_{i,0}$ are positive for hard rods, disks, and spheres. The $\Delta B_{i,1}$ are negative for rods and disks, but have alternating sign for spheres. $\Delta B_{i,n}$ with $n > 1$ vanish for rods and alternate in sign for disks and spheres, n being held fixed. The absolute values $|\Delta B_{i,n}|$, $n > 1$, increase rapidly when passing from rods to spheres. Both B_i and $\Delta B_{i,1}$ exhibit the slowest convergence for rods, the quickest for spheres. It is remarkable that $|\Delta B_{i,1}| < B_i$ for disks and, even more pronounced, for spheres. As Tables I–V show, $\Delta B_{i,1}$ is built up from contributions of different products $\prod B_m$ with large factors. However, the contributions almost cancel in order to yield a small $\Delta B_{i,1}$. Incidentally, the same is already the case with the cluster integrals contributing to B_m; see Ref. 16. For hard spheres, $\Delta B_{7,1} = 0.002 \pm 0.004$ cannot even be discriminated from zero. The approximation $\Delta B_{i,1} = 0$ for $i \geqslant 7$ probably yields very accurate estimates of B_i, $i \geqslant 7$. On the other hand, *volume-dependent* cluster integrals (due to the implicit correction) may *not* cancel in the above sense. Thus slight changes in the implicit correction may change the total pressure considerably. This means that the approximation $\Delta Z_{(NV)} = 0$ is probably not so good as it seemed to be.

In Ref. 17, the *hard-sphere fluid* was studied via computer simulation. The accuracy of pressure was much higher than in older papers. Thus finiteness effects could be investigated in detail. It turned out that in most cases the approximation

$$Z = Z_{\text{TDL}} + \Delta Z_{(N)}^1 N^{-1} \tag{69}$$

was accurate enough. In this representation, Z is a straight line as a function of N^{-1} for given density. Only for the highest fluid density ($B_2 \rho = 1.8512$) and the smallest particle number ($N = 108$) studied, the deviation from this simple behavior was unquestionable. The case

Table VII. $\Delta B_{i,n}$ up to $i=7$ for Hard Spheres

i	$B_i = \Delta B_{i,0}$	$\Delta B_{i,1}$	$\Delta B_{i,2}$	$\Delta B_{i,3}$	$\Delta B_{i,4}$	$\Delta B_{i,5}$	$\Delta B_{i,6}$
1	1.						
2	1.	−1.					
3	0.6250000	0.1250	−0.7500				
4	0.2869495	−0.0967	2.2814	−2.4717			
5	0.110252(1)	0.0043	−3.6102	17.1468	−13.651		
6	0.0390(2)	0.004(3)	4.00(2)	−57.34(4)	158.86(5)	−105.56(2)	
7	0.0131(2)	0.002(4)	−3.53(11)	126.7(6)	−864.(2)	1789.(2)	−1048.6(8)

$(B_2\rho = 1.4810, \quad N = 108)$ was doubtful. Eighteen other experimental $Z(B_2\rho, N)$ remained which were used for a least-squares fit of Padé approximant [3/2] for Z_{TDL}. Virial coefficients $B_2 - B_5$ were taken from Ref. 16, B_6 and B_7 were determined by the least-squares fit mentioned. Thus the results for B_6 and B_7 (cf. Table VII) are not independent.[3] Unlike the present paper, $\Delta Z^1_{(N)}$ was indirectly evaluated via the ensemble correction for the NPT ensemble.[18] This roundabout way will be treated in the Appendix. We can use Table VII for checking the results of Ref. 17 concerning $\Delta Z^1_{(N)}$. As mentioned above, $\Delta B_{i,1}$ have alternating sign, the absolute values quickly decreasing. No Padé approximant is necessary. A simple but very good approximation is cutting the series after $i = 5$ (or even after $i = 4$):

$$\Delta Z^1_{(N)} = -(B_2\rho) + 0.1250(B_2\rho)^2 - 0.0967(B_2\rho)^3 + 0.0043(B_2\rho)^4 \quad (70)$$

The terms for $i > 5$ being negligible, Eq. (70) remains unchanged when improving B_6 and B_7 from the old values (Ref. 16) to the new ones (Ref. 17). This is not the case for Z_{TDL} itself, where a Padé approximant including B_6 and B_7 is necessary for accurate representation. Thus the straight line Z [Eq. (69)] is shifted in a parallel way when improving B_6 and B_7. This is confirmed by the figures of Ref. 17. Moreover, from these figures it can be deduced that the indirect method via the NPT ensemble is consistent with the direct method treated in the present paper.

