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# Singularities of the canonical partition functions of fluid systems with continuous interaction potentials

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We observe that for finite $N$ and $V$, the canonical partition function $Q_N$ of a fluid system of $N$ particles is a polynomial of degree $N$ in variable $V/N\lambda^3$, which has $N$ zeros that depend only on the cluster integrals $b_2(V,T),\ldots,b_N(V,T)$. In the thermodynamic limit, if the zero distribution approaches the positive real axis, a phase transition arises. The behavior of phase transition is determined solely by the zero distribution near the positive real axis. Below the critical temperature, the Maxwell's equal-area rule must be used to obtain the gas-liquid coexistence regime. Several examples are given.

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## I. INTRODUCTION

In 1952, Yang and Lee [1] proposed a general theory of phase transition. They observed that in a finite volume, the grand partition function of a real gas with a hard core is a finite polynomial in fugacity and is determined completely by the zeros of the polynomial. They showed that in the thermodynamic limit if the zero distribution approaches the positive real axis, a phase transition arises. They further applied their theory to a ferromagnetic Ising model and to an attractive lattice gas model and proved the famous circle theorem, which states that the zeros are distributed on the unit circle in the complex fugacity plane. Fisher [2], Jones [3] and Grossmann *et al.* [4] extended this approach to the canonical ensemble. Grossmann *et al.* [4] observed that the free energy of a many-body system is represented by a finite Laplace transform of the interaction phase volume, which has an infinite number of zeros. Possible phase transitions are classified by the behavior of the zero distribution near the positive real axis. Recently, this approach has been applied to the classification of phase transitions in small systems [5,6].

Despite its spectacular success when applied to lattice systems, the Yang-Lee theory meets with two difficulties when applied to a fluid system with a continuous interaction potential. One difficulty is the evaluation of the Yang-Lee zeros. To our knowledge, only the zeros of some one-dimensional (1D) gases are known [7–10]. Another difficulty is that the Yang-Lee theory relies heavily on the condition of the hard core. As is well known, the condition of the hard core is nothing but a good approximation for a real fluid system. The more accurate interaction of atoms of a real fluid system is, for example, the Lennard-Jones potential. In this case the hard core does not exist. The grand partition function is an infinite polynomial. It is impossible to introduce the zeros. In order to avoid these difficulties, we will turn to the canonical ensemble.

## II. FORMULATION

Let us consider a three-dimensional (3D) classical or quantum fluid system of $N$ particles in a finite volume $V$. The canonical partition function is

$$Q_N=\frac{1}{N!\lambda^{3N}}\int d^3r_1\cdots d^3r_N W_N(\vec{r}_1,\ldots,\vec{r}_N), \tag{1}$$

where

$$W_N(\vec{r}_1,\ldots,\vec{r}_N)=\exp[-\beta V_N(\vec{r}_1,\ldots,\vec{r}_N)], \tag{2}$$

for a classical system and

$$W_N(\vec{r}_1,\ldots,\vec{r}_N)=N!\lambda^{3N}\sum_i \Psi_i(\vec{r}_1,\ldots,\vec{r}_N)\Psi_i^*(\vec{r}_1,\ldots,\vec{r}_N)e^{-\beta E_i}, \tag{3}$$

for a quantum system. Here $V_N(\vec{r}_1,\ldots,\vec{r}_N)$ are the potential energies of the classical system, $\beta=1/k_BT$, $\lambda=h(2\pi mk_BT)^{-1/2}$ is the thermal wavelength, $\Psi_i$ are a complete set of normalized orthonormal wave functions of the quantum system, $E_i$ are the energy eigenvalues.

For both systems, $Q_N$ may be written as [11,12]

$$Q_N=\sum_{\{m_l\}}{}' \prod_{l=1}^{N}\left\{\frac{1}{m_l!}\left[b_l(V,T)\frac{V}{\lambda^3}\right]^{m_l}\right\}, \tag{4}$$

where the primed summation goes over all the sets $\{m_l\}$ that satisfy the condition $\Sigma_{l=1}^N l m_l=N$, $m_l=0,1,2,\ldots$. $b_l(V,T)$ are the cluster integrals, defined by

$$b_l(V,T)=\frac{1}{Vl!\lambda^{3(l-1)}}\int d^3r_1\cdots d^3r_l U_l(\vec{r}_1,\ldots,\vec{r}_l), \tag{5}$$

where $U_l(\vec{r}_1,\ldots,\vec{r}_l)$ are Ursell functions, determined by $W_1,W_2,\ldots,W_l$.

