van der Waals–Tonks-type equations of state for hard-disk and hard-sphere fluids

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Using the known virial coefficients of hard-disk and hard-sphere fluids, we develop van der Waals–Tonks–type equations of state for hard-disk and hard-sphere fluids. In the low-density fluid regime, these equations of state are in good agreement with the simulation results and the existing equations of state.

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I. INTRODUCTION

The short-range repulsive interaction between particles is responsible for the occurrence of the first-order liquid-solid phase transition. The simplest such models are the hard-disk and hard-sphere models, which have merely excluded area (volume) interactions [1–3]. There exists a long history of studying these hard-core models. As early as 1936, Tonks [4] solved exactly the one-dimensional hard rod model and found its equation of state to be $P(L-Nd)=Nk_BT$. Here d is the length of a hard rod. It is well known that an exact solution exists only for one dimension.

The van der Waals equation of state is the simplest equation of state that exhibits the gas-liquid phase transition, which historically proceeded the development of the kinetic theory of molecules and the theory of phase transition. In recent years, in order to make it work better at high densities, some researchers [5,6] modified the excluded volume term in the van der Waals equation. Recently, Eu and Rah [7] have proposed a generic van der Waals equation of state for a fluid with the potential made up of a repulsive and an attractive part by using the virial equation of state. One may raise an interesting question: Does the van der Waals–Tonks–type equation of state exist for hard-disk and hard-sphere fluids? In this paper, we will answer this question.

This paper is organized as follows. In Secs. II and III, the van der Waals–Tonks–type equations of state for a hard-disk fluid and for a hard-sphere fluid are derived, respectively. In Sec. IV, a summary of this paper is given.

II. HARD-DISK FLUIDS

The virial expansion is

$$\begin{aligned}\frac{Ps}{k_BT}&=1+B_2/s+B_3/s^2+\cdots+B_{n+1}/s^n+\cdots\\&=1+B_2'(B_2/s)+B_3'(B_2/s)^2\\&\quad+\cdots+B_{n+1}'(B_2/s)^n+\cdots,\end{aligned}\tag{1}$$

where s is the area per disk, $B_{n+1}'=B_{n+1}/B_2^n$. The virial coefficients are known up to B_7 [8]: $B_2=\pi d^2/2$, $B_2'=1$, $B_3'=4/3-\sqrt{3}/\pi=0.782\,004\,4$, $B_4'=2-4.5(\sqrt{3}/\pi)+10/\pi^2=0.532\,231\,8$, $B_5'=0.333\,556\,1$, $B_6'=0.198\,93$, $B_7'=0.1148$. Here d is the diameter of a hard disk.

Using the virial coefficients, Ree and Hoover (RH) [9] developed a Padé approximation to the equation of state

$$\frac{Ps}{k_BT}=1+\left(\frac{B_2}{s}\right)\frac{1-0.196\,703(B_2/s)+0.006\,519(B_2/s)^2}{1-0.978\,703(B_2/s)+0.239\,465(B_2/s)^2}.\tag{2}$$

By modifying the equation of state of scaled-particle theory empirically, Henderson [10,11] obtained a very accurate equation of state,

$$\frac{Ps}{k_BT}=\frac{1+y^2/8}{(1-y)^2},\tag{3}$$

where $y=\pi d^2/4s$.

The close-packing limit is that for $s>s_0$, as $s\to s_0$, the pressure approaches infinity. Here $s_0=\sqrt{3}d^2/2$ is the close-packing area per disk. We note that none of the above equations of state for a hard-disk fluid gives the close-packing limit.