The last point which remains open is the inappropriateness[17] of Eq. (69) for $B_2\rho = 1.8512$ and $N = 108$. In this case, summing up all terms up to $i = 7$ (Table VII) yields

$$Z_{(N)}[\text{up to } i = 7] = 9.483(1) - 0.017(2) - 0.0073(5) + 0.0032(2)$$
$$- 0.0002(0) + 0.0000(0) - 0.0000(0) \quad (71)$$

This may be compared with $Z_{(N)}$ up to $i = 7$ for hard disks [Eq. (66)]. As already mentioned, the contributions to $\Delta Z^n_{(N)}$, $n > 1$, are larger for spheres than for disks. For instance, $\Delta Z^2_{(N)}$ cannot simply be neglected without further consideration. The Padé approximant [2/2] for $\Delta Z^2_{(N)}$ is

$$\Delta Z^2_{(N)} = -0.7500(B_2\rho)^2 \frac{1 - 1.4075(B_2\rho) + 0.6749(B_2\rho)^2}{1 + 1.6344(B_2\rho) + 0.8331(B_2\rho)^2} \quad (72)$$

the approximant being based on $\Delta B_{i,2}$, $i \leqslant 7$. It turns out that the alter-

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[3] However, we assumed independence when calculating the error of $\Delta B_{7,n}$, $n \geqslant 1$, which slightly underestimates the error.

nating contributions of $\Delta B_{i,2}$ cancel to a high amount, resulting in $\Delta Z^2_{(N)} = -0.264$ for $B_2\rho = 1.8512$. With $N = 108$ this yields

$$\Delta Z^2_{(N)} N^{-2} = -0.00002 \tag{73}$$

Therefore, this contribution to $Z_{(N)}$ is really negligible. It turns out that the same is true for $\Delta Z^n_{(N)}$ with $n > 2$. Thus the deviation of Z from approximation (69) must be due to the implicit finiteness effect, $\Delta Z_{(V)}$, and (possibly) $\Delta Z_{(NV)}$. In fact, $B_2\rho = \frac{2}{3}\pi\sigma^3 N/V = 1.8512$ means $(L_{\min}/\sigma) = 4.96$ for a cubic box $(V = L^3_{\min})$ and $N = 108$. From Eq. (45) it follows that virial coefficients starting with the fifth are effected by the implicit correction. Since at the high fluid density $B_2\rho = 1.8512$ virial coefficients beyond the fifth contribute considerably, the implicit finiteness correction is really responsible for the deviations mentioned.

In this paper, the finiteness dependence of virial coefficients $B_i(N, \tilde{V})$ has been studied. *Two types of correction* occur: the explicit and the implicit finiteness correction. As to the former one, expressions in terms of B_i, the virial coefficients in the thermodynamic limit, have been exhibited for $i \leqslant 8$. Best use of these expressions can be made for hard disks and spheres since the B_i up to $i = 7$ are known quite accurately for these potentials. Owing to a new graph expansion,[2,19] also B_8 seems within reach, at least for hard disks. Including the implicit finiteness correction is no problem formally, but the practical evaluation is difficult. Approximate treatment can be found in Refs. 6, 10, 12, and 14. A special problem is the cross-correlation between explicit and implicit corrections. Up to now, the corresponding cross-terms have been neglected, which may be an explanation of discrepancies theory–computer experiment.[10,17] Thus a better knowledge of the implicit correction including the cross-terms would be desirable.

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APPENDIX

In the *pressure ensemble* N, P, T, and the shape of the volume are fixed. In $Z = P/(\rho k_B T)$, ρ is now the mean value of fluctuating density. Z may be expanded in powers of $(P/k_B T)$,

$$Z_{NPT} = \sum_{i=1}^{\infty} D_i(N, \text{shape})(P/k_B T)^{i-1} \tag{A1}$$

The finiteness dependence of $D_i(N, \text{shape})$ is much simpler than the correction in the canonical ensemble[17,18]:

$$D_i(N, \text{shape}) = D_i(N), \qquad i \leqslant N \tag{A2}$$

$$D_i(N) = D_i + \Delta D_{i,1} N^{-1} \tag{A3}$$

To a given N, P, and T, the according ρ_{TDL} may be attributed according to Eq. (1). Inserting (1) in (A1) results in

$$Z_{\text{NPT}} = \sum_{i=1}^{\infty} E_i(N, \text{shape}) \, \rho_{\text{TDL}}^{i-1} \tag{A4}$$

the $E_i(N, \text{shape})$ having the same properties as the $D_i(N, \text{shape})$ [cf. (A2), (A3)]. Implicit finiteness correction may be neglected now since the contributions of the coefficients with $i > N$ usually are small. (Compare, however, Ref. 20). Thus