Equation (4) is an exact identity. Hence $Q_N$ may be expressed as a polynomial of degree $N$ in variable $V/N\lambda^3$,

$$Q_N\left(\frac{V}{N\lambda^3}\right)=\sum_{n=0}^{N}A_n(N,V,T)\left(\frac{V}{N\lambda^3}\right)^n$$
$$=A_N(N,V,T)\prod_{j=1}^{N}\left[\frac{V}{N\lambda^3}-z_j(N,V,T)\right], \tag{6}$$

where $A_n(N,V,T)$ are coefficients that depend only on the cluster integrals $b_2(V,T),\ldots,b_N(V,T)$. $z_j=z_j(N,V,T)$ are the zeros of $Q_N$, i.e., $Q_N(z_j)=0$. These zeros are determined only by $b_2(V,T),\ldots,b_N(V,T)$. If some $b_l(V,T)$ are negative, $Q_N$ may have positive real zeros and the zero distribution may cross the positive real axis. Since $Q_N>0$ for all physical values of $N$ and $V$, $Q_N$ is analytic for finite $N$ and $V$. These positive real zeros are not physical singularities of $Q_N$. In the thermodynamic limit, if the zero distribution approaches the positive real axis, $Q_N$ may have a singularity and a phase transition may arise.

It is well known that in the infinite volume limit, the cluster integrals become volume-independent [12], i.e.,

$$\lim_{V\to\infty} b_l(V,T)=b_l(T). \tag{7}$$

In Eq. (4), replacing $b_l(V,T)$ with $b_l(T)$, we obtain the limiting canonical partition function

$$\mathcal{Q}_N\equiv\sum_{\{m_l\}}{}' \prod_{l=1}^{N}\left\{\frac{1}{m_l!}\left[b_l(T)\frac{V}{\lambda^3}\right]^{m_l}\right\}, \tag{8}$$

$\mathcal{Q}_N$ is also a polynomial of degree $N$ in variable $V/N\lambda^3$,

$$\begin{aligned}\mathcal{Q}_N\left(\frac{V}{N\lambda^3}\right)&=\sum_{n=0}^{N}A_n(N,T)\left(\frac{V}{N\lambda^3}\right)^n\\&=A_N(N,T)\prod_{j=1}^{N}\left[\frac{V}{N\lambda^3}-z_j(N,T)\right],\end{aligned} \tag{9}$$

where $z_j=z_j(N,T)$ are the zeros of $\mathcal{Q}_N$, i.e., $\mathcal{Q}_N(z_j)=0$. These zeros are determined only by $b_2(T),\ldots,b_N(T)$. For finite $N$, if some $b_l(T)$ are negative, $\mathcal{Q}_N$ may have positive real zeros and the zero distribution may cross the positive real axis.

From Eq. (7), we obtain

$$\lim_{V\to\infty}A_n(N,V,T)=A_n(N,T), \tag{10}$$

$$\lim_{V\to\infty}z_j(N,V,T)=z_j(N,T). \tag{11}$$

This means that for finite $N$, as $V\to\infty$, the zeros of $Q_N$ approach the zeros of $\mathcal{Q}_N$.

From Eqs. (4) and (8), we obtain the recursive formulas for the canonical partition functions

$$Q_N=\frac{V}{\lambda^3}\frac{1}{N}\sum_{n=1}^{N}nb_n(V,T)Q_{N-n}, \tag{12}$$

$$\mathcal{Q}_N=\frac{V}{\lambda^3}\frac{1}{N}\sum_{n=1}^{N}nb_n(T)\mathcal{Q}_{N-n}, \tag{13}$$

where $Q_0=\mathcal{Q}_0=1$.

## III. ASYMPTOTIC ZERO DISTRIBUTION

Using Eqs. (7), (10), and (11), it is easy to verify that

$$\left(\lim_{N\to\infty}\lim_{V\to\infty}\right)\Big|_{V/N=\mathrm{const}}\quad z_j(N,V,T)=\lim_{N\to\infty}z_j(N,T), \tag{14}$$

$$\left(\lim_{N\to\infty}\lim_{V\to\infty}\right)\Big|_{V/N=\mathrm{const}}\quad (Q_N-\mathcal{Q}_N)=0. \tag{15}$$

This means that in the thermodynamic limit, both $Q_N$ and $\mathcal{Q}_N$ are identical. Their asymptotic zero distributions are also identical.

