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Exact equilibrium statistical mechanics of two particles interacting via Lennard-Jones and Morse potentials

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The exact classical statistical phase-space volume is obtained for a finite system consisting of two particles interacting via both Lennard-Jones and Morse potentials and confined in a spherical volume. The case when the center of mass of the system is fixed at the center of the sphere is also considered. It is shown that the microcanonical caloric curve of the system can have properties similar to those of large clusters, and the equation of state of the system can have behavior similar to that of bulk systems. It is also shown that the fixing of the center of mass of the system can appreciably change the properties of the microcanonical caloric curve and the equation of state of the system.

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Knowing the partition function for the canonical ensemble of many particle systems it is easy to define the thermodynamic properties of the system [1,2], but the partition function of a system confined in a finite volume can be calculated explicitly for the ideal gas only [1,2]. The classical statistical partition function cannot be calculated explicitly even for a two particle system with a Morse interaction potential in a finite volume because there is a Boltzmann exponent in the expression for the partition function. However, it is possible to compute the quantum statistical partition function of the bound states of a free system of two particles interacting via a Morse potential and having zero angular momentum, because the bound quantum levels of this system can be obtained from a very complicated transcendental equation [3]. Therefore it is interesting to consider a microcanonical ensemble of systems where there is no Boltzmann exponent in the expression for the classical statistical phase-space volume. The phase-space volume plays a key role in defining the thermodynamic properties of a system in the microcanonical ensemble.

In the present work we consider a system consisting of two particles with total energy E in the volume V. The classical statistical phase-space volume of the two particle system is given by [4]

$$\Omega(E,V)=c\int_V\int_V (E-U)^3\,\theta(E-U)\,d\mathbf{r}_1\,d\mathbf{r}_2. \tag{1}$$

Here $c=\frac{1}{6}(\sqrt{m_1 m_2}/2\pi\hbar^2)^3$, m_1 and m_2 are the masses of the particles, $\hbar$ is Planck's constant, $\mathbf{r}_1$ and $\mathbf{r}_2$ are vectors of the coordinates of the particles, and $\theta(x)$ is the Heaviside step function [$\theta(x)=0,\ x\leqslant 0;\ \theta(x)=1,\ x>0$]. $U=u(|\mathbf{r}_1-\mathbf{r}_2|)+u_w(r_{1w})+u_w(r_{2w})$ is the total interaction potential, $u(|\mathbf{r}_1-\mathbf{r}_2|)$ is the potential of interparticle interaction, r_{1w} and r_{2w} are the distances from the particles to the wall, and $u_w(r_{1w})$ and $u_w(r_{2w})$ are the interaction potentials of the particles with the wall.

Knowing the phase-space volume, one can easily obtain the entropy, the microcanonical caloric curve, and the equation of state of the system from

$$S(E,V)=k\ln\Omega(E,V), \tag{2}$$

$$T(E,V)=\left(\frac{\partial S(E,V)}{\partial E}\right)_V^{-1}, \tag{3}$$

and

$$p(E,V)=T(E,V)\left(\frac{\partial S(E,V)}{\partial V}\right)_E, \tag{4}$$

respectively [2,4]. Here k is the Boltzmann constant, $T(E,V)$ is the microcanonical temperature, and $p(E,V)$ is the pressure.

We assume that the system is placed in a sphere of radius R_s[$V=(4\pi/3)R_s^3$], the hard core potential [$u_w(r)=\infty$, $0\leqslant r\leqslant r_c$; $u_w(r)=0$, $r>r_c$] is the interaction potential of the particles with the wall, and the system of coordinates has its origin at the center of the sphere. We will consider the cases when the center of mass of the system is not fixed (case A) and when the center of mass is fixed at the center of the sphere (case B) for the Lennard-Jones potential $u(r)=4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^6]$ and Morse potential $u(r)=\varepsilon(e^{-2g(r-r_m)}-2e^{-g(r-r_m)})$, where ε, σ, g, and r_m are the parameters of the potentials. We will measure the energy, all the distances, and the parameter g in units of ε, r_0, and r_0^{-1}, respectively, where $r_0=2^{1/6}\sigma$ for the Lennard-Jones potential and $r_0=r_m$ for the Morse potential.

