Equation of state of the classical hard-disk fluid

Jerome J. Erpenbeck
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

Marshall Luban
Ames Laboratory and Department of Physics, Iowa State University, Ames, Iowa 50011
(Received 24 June 1985)

We present data with an accuracy of 1 part in 10^4 for the equation of state of the classical hard-disk fluid obtained by a Monte Carlo—molecular-dynamics method for a system of as many as 5822 particles when $\tau=\rho_0/\rho$ ranges from $\tau=30$ to 1.4, where ρ_0 is the value of the number density ρ for closest packing. The data are in excellent agreement with those obtained using a Levin approximant applied to the first six terms of the virial series.

A central problem of classical statistical mechanics is to obtain the equation of state of the hard-disk fluid. Over three decades ago the pioneering efforts of Metropolis *et al.*[1] using the Monte Carlo method provided the first numerical results for the equation of state. During the ensuing years the Monte Carlo and molecular-dynamics (MCMD) calculational procedures have been perfected and these have been used to study hard-disk systems typically consisting of at most a few hundred particles.[2–4] One study[5] for a limited interval of densities of a system of 870 particles showed that the hard-disk fluid, as does the hard-sphere fluid, undergoes a freezing transition when $\tau=\rho_0/\rho$ is reduced to approximately $\tau=1.32$, where ρ_0 is the value of the number density ρ when the disks are in the closest-packing configuration.

Parallel efforts to obtain an accurate equation of state of the fluid based on an expansion in powers of ρ, the virial series, have been hampered because of the extreme difficulties arising in the calculation of the virial coefficients. Writing the expansion as

$$Z(x)\equiv p/(\rho k_B T)=\sum_{n=0}^{\infty} a_n x^n \;, \tag{1}$$

where p is the pressure, $x=1/\tau$, and $a_n=[B_{n+1}/(B_2)^n](B_2\rho_0)^n$, we recall that B_n has been calculated[6–9] for hard disks only for $n\leq 7$. In fact, $B_7/(B_2)^6$ is currently known[7] to an accuracy of only 4 parts in 10^3. In practice, the straightforward summation of the first seven terms of (1) provides values of Z of 1% accuracy only for $\tau\gtrsim 2.2$. To overcome this obstacle, efforts have been made in the past to employ various series acceleration methods (e.g., Padé,[7,10] Levin,[11] and Tova[11] approximants) to the available terms of (1). Ultimately, the precision of the expansion coefficients employed is a primary factor limiting the effectiveness of such methods.

It is our purpose here to report accurate (1 part in 10^4) MCMD data for the equation of state of the hard-disk system and to compare it with the equations of state obtained by applying several series acceleration methods to the virial series. We find excellent agreement between the MCMD data and the equation of state obtained by constructing a Levin approximant using the first six terms of (1). The present level of accuracy of the MCMD data was achieved by considering the order of 10^8 particle collisions in systems of 5822 and 1512 hard disks for $1.4\leq\tau\leq 10$ and $\tau\geq 20$, respectively. The very small uncertainties of the present Levin estimate even at the smallest values of τ have become possible because of Kratky's[9] remarkably accurate calculation (5 parts in 10^5) of $B_6/(B_2)^5$. Furthermore, an accuracy of $B_7/(B_2)^6$ at the level of 1 part in 10^4 will be required before this coefficient can be utilized for constructing a meaningful, yet higher-order Levin approximant.

Our MCMD program for the calculation of statistical mechanical averages has been described in some detail.[12] Its application to the calculation of the equation of state has been described for the case of hard spheres.[13] The present calculations were similarly done in the microcanonical ensemble, but were used to obtain estimates of the canonical-ensemble pressure from the time-averaged virial [see Eq. (12) of Ref. 13].

In order to extrapolate our MCMD data to the infinite-system limit, we have used the approximate expression of Schreiner and Kratky,[14] based on the "normal" $1/N$ corrections to the virial coefficients. The values of $Z=P/(\rho k_B T)$ given in Table I, for values of τ ranging from $\tau=1.4$ to 3 include this correction. In no instance is the finite-system correction appreciably larger than the statistical uncertainty of the data; for $\tau\geq 5$, the corrections are entirely negligible.