For a tempered and stable potential, the thermodynamic limit exists [13], which implies that as $N\to\infty$, $V\to\infty$, $V/N=\mathrm{const}$,

$$F(N,V,T)=-k_BT\ln Q_N\to -k_BT\ln\mathcal{Q}_N\to Nf(V/N,T). \tag{16}$$

The zeros are generally located in areas. The curve distribution is a limiting case of the area distribution. For finite $N$, the zeros are isolated points. As $N\to\infty$, the zeros become everywhere dense within these areas. In this case, we may introduce the zero density, $g(N,V,T,x,y)=\lim_{\Delta S\to 0}\Delta N/(N\Delta S)$. Here $\Delta S=\Delta x\Delta y$, $\Delta N$ is the number of zeros in the area $\Delta S$. As $N\to\infty$, $V\to\infty$, $V/N=\mathrm{const}$, we obtain

$$\begin{aligned}\ln Q_N&=\ln A_N(N,V,T)+\sum_{j=1}^{N}\ln\left[\frac{V}{N\lambda^3}-z_j(N,V,T)\right]\\&\to\ln A_N(N,V,T)+N\int_\Omega dxdy\,g(N,V,T,x,y)\\&\quad\times\ln\left[\frac{V}{N\lambda^3}-z(N,V,T)\right]\\&\to\ln\mathcal{Q}_N=\ln A_N(N,T)+\sum_{j=1}^{N}\ln\left[\frac{V}{N\lambda^3}-z_j(N,T)\right]\\&\to\ln A_N(N,T)+N\int_\Omega dxdy\,g(N,T,x,y)\\&\quad\times\ln\left[\frac{V}{N\lambda^3}-z(N,T)\right],\end{aligned} \tag{17}$$

where $\Omega$ represent the zero distribution areas.

Comparing Eq. (17) with (16), we obtain the asymptotic zero distribution,

$$\begin{aligned}\left(\lim_{N\to\infty}\lim_{V\to\infty}\right)\Big|_{V/N=\mathrm{const}}\quad z_j(N,V,T)&=\lim_{N\to\infty}z(N,T)=z(T)\\&=x+iy,\end{aligned} \tag{18}$$

$$\begin{aligned}\left(\lim_{N\to\infty}\lim_{V\to\infty}\right)\Big|_{V/N=\mathrm{const}}\quad g(N,V,T,x,y)&=\lim_{N\to\infty}g(N,T,x,y)\\&=g(T,x,y).\end{aligned} \tag{19}$$

The normalization condition is

$$\int_\Omega dxdy\,g(T,x,y)=1. \tag{20}$$

We obtain

$$F(V/N,T)=-k_BT\ln A_N-Nk_BT\int_\Omega dxdy\, g(T,x,y)\times\ln\left[\frac{V}{N\lambda^3}-x-iy\right]. \tag{21}$$

From Eq. (21), we obtain

$$P=-\left(\frac{\partial F}{\partial V}\right)_T=\frac{k_BT}{\lambda^3}\int_\Omega dxdy\frac{g(T,x,y)}{\frac{V}{N\lambda^3}-x-iy}. \tag{22}$$

Using $Q_N$, we obtain the criterion for the occurrence of phase transition: As $N\to\infty$, $V\to\infty$, $V/N=\text{const}$, the zero distribution of $Q_N$ approaches the positive real axis, with the zero density $g(T,x,y)\neq 0$.

Using $\mathcal{Q}_N$, we obtain the criterion for the occurrence of phase transition: As $N\to\infty$, the zero distribution of $\mathcal{Q}_N$ approaches the positive real axis, with the zero density $g(T,x,y)\neq 0$.

Both criteria are equivalent. Since evaluating $b_l(T)$ is much easier than evaluating $b_l(V,T)$, in practical calculations, we may prefer to use $\mathcal{Q}_N$ instead of using $Q_N$.