Case A. We enter the vector of the relative interparticle distance $\mathbf{r}=\mathbf{r}_1-\mathbf{r}_2$ instead of $\mathbf{r}_2$ and introduce systems of spherical coordinates for $\mathbf{r}_1$ and $\mathbf{r}$. Integrating over the spherical angles we obtain from Eq. (1)

$$\frac{\Omega(E,V)}{4\pi c}=F(a)\,\theta(D-a)-F(b)\,\theta(D-b)\,\theta(-E), \tag{5}$$

where

$$\frac{F(x)}{\pi r_0^6\varepsilon^3}=\int_{x-R}^{R} r_1\,dr_1\int_x^{R+r_1}[E-u(r)]^3[R^2-(r-r_1)^2]\,r\,dr. \tag{6}$$

Here $r_1=|\mathbf{r}_1|$, $r=|\mathbf{r}|$, $D=2R$, $R=R_s-r_c$ is the radius of the sphere where the particles can move, and a and b are the turning points: $u(a)=E$, $u(b)=E$, $(a\leqslant b)$.

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Note that if a and b can be explicitly expressed via E and parameters of the potential $u(r)$ and the integral in Eq. (6) can be calculated, then one can obtain an analytical expression for the phase-space volume.

From Eq. (6) we obtain

$$\frac{F(x)}{\pi r_0^6 \varepsilon^3} = \sum_{n=0}^{6} a_n [Rf(0,3,n,x) + 3Rf(2,1,n,x) - 4Rf(1,2,n,x) + 2R^2 f(0,2,n,x) - 2R^2 f(1,1,n,x) - f(1,3,n,x) - f(3,1,n,x) + 2f(2,2,n,x)], \tag{7}$$

$$a_0 = E^3, \quad a_1 = 6E^2, \quad a_2 = 12E - 3E^2,$$

$$a_3 = 8 - 12E, \quad a_4 = 3E - 12, \quad a_5 = 6, \quad a_6 = -1,$$

where

$$f(l,m,n,x) = \frac{D^{l+m-6n+2} - x^{l+m-6n+2}}{(m-6n+1)(l+m-6n+2)} - x^{m-6n+1}\frac{D^{l+1} - x^{l+1}}{(m-6n+1)(l+1)} \quad \text{at} \quad l+m-6n+2 \neq 0, \tag{8}$$

$$f(l,m,n,x) = -\frac{1}{l+1}\ln\frac{D}{x} + \frac{(D/x)^{l+1} - 1}{(l+1)^2} \quad \text{at} \quad l+m-6n+2 = 0,$$

for the Lennard-Jones potential, and

$$f(l,m,n,x) = \frac{e^{ng}}{(ng)^{l+m+2}} \sum_{i=0}^{m} \frac{m!}{(m-i)!} \times \Bigg(e^{-ngx}(ngx)^{m-i} \frac{(ngD)^{l+1} - (ngx)^{l+1}}{l+1} + \sum_{j=0}^{l+m-i} \frac{(l+m-i)!}{(l+m-i-j)!} [e^{-ngD}(ngD)^{l+m-i-j} - e^{-ngx}(ngx)^{l+m-i-j}] \Bigg),$$

$$f(l,m,0,x) = \frac{D^{l+m+2} - x^{l+m+2}}{(m+1)(l+m+2)} - x^{m+1}\frac{D^{l+1} - x^{l+1}}{(m+1)(l+1)}, \tag{9}$$

for the Morse potential. It is necessary to put in Eq. (5) $a = (1+\sqrt{E+1})^{-1/6}$ and $b = (1-\sqrt{E+1})^{-1/6}$ for the Lennard-Jones potential, and $a = 1-(1/g)\ln(1+\sqrt{E+1})$ and $b = 1-(1/g)\ln(1-\sqrt{E+1})$ for the Morse potential.

Case B. We enter the vector of the center-of-mass coordinates $\mathbf{R} = (m_1\mathbf{r}_1 + m_2\mathbf{r}_2)/(m_1+m_2)$ and the vector $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ instead of $\mathbf{r}_1$ and $\mathbf{r}_2$ and introduce a system of spherical coordinates for $\mathbf{r}$. Integrating over $\mathbf{R}$ and the spherical angles we obtain from Eq. (1) that the phase-space volume is given by Eq. (6), where

$$\frac{F(x)}{r_0^3 \varepsilon^3} = \int_x^D [E - u(r)]^3 r^2 dr.$$

It is easy to obtain

$$\frac{F(x)}{r_0^3 \varepsilon^3} = \sum_{n=0}^{6} a_n \frac{D^{3-6n} - x^{3-6n}}{3-6n} \tag{10}$$

for the Lennard-Jones potential, and

$$\frac{F(x)}{r_0^3 \varepsilon^3} = a_0 \frac{D^3 - x^3}{3} + \sum_{n=1}^{6} a_n \frac{e^{ng}}{n^3 g^3} g_n(x), \tag{11}$$

where

$$g_n(x) = (n^2g^2x^2 + 2ngx + 2)e^{-ngx} - (n^2g^2D^2 + 2ngD + 2)e^{-ngD},$$

for the Morse potential.