$$Z_{NPT} = Z_{\text{TDL}} + \Delta Z_{NPT}^1 N^{-1}, \tag{A5}$$

ΔZ_{NPT}^1 meaning $\Delta Z_{(N)}^1$ in the NPT ensemble. In Ref. 17, a connection between this quantity and $\Delta Z_{NVT}^1 \equiv \Delta Z_{(N)}^1$ in the *canonical* ensemble is provided. This connection can be formulated in terms of $x = B_2 \rho_{\text{TDL}}$ in the following way:

$$\Delta Z_{NVT}^1 = \Delta Z_{NPT}^1 \left[\frac{Z_{\text{TDL}} + \dot{Z}_{\text{TDL}}}{Z_{\text{TDL}}} \right] - 1 - \frac{1}{2} \left[\frac{\dot{Z}_{\text{TDL}} + \ddot{Z}_{\text{TDL}}}{Z_{\text{TDL}} + \dot{Z}_{\text{TDL}}} \right] \tag{A6}$$

where

$$\dot{Z}_{\text{TDL}} \equiv x(\partial Z_{\text{TDL}}/\partial x), \qquad \ddot{Z}_{\text{TDL}} \equiv x(\partial \dot{Z}_{\text{TDL}}/\partial x) \tag{A7}$$

This was used in Ref. 17 to calculate ΔZ_{NVT}^1 via ΔZ_{NPT}^1. Concerning the last quantity, the results of Ref. 18 were inserted. This method, however, seems unnecessarily complicated: From Ref. 6 it follows that

$$\Delta Z_{NVT}^1 = -\tfrac{1}{2}(\dot{Z}_{\text{TDL}} + \ddot{Z}_{\text{TDL}})/(Z_{\text{TDL}} + \dot{Z}_{\text{TDL}}) \tag{A8}$$

This may also be obtained from Eqs. (21) and (22) using

$$\mathcal{O} = 1 + (2!V)^{-1}(F^1\rho)(\partial/\partial\rho)^2 + O(V^{-2}) \tag{A9}$$

Comparing the indirect method (A6) with the direct one (A8) reveals the interesting identity

$$\Delta Z_{NPT}^1 [1 + (\dot{Z}_{\text{TDL}}/Z_{\text{TDL}})] - 1 = 0 \tag{A10}$$

If the implicit finiteness correction can be neglected in the *NPT* ensemble, combination of (A5) and (A10) yields

$$Z_{NPT} = Z_{\text{TDL}} + N^{-1}(1 + x\partial \ln Z_{\text{TDL}}/\partial x)^{-1} \qquad \text{(A11)}$$

This apparently new formula provides a very simple representation of Z_{NPT} in terms of Z_{TDL}.

REFERENCES

1. C. A. Croxton, *Liquid State Physics—A Statistical Mechanical Introduction* (Cambridge University Press, Cambridge, England, 1974), Chap. 1.
2. K. W. Kratky, *J. Stat. Phys.* **27**:533 (1982).
3. K. W. Kratky, *J. Comput. Phys.* **37**:205 (1980).
4. W. Schreiner and K. W. Kratky, *Mol. Phys.* **50**:435 (1984).
5. O. Oppenheim and P. Mazur, *Physica* **23**:197 (1957).
6. J. L. Lebowitz and J. K. Percus, *Phys. Rev.* **124**:1673 (1961).
7. G. Horwitz, *J. Math. Phys.* **7**:2261 (1966).
8. J. B. Hubbard, *J. Comput. Phys.* **7**:502 (1971).
9. J. B. Hubbard, *J. Chem. Phys.* **55**:1382 (1971).
10. W. Schreiner and K. W. Kratky, *Chem. Phys.* **89**:177 (1984).
11. F. H. Ree and W. G. Hoover, *J. Chem. Phys.* **46**:4181 (1967).
12. W. Schreiner and K. W. Kratky, *Chem. Phys.* **80**:245 (1983).
13. J. W. Haus and H. S. Raveché, *J. Chem. Phys.* **68**:4969 (1978).
14. L. R. Pratt and S. W. Haan, *J. Chem. Phys.* **74**:1864 (1981); **74**:1873 (1981).
15. W. W. Wood and J. J. Erpenbeck, private communication.
16. K. W. Kratky, *Physica* **87A**:584 (1977).
17. J. J. Erpenbeck and W. W. Wood, *J. Stat. Phys.* **35**:321 (1984).
18. Z. W. Salsburg, *J. Chem. Phys.* **44**:3090 (1966); **45**:2719 (1966).
19. K. W. Kratky, *J. Stat. Phys.* **29**:129 (1982).
20. W. W. Wood, *J. Chem. Phys.* **52**:729 (1970).