## IV. CONTINUOUS PHASE TRANSITION

Let us assume that the system has a continuous phase transition. As $N\to\infty$, the zeros close to the positive real axis are assumed to be on lines, i.e., $z_j=x_j+iy_j$ with $x_j-z_c=k|y_j|$. Here $z_c$ is the critical value of $V/N\lambda^3$ and $k$ is a constant. Then the singular part of the free energy is given by

$$-F_s\sim\sum_j\ln\left[\frac{V}{N\lambda^3}-z_j\right]=N\int_{-y_0}^{y_0}g(y,t)\ln\left[\frac{V}{N\lambda^3}-z_c-k|y|-iy\right]dy, \tag{23}$$

and hence

$$P-P_c\sim-\left(\frac{\partial F_s}{\partial V}\right)_T\sim\int_{-y_0}^{y_0}\frac{g(y,t)}{\frac{V}{N\lambda^3}-z_c-k|y|-iy}dy, \tag{24}$$

where $g(y,t)=dj/(Ndy)$ is the zero density near the positive real axis, $t=(T-T_c)/T_c$, and $y_0$ is a small number. If $g(y,t)\sim|y|^\delta$ with $\delta>0$ [14,15], then from Eq. (24) we obtain $(P-P_c)|_{T=T_c}\sim|V-V_c|^\delta$.

If $b_l(T)$ is independent of $T$, it follows that the zeros are independent of $T$. From Eq. (23), we obtain

$$C_{V=V_c}=-T\frac{\partial^2F(V_c/N,T)}{\partial T^2}\sim-T\frac{\partial^2F_s(V_c/N,T)}{\partial T^2}\sim\int_{-y_0}^{y_0}\frac{g(y)}{\left[\frac{V_c}{N\lambda^3}-z_c-k|y|-iy\right]^2}dy\sim|t|^{\delta-1}. \tag{25}$$

Thus we obtain $(P-P_c)|_{T=T_c}\sim|V-V_c|^\delta$ and $C_{V=V_c}\sim|t|^{\delta-1}$.

## V. FIRST-ORDER GAS-LIQUID PHASE TRANSITION

Below the critical temperature, the fluid has a first-order gas-liquid phase transition. In the gas-liquid coexistence regime, the fluid is not uniform. As is well known, in order to obtain the gas-liquid coexistence regime, the exact canonical partition function in the thermodynamic limit must be used [13]. In writing out the canonical partition function Eq. (4), we make an implicit assumption that the system is uniform. If we use Eq. (22) to calculate the equation of state, $P=P(V/N,T)$, then van der Waals loops will appear (see Sec. 12.1 of Ref. [12]). It is necessary to use the Maxwell's equal-area rule to obtain the gas-liquid coexistence regime, i.e., for $v_l\leqslant v\leqslant v_g$, the free energy is given by

$$F_{coe}(v,T)=\frac{v_g-v}{v_g-v_l}F(v_l,T)+\frac{v-v_l}{v_g-v_l}F(v_g,T), \tag{26}$$

where $v\equiv V/N$, $v_g$ and $v_l$ are the volumes per particle for the pure gas and the pure liquid at the edges of the coexistence regime, respectively. $F(v_g,T)$ and $F(v_l,T)$ are given by Eq. (21). $v_l$ and $v_g$ are given by

$$P(v_g,T)=P(v_l,T), \tag{27}$$

$$NP(v_g,T)(v_g-v_l)+F(v_g,T)-F(v_l,T)=0. \tag{28}$$

The obtained gas-liquid coexistence regime is exact.

In the single gas phase $(v>v_g)$ or the single liquid phase $(v<v_l)$, the free energy is still given by Eq. (21).

## VI. EXAMPLES

Let us give several examples.

### A. 3D ideal Bose gas

The cluster integrals are given by $b_l(T)=l^{-5/2}$ [12]. $W_N$ is given by

$$W_N=\sum_P\delta_P[f(\vec{r}_{P1}-\vec{r}_1)\cdots f(\vec{r}_{PN}-\vec{r}_N)], \tag{29}$$

where $P$ are $N!$ possible permutations, $\delta_P=1$, and $f(\vec{r})=\exp(-\pi r^2/\lambda^2)$. Since all $b_l$ are positive, the zeros are complex or negative.