Thus we have obtained analytical expressions for the classical statistical phase-space volume of a system consisting of two particles interacting via both the Lennard-Jones and Morse potentials in a spherical volume. The phase-space volume cannot be expressed explicitly even for the one dimensional Lennard-Jones oscillator, and it is known for the bound states of the one dimensional Morse oscillator in the interval $(-\infty, +\infty)$ [5]. It is also possible to compute the quantum statistical phase-space volume of bound states of a free system of two particles interacting via the Morse potential and having zero angular momentum [3]. Note that exact phase-space volumes for the same systems can also be obtained for a finite interval in one dimensional space and for a ring in two dimensional space.

Figure 1(a) represents microcanonical caloric curves of the system for both Lennard-Jones and Morse potentials obtained from Eqs. (2), (3), (5) and (7)–(11) at various diameters D. For simplicity we use here $2^{1/6}\sigma = r_m$ so the minima of the potentials are at the same distances, and $g = 6$ so the potentials have the same curvatures at their minima. One can see that the caloric curves for case A (curves 1–4) lie below those for case B (curves 5–8) because in case A the particles can move in the sphere without any restriction and therefore they have more kinetic energy than in case B. At sufficiently large values of D there is a region where temperature decreases with increasing energy. The analysis shows that the existence of the region is related to the influence of the attractive forces. The greater [smaller] is the value of D [the density $n = 2/(\pi D^3/6)$], the more the region becomes expressed. This is due to the increase of the influence of the attractive forces with decreasing density. The region disappears at small values of D.

Such a region can occur in microcanonical caloric curves of large clusters such as Ar_{55} and Ar_{147} [6]. This region is usually named a van der Waals type loop or ''S bend'' and is related to the melting phenomenon (the coexistence of liquidlike and solidlike states) in the clusters [7,8]. The sufficient and necessary conditions for such loops to occur have been obtained in [8]. In most cases the cluster is placed in the sphere in order to keep it bonded, and the center of mass of

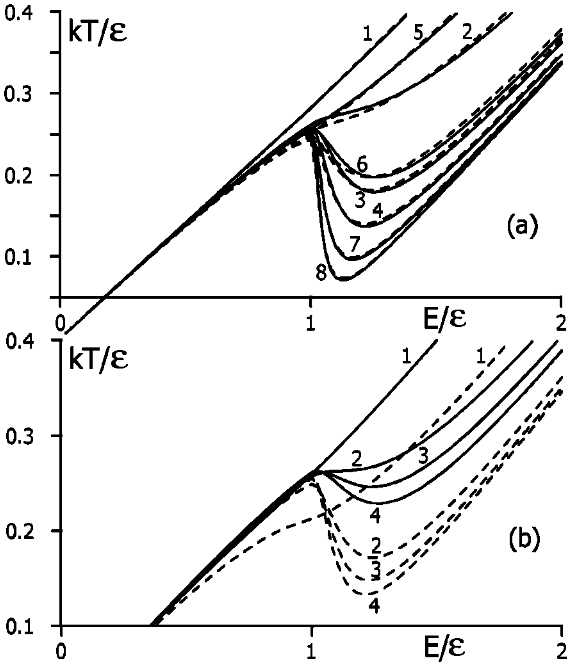

FIG. 1. Microcanonical caloric curves. (a) Solid lines correspond to Morse potential with $g=6$ and dashed lines to Lennard-Jones potential. $D=1.5$ corresponds to curves 1 and 5, $D=3$ to 2 and 6, $D=6$ to 3 and 7, and $D=8$ to 4 and 8. Curves 1–4 correspond to case A, and curves 5–8 to case B. (b) Morse potential, $D=4$; $g=1$ corresponds to curves 1, $g=4$ to curves 2, $g=6$ to curves 3, and $g=8$ to curves 4. Solid lines correspond to case A and dashed lines to case B.