A Levin approximant[11,15,16] is a ratio of two polynomials which provides estimates for the values of a function $Z(x)$ represented by an infinite series of the form (1). The Levin method is most effective if the sequence of ratios a_n/a_{n+1} is a slowly varying function of n. This condition is fulfilled for the coefficients a_n of the virial series (1). The Levin approximant $Z[x;N]$ utilizes the first N expansion coefficients of (1) and is of the form

$$Z[x;N]=P[x;N]/Q[x;N] \;, \tag{2}$$

where P and Q are polynomials in x of degrees $N-2$ and $N-1$, respectively. The explicit formulas are

 ©1985 The American Physical Society

TABLE I. Values of $Z=p/\rho k_B T$ for hard disks: the present MCMD data, the seven-term virial series, and the Levin and Padé approximants derived from the six-term virial series.

τ	MCMD	Seven-term virial series	Levin	Padé [3/2]	Padé [2/3]
1.4	8.306(1)	6.974	8.343(2)	8.278(2)	8.456(4)
1.5	6.6074(6)	5.880	6.6087(9)	6.5812(9)	6.655(2)
1.6	5.4963(6)	5.081	5.4948(5)	5.4818(5)	5.516(1)
1.8	4.1715(4)	4.017	4.1707(2)	4.1670(2)	4.1767(3)
2.0	3.4243(3)	3.359	3.424 03(7)	3.422 68(7)	3.4261(1)
3.0	2.0771(2)	2.0743	2.077 20	2.077 15	2.077 26
5.0	1.4983(1)	1.498 36	1.498 43	1.498 43	1.498 43
10.0	1.210 68(3)	1.210 69	1.210 69	1.210 69	1.210 69
20.0	1.097 43(3)	1.097 54	1.097 54	1.097 54	1.097 54
30.0	1.063 37(2)	1.063 44	1.063 44	1.063 44	1.063 44

$$P[x;N]=\sum_{n=0}^{N-2} p_n x^n,\quad p_n=\sum_{k=0}^{n} a_{n-k}q_k\ , \tag{3}$$

$$Q[x;N]=\sum_{n=0}^{N-1} q_n x^n\ ,$$

$$q_n=(-1)^n\binom{N}{n}[1-(n/N)]^{N-1}\frac{a_{N-1}}{a_{N-1-n}}\ , \tag{4}$$

where the symbol $\binom{N}{n}$ denotes the binomial coefficient. If the ratio of polynomials in (2) is expanded in powers of x, then the first N terms are identical to the given first N terms of the expansion (1) for $Z(x)$. The coefficients of the $x^N, x^{N+1}, \ldots$ terms then serve as estimates for the unknown coefficients $a_N, a_{N+1}, \ldots$.

Turning to the problem at hand, we construct the Levin approximant $Z[x;6]$ using the accurately known values of $B_n/(B_2)^{n-1}$, $n\le 6$, listed in Table II. The corresponding estimates for $Z(x)$ are listed in Table I. We note the excellent agreement with the MCMD data. For $\tau=1.5$, 1.6, and 1.8 the MCMD and Levin data are consistent at the 1.2, 1.9, and 1.8 standard-deviation levels, respectively, when we totally ignore any possible error in the Schreiner-Kratky[14] correction procedure. For $\tau=1.4$ there is about a one-half percent discrepancy between the estimates.

We have also listed in Table I values of the equation of state as obtained by constructing the [2/3] and [3/2] Padé approximants using the values of the virial coefficients given in Table II. Clearly, the Levin approximant provides a much more accurate representation of the data than either of these two Padé approximants. It should be noted that the latter are also constructed using the first six terms of the virial series.

By expanding $Z[x;6]$ in powers of x we obtain the following estimates for $B_7/(B_2)^6$ and $B_8/(B_2)^7$,

$$B_7^{\text{est}}/(B_2)^6=0.114\,78(2)\ , \tag{5}$$

$$B_8^{\text{est}}/(B_2)^7=0.064\,843(25)\ . \tag{6}$$

Note that (5) is consistent with the currently known value of $B_7/(B_2)^6$ listed in Table II. Although there is excellent agreement between the MCMD data and the values of $Z[x;6]$, additional support for our contention, that $Z[x;6]$ provides a highly accurate theoretical equation of state for the hard-disk system in the thermodynamic limit, would be provided by an improved direct calculation of B_7 which can be compared with (5). We hope that such an improved calculation will be performed in the near future. A direct calculation of B_8, especially at the level of accuracy given in (6), seems out of reach for the foreseeable future.