By observing $B_3'/B_2'=1/1.278\,77$, $B_4'/B_3'=1/1.469\,29$, $B_5'/B_4'=1/1.595\,63$, $B_6'/B_5'=1/1.676\,75$, and $B_7'/B_6'=1/1.732\,84$, we find that the larger n becomes, the nearer B_{n+1}'/B_n' comes to a limit $\sqrt{3}/\pi=1/1.813\,80$, i.e.,

$$\lim_{n\to\infty}B_{n+1}'/B_n'=\sqrt{3}/\pi=1/1.813\,80.\tag{4}$$

The condition of convergence of the virial series Eq. (1) is

$$\lim_{n\to\infty}(B_{n+1}'/B_n')(B_2/s)<1.\tag{5}$$

Substitution of Eq. (4) into Eq. (5) gives $s>s_0$, which indicates that the limit Eq. (4) is relevant to the close-packing limit. Equation (4) suggests the following equation of state:

$$\begin{aligned}\frac{Ps}{k_BT}&=1+C_2\left(\frac{B_2}{s}\right)+C_3\left(\frac{B_2}{s}\right)^2+\cdots+C_{n+1}\left(\frac{B_2}{s}\right)^n\\&\quad+\cdots+D\frac{s_0/s}{1-s_0/s},\end{aligned}\tag{6}$$

where $D,C_2,\ldots$ are constants to be determined. By properly choosing the value of D, we find that as n becomes larger and larger, C_n becomes smaller and smaller. Hence C_n may be neglected for n large enough. The result is

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TABLE I. The virial coefficients B_n' for a hard-disk fluid.

B_n'	Exact	Wang	RH	Henderson
B_2'	1	1	1	1
B_3'	0.782 00	0.782 00	0.782	0.781 25
B_4'	0.532 23	0.532 23	0.5324	0.531 25
B_5'	0.333 56	0.333 56	0.3338	0.335 94
B_6'	0.198 93	0.198 93	0.1992	0.203 13
B_7'	0.1148	0.1148	0.115 02	0.119 14
B_8'		0.063 293	0.064 873	0.068 359
B_9'		0.034 895	0.035 947	0.038 574

$$\left[\frac{Ps}{k_BT}+3.087\,68+1.253\,66\left(\frac{B_2}{s}\right)+0.460\,51\left(\frac{B_2}{s}\right)^2+0.152\,797\left(\frac{B_2}{s}\right)^3+0.044\,12\left(\frac{B_2}{s}\right)^4+0.009\,29\left(\frac{B_2}{s}\right)^5\right](1-s_0/s)=4.087\,68. \tag{7}$$

The virial coefficients given by the RH equation, the Henderson equation, and Eq. (7) are listed in Table I. The calculated values and the simulation values [9,12] of Pv/k_BT in the low-density fluid regime are listed in Table II. The equations of state are shown in Fig. 1(a). We see that in the low-density fluid regime, our equation of state is in good agreement with the simulation results, the RH equation, and the Henderson equation.

As the density becomes high enough ($s_0/s>0.761$), the hard-disk system undergoes a fluid-solid phase transition. The equation of state splits into two branches, i.e., the metastable branch and the stable branch [14,15]. The stable branch is composed of two parts, i.e., the fluid-solid coexistence part ($0.761<s_0/s<0.798$) and the solid part ($0.798<s_0/s<1$). From Fig. 1(b), we see that in the high-density regime, Eq. (7) does not agree with the simulation results of the stable branch [9,12–14]. The reason is that the virial expansion is only valid in the low-density regime.

TABLE II. Values of Ps/k_BT for a hard-disk fluid.

s/s_0	Exact	Wang	RH	Henderson
1.312	10.13	10.8765	10.7832	11.1157
1.40	8.25	8.3315	8.3123	8.4838
1.45	7.47	7.3594	7.3536	7.4767
1.50	6.67	6.5976	6.5979	6.6885
1.55	6.08	5.9866	5.9895	6.0577
1.60	5.56	5.4870	5.4909	5.5430
1.65	5.13	5.0718	5.0759	5.1165
1.70	4.76	4.7221	4.7260	4.7580
1.80	4.24	4.1673	4.1704	4.1909
1.90	3.78	3.7485	3.7508	3.7646
2.00	3.39	3.4225	3.4242	3.4337