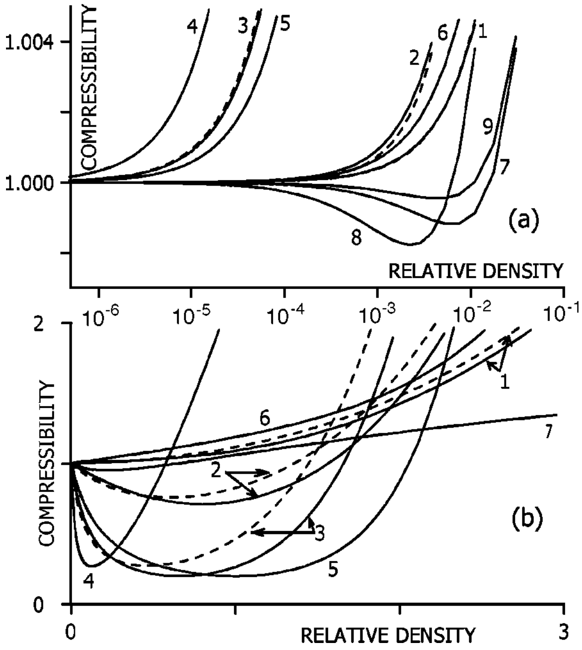

FIG. 2. Equation of state: solid lines correspond to Morse potential and dashed lines to Lennard-Jones potential. (a) case A and (b) case B. Curve 1, $g=6$ and $E=7$; curve 2, $g=6$ and $E=1$; curve 3, $g=6$ and $E=0.2$; curve 4, $g=2$ and $E=0.2$; curve 5, $g=9$ and $E=0.2$; curve 6, $g=12$ and $E=7$; curve 7, $g=2$ and $E=7$; curve 8, $g=1$ and $E=7$; and curve 9, $g=2.5$, and $E=7$.

the cluster is fixed at the center of the sphere. We see from Fig. 1(a) that the existence of the S bend in the caloric curve of the cluster depends on the diameter of the sphere. Curves 2 and 6 show that the S bend can exist for case B and cannot exist for case A because the influence of the attractive forces in case B is more than in case A.

Figure 1(b) represents caloric curves for the Morse potential at various values of the parameter g and fixed value of D. It is known that g^{-1} characterizes the size of the region of action of the attractive forces. We see that the smaller the value of g^{-1}, the more the S bend becomes expressed. The S bend disappears at small values of g^{-1} (curves 1). Curves 2 show that the S bend can exist for case B and cannot exist for case A.

Figure 2(a) shows the equation of state of the system for case A (the dependence of the compressibility p/p_{ideal} on the relative density n/n_0, where $n_0=r_0^{-3}$ and $p_{ideal}=2E/3V$) obtained from Eqs. (2)–(5) and Eqs. (7)–(9) for the two potentials at various values of the energy. One can see that for the Lennard-Jones potential and the Morse potential with $g=6$ the compressibility grows with increasing relative density (curves 1–3), and this growth becomes more pronounced with decreasing energy (curves 1–3) and increasing g^{-1} (solid curves 3–5; see also curves 1 and 6). Curves 7–9 show that at large values of g^{-1} the compressibility first decreases with increasing relative density, passes through a minimum, and then increases. This behavior of the compressibility is due to the prevalence of attractive forces at low densities resulting in reduction of the pressure in comparison with that for the ideal gas, and the prevalence of repulsive forces at high densities resulting in rapid growth of the pressure in comparison with the pressure of the ideal gas. The greater the value of g^{-1}, the more pronounced this behavior becomes.

Figure 2(b) represents the equation of state of the system for case B (the dependence of the compressibility p/p_{ideal} on the relative density n/n_0, where $p_{ideal}=E/3V$) obtained from Eqs. (2)–(5), (7),(10), and (11) for the two potentials at various values of the energy. As one can see, the compressibility at low energies first decreases with increasing relative density, passes through a minimum, and then increases (curves 2 and 3). This behavior becomes more pronounced with decreasing energy (curves 2 and 3) and g^{-1} (solid curves 3–5). The existence of this behavior depends on the value of g^{-1} at high energies (see solid curves 1, 6, and 7). From comparison of curves 2–5 in Fig. 2(a) and Fig. 2(b), we see that the equation of state can have this behavior in case B while it cannot have this behavior in case A. The equations of state of bulk Ar and Xe have similar behavior [9]. Figure 2(b) also shows that the role of the attractive forces decreases with increasing energy (see curves 1–3).

We have obtained the exact phase-space volume for a finite system consisting of two particles interacting via both Lennard-Jones and Morse potentials and confined in a spherical volume. We have shown that the microcanonical caloric curve of the system can have properties similar to those of large clusters, and the equation of state of the system can have behavior similar to that of the bulk. We have also shown that fixing the center of mass of the system can appreciably change the properties of the microcanonical caloric curve and the equation of state of the finite system.

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