We also note that $Z[x;6]$ possesses five simple poles, corresponding to the simple zeros of the denominator polynomial $Q[x;6]$. All of these poles occur for real positive values of x. The pole at $x_s=1.0324(9)$ lies closest to the origin of the complex x plane and it provides an estimate for the radius of convergence of the virial series (1). This corresponds to a density ρ which is 3% above the density ρ_0 of closest packing. Baram and Luban[11] have previously suggested that the radius of convergence of the virial series for both the hard-disk and hard-sphere systems coincides with the density ρ_0. On the face of it, the present result is consistent with their contention for the hard-disk system.

The excellent agreement between the MCMD data for the equation of state and the Levin approximant estimates based on the virial series (1) suggests that this route might be useful for other fluids of interest. For the hard-sphere system, where MCMD data of comparable accuracy exists for 4000 particles,[13] the current value of $B_6/(B_2)^5$, which

TABLE II. Values of $B_n/(B_2)^{n-1}$ for hard disks of diameter a. The values of B_2 and ρ_0 are $B_2=\frac{1}{2}\pi a^2$ and $\rho_0=2/(3^{1/2}a^2)$, respectively. The figures enclosed in parentheses are the one-standard-deviation uncertainties in the last digit.

n	3	4	5	6	7
$B_n/(B_2)^{n-1}$	$\frac{4}{3}-(3^{1/2}/\pi)$	$2-\frac{9}{2}(3^{1/2}/\pi)+(10/\pi^2)$	0.333 556 04(4)	0.198 83(1)	0.1148(5)

is accurate to only 1 part in 10^2, is inadequate for constructing a meaningful Levin approximant $Z[x;6]$. However, only a modest reduction in the uncertainty is required; an accuracy of even 2 parts in 10^3 would suffice to provide a meaningful comparison between $Z[x;6]$ and the MCMD data. We hope that the present work will in fact motivate such theoretical improvements.

We wish to thank W. W. Wood for many helpful discussions. This work was supported by the U.S. Department of Energy, Divisions of Chemical Sciences (Los Alamos) and Material Sciences (Ames), Office of Basic Energy Sciences. The Ames Laboratory is operated for the USDOE by Iowa State University under Contract No. W-7405-Eng-82.

[1]N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, J. Chem. Phys. **21**, 1087 (1953).
[2]W. W. Wood, J. Chem. Phys. **48**, 415 (1968); **52**, 729 (1970).
[3]W. G. Hoover and B. J. Alder, J. Chem. Phys. **46**, 686 (1967).
[4]D. G. Chae, F. H. Ree, and T. Ree, J. Chem. Phys. **50**, 1581 (1969).
[5]B. J. Alder and T. E. Wainwright, Phys. Rev. **127**, 359 (1962).
[6]J. S. Rowlinson, Mol. Phys. **7**, 593 (1963).
[7]K. W. Kratky, J. Chem. Phys. **69**, 2251 (1978).
[8]K. W. Kratky, J. Stat. Phys. **27**, 533 (1982).
[9]K. W. Kratky, J. Stat. Phys. **29**, 129 (1982).
[10]F. H. Ree and W. G. Hoover, J. Chem. Phys. **40**, 939 (1964); **46**, 4181 (1967).
[11]A. Baram and M. Luban, J. Phys. C **12**, L659 (1979).
[12]J. J. Erpenbeck and W. W. Wood, in *Modern Theoretical Chemistry, Statistical Mechanics, Part B: Time Dependent Processes,* edited by B. J. Berne (Plenum, New York, 1977), Vol. 6.
[13]J. J. Erpenbeck and W. W. Wood, J. Stat. Phys. **35**, 321 (1984).
[14]W. Schreiner and K. W. Kratky, Chem. Phys. **80**, 245 (1983).
[15]D. Levin, Int. J. Comput. Math. **3**, 371 (1973).
[16]A fairly detailed exposition of the method of Levin approximants can be found in M. Luban and H. W. Chew, Phys. Rev. D **31**, 2643 (1985).