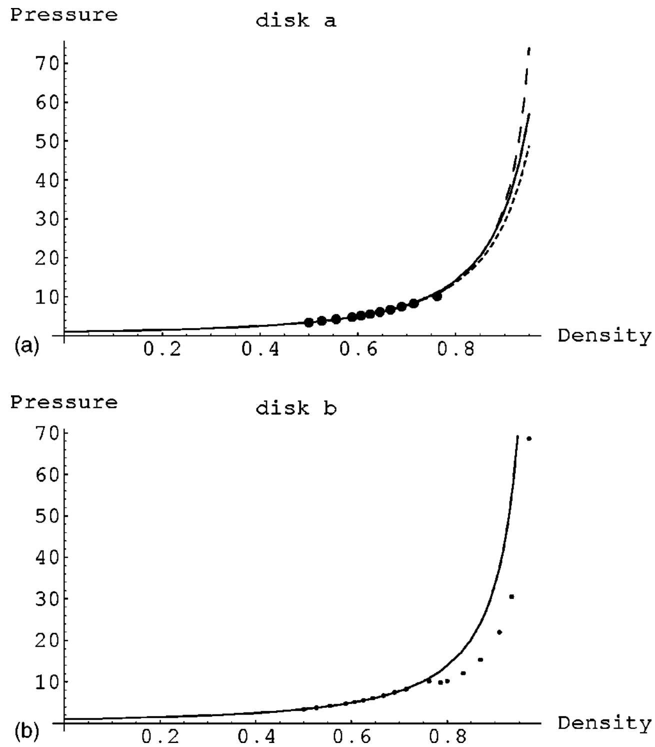

FIG. 1. Equation of state in the Ps/k_BT-s_0/s plane for a hard-disk system. (a) The low-density fluid regime. The dots represent the simulation results [9,12]. The curves marked by a solid line, a short dashed line, and a long dashed line represent the Henderson equation, the RH equation, and Eq. (7), respectively. (b) The fluid regime, the fluid-solid coexistence regime, and the solid regime. The solid curve represents Eq. (7). The dots represent the simulation results [9,12–14].

III. HARD-SPHERE FLUIDS

The virial expansion is

$$\frac{Pv}{k_BT}=1+\frac{B_2}{v}+\frac{B_3}{v^2}+\cdots+\frac{B_{n+1}}{v^n}+\cdots=1+B_2'\left(\frac{B_2}{v}\right)+B_3'\left(\frac{B_2}{v}\right)^2+\cdots+B_{n+1}'\left(\frac{B_2}{v}\right)^n+\cdots, \tag{8}$$

where $v=V/N$ is the volume per sphere and $B_{n+1}'=B_{n+1}/B_2^n$. The virial coefficients are known up to B_{10} [8]: $B_2=4\pi d^3/6$, $B_2'=1$, $B_3'=0.625$, $B_4'=0.28695$, $B_5'=0.11025$, $B_6'=0.0389$, $B_7'=0.0137$, $B_8'=0.004\,45$, $B_9'=0.001\,50$, and $B_{10}'=0.000\,51$. Here d is the diameter of a hard sphere.

Although no exact solution exists, there exists an exact solution of the Percus-Yevick integration equation for a hard-sphere fluid [16,17]. Two equations of states obtained from the compressibility equation and from the virial equation are

$$\frac{Pv}{k_BT}=\frac{1+y+y^2}{(1-y)^3} \tag{9}$$

TABLE III. The virial coefficients B'_n for a hard-sphere fluid.

B'_n	Exact	Wang	RH	CS
B'_2	1	1	1	1
B'_3	0.625	0.625	0.625	0.625
B'_4	0.286 95	0.286 95	0.286 95	0.281 25
B'_5	0.110 25	0.110 25	0.1103	0.1094
B'_6	0.0389	0.038 95	0.0386	0.039 06
B'_7	0.0137	0.0137	0.0127	0.013 18
B'_8	0.004 45	0.004 44	0.0040	0.004 27
B'_9	0.001 50	0.001 50	0.001 21	0.001 34
B'_{10}	0.000 51	0.000 506	0.000 35	0.000 41

and

$$\frac{Pv}{k_BT}=\frac{1+2y+3y^2}{(1-y)^2}, \tag{10}$$

where $y=\pi d^3/6v$.

Based on the virial coefficients, Carnahan and Starling (CS) [18] developed a Padé approximation to the equation of state

$$\frac{Pv}{k_BT}=\frac{1+y+y^2-y^3}{(1-y)^3}. \tag{11}$$

It is obtained by taking a (1/3:2/3) average of the virial pressure Eq. (10) and the compressibility pressure Eq. (9).

Using the virial coefficients, Ree and Hoover (RH) [9] developed a Padé approximation to the equation of state,

$$\frac{Pv}{k_BT}=1+\left(\frac{B_2}{v}\right)\frac{1+0.063\,507(B_2/v)+0.017\,329(B_2/v)^2}{1-0.561\,493(B_2/v)+0.081\,313(B_2/v)^2}. \tag{12}$$

The close-packing limit is that for $v>v_0$, as $v\to v_0$, the pressure goes to infinity. Here $v_0=d^3/\sqrt{2}$ is the close-packing volume per sphere. We note that none of the above equations of state for a hard-sphere fluid gives the close-packing limit.

TABLE IV. Values Pv/k_BT for a hard-sphere fluid.

v_0/v	Exact	Wang	RH	CS
0.10	1.36	1.3594	1.3594	1.3593
0.141 42	1.55	1.5536	1.5536	1.5532
0.212 13	1.97	1.9682	1.9682	1.9667
0.282 84	2.52	2.5219	2.5213	2.5180
0.333 33	3.05	3.0326	3.0307	3.0256
0.353 55	3.26	3.2711	3.2682	3.2624
0.424 26	4.28	4.3018	4.2906	4.2834
0.494 97	5.70	5.7504	5.7135	5.7102
0.50	5.89	5.8744	5.8344	5.8318
0.565 69	7.78	7.8445	7.7319	7.7500
0.588 23	8.59	8.7066	8.5472	8.5794
0.625	10.17	10.3876	10.1079	10.1780
0.636 40	10.74	10.9921	10.6593	10.7461
0.650 54	11.60	11.8073	11.3944	11.5064

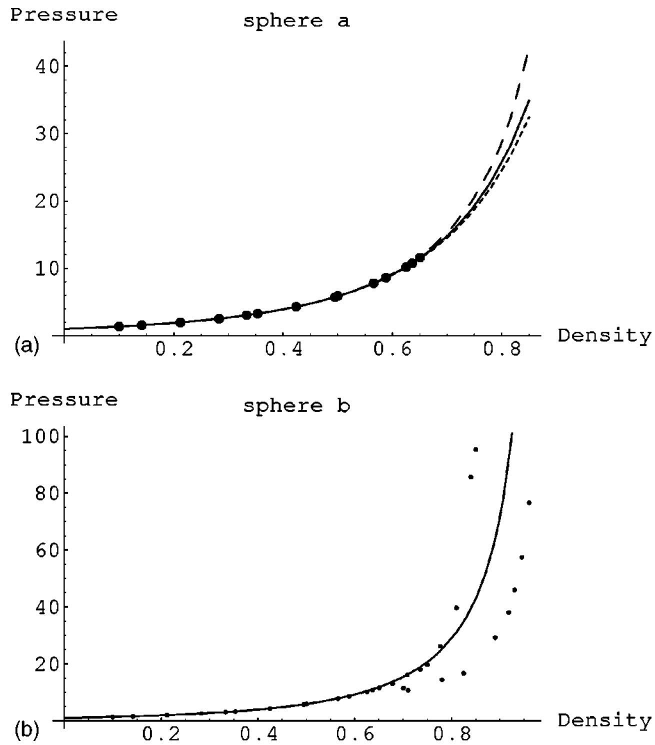

FIG. 2. Equation of state in the Pv/k_BT-v_0/v plane for a hard-sphere system. (a) The low-density fluid regime. The dots represent the simulation results [9,12,19]. The curves marked by a solid line, a short dashed line, and a long dashed line represent the CS equation, the RH equation, and Eq. (16), respectively. (b) The fluid regime, the metastable regime, the fluid-solid coexistence regime, and the solid regime. The solid curve represents Eq. (16). The dots represent the simulation results [3,9,12,14,19].

By observing $B'_3/B'_2=1/1.6$, $B'_4/B'_3=1/2.178\,08$, $B'_5/B'_4=1/2.602\,72$, $B'_6/B'_5=1/2.834\,19$, $B'_7/B'_6=1/2.839\,416$, $B'_8/B'_7=1/3.078\,65$, $B'_9/B'_8=1/2.966\,67$, and $B'_{10}/B'_9=1/2.941\,18$, we find that there exists a tendency that the larger n becomes, the nearer B'_{n+1}/B'_n comes to a limit $3/2\pi\sqrt{2}=1/2.961\,92$, i.e.,

$$\lim_{n\to\infty} B'_{n+1}/B'_n=3/2\pi\sqrt{2}=1/2.961\,92. \tag{13}$$

The condition of convergence of the virial series Eq. (8) is

$$\lim_{n\to\infty}(B'_{n+1}/B'_n)(B_2/v)<1. \tag{14}$$

Combination of Eqs. (13) and (14) gives $v>v_0$, which indicates that the limit Eq. (13) is relevant to the close-packing limit. Equation (13) suggests the following equation of state:

$$\frac{Pv}{k_BT}=1+C_2\left(\frac{B_2}{v}\right)+C_3\left(\frac{B_2}{v}\right)^2+\cdots+C_{n+1}\left(\frac{B_2}{v}\right)^n+\cdots+D\frac{v_0/v}{1-v_0/v}, \tag{15}$$

where $D, C_2, \ldots$ are constants to be determined. By properly choosing the value of D, we find that as n becomes larger and larger, C_n becomes smaller and smaller. Hence C_n may be neglected for n large enough. The result is

$$\left[\frac{Pv}{k_BT}+7.8854+2.0\left(\frac{B_2}{v}\right)+0.387\,86\left(\frac{B_2}{v}\right)^2+0.055\left(\frac{B_2}{v}\right)^3+0.0052\left(\frac{B_2}{v}\right)^4-0.0005\left(\frac{B_2}{v}\right)^6\right](1-v_0/v)=8.8854. \tag{16}$$

The virial coefficients given by the RH equation, the CS equation, and Eq. (16) are listed in Table III. The CS equation gives $B_6'=0.039\,06$ while Refs. [8,11] gave a wrong result $B_6'=0.0156$ for the CS equation. The calculated values and the simulation values [9,12,19] of Pv/k_BT in the low-density fluid regime are listed in Table IV. The equations of state are shown in Fig. 2(a). We see that in the low-density fluid regime, our equation of state is in good agreement with the simulation results, the RH equation, and the CS equation.

As the density becomes high enough ($v_0/v>0.667$), the hard-sphere system undergoes a fluid-solid phase transition. The equation of state splits into two branches, i.e., the metastable branch ($0.667<v_0/v<0.8754$) [20,21] and the stable branch [14,22]. The stable branch is composed of two parts, i.e., the fluid-solid coexistence part ($0.667<v_0/v<0.736$) and the solid part ($0.736<v_0/v<1$). From Fig. 2(b), we see that in the high-density regime, Eq. (16) does not agree with the simulation results of the metastable branch and the stable branch [3]. The reason is that the virial expansion is only valid in the low-density regime.

IV. CONCLUSION

We observe that for hard-disk and hard-sphere fluids, as n becomes large enough, B_{n+1}'/B_n' approaches a limit that is relevant to the close-packing limit. This reflects the fact that the interaction is merely an excluded volume effect and hence the models have a purely geometric character [1,3]. Indeed, the central idea of "scaled particle theory" and "statistical geometry" [2] is also that the thermodynamic properties of hard-sphere systems are dominated by the constraints of geometry. Using our observation, we develop accurate van der Waals–Tonks–type equations of state, which reproduce the known virial coefficients and also give the close-packing limit. In the low-density fluid regime, our equations of state are in good agreement with the simulation results and the existing equations of state. These equations are useful as a guide when treating more complicated potentials.

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