Let us use the recursive formula of the canonical partition function for ideal Bose gas [16]

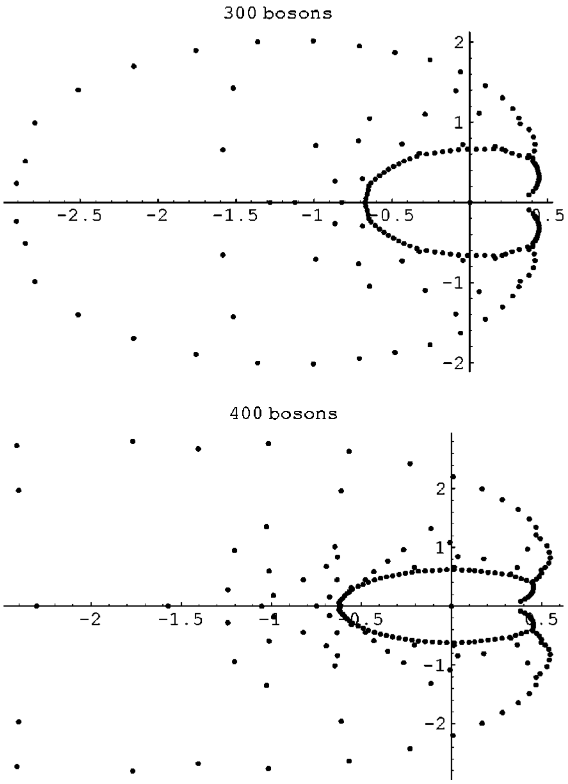

FIG. 1. The zeros of $\mathcal{Q}_{300}$ and $\mathcal{Q}_{400}$ in variable $V/N\lambda^3$ for 3D ideal Bose gas.

$$\mathcal{Q}_N(\beta)=\frac{1}{N}\sum_{n=1}^{N}\mathcal{Q}_1(n\beta)\mathcal{Q}_{N-n}(\beta), \tag{30}$$

where $\mathcal{Q}_0=1$, $\mathcal{Q}_1(\beta)=V/\lambda^3\sim\beta^{-3/2}$. It is easy to show that Eq. (30) is a special case of the general recursive formula Eq. (13). The zeros are shown in Fig. 1. We see that the zeros close to the positive real axis are on lines. For example, $|y|=1.965\,35x-0.653\,769$ for $N=300$, and $|y|=-0.585\,243+1.732\,66x$ for $N=400$. It is estimated that the zero density $g(y)\sim|y|^{\delta}$ with $\delta=2$. Hence near the critical point, we have $(P-P_c)|_T\sim(V-V_c)^2$ for $V>V_c$ and $C_V(t>0)-C_V(t=0)\sim t$. Here $V_c$ is defined by $V_c/N=\lambda^3/\zeta(3/2)$ for given $T$ and $P_c$ is given by $P_c=P(V_c/N,T)$. $T_c$ is defined by $V/N=\lambda_c^3/\zeta(3/2)$ for given $V$ and $\lambda_c=h(2\pi mk_BT_c)^{-1/2}$. As $N\to\infty$, the zero $z_1$ closest to the positive real axis approaches the positive real axis with a scaling relation

$$|z_1-z_c|=1.5743N^{-0.494\,596}, \tag{31}$$

where $z_c=1/\zeta(3/2)=0.382\,793$. For example, $z_1=0.379\,307\pm0.093\,650\,8i$ for $N=300$ and $z_1=0.383\,891\pm0.081\,288\,3i$ for $N=400$.

For given $T$, there exists a first-order phase transion for $v<v_c$, with $v_c=V_c/N=\lambda^3/\zeta(3/2)$. Here $v_g=v_c$, $v_l=0$, $F(v_l,T)=0$. Hence Eq. (26) becomes, for $0<v<v_c$,

$$F_{coe}(v,T)=\frac{v}{v_c}F(v_c,T). \tag{32}$$

### B. 3D ideal Fermi gas

The cluster integrals are given by $b_l(T)=(-1)^{l-1}l^{-5/2}$ [12]. $W_N$ is given by Eq. (29) with $\delta_P=\pm1$ if the permutation $P$ is even or odd. So the canonical partition function is given by

$$\mathcal{Q}_N^{Fermi}\left(\frac{V}{N\lambda^3}\right)=(-1)^N\mathcal{Q}_N^{Bose}\left(-\frac{V}{N\lambda^3}\right). \tag{33}$$

Therefore, the zeros of the ideal Fermi gas are the negative of those of ideal Bose gas, i.e., $z_j^{Fermi}=-z_j^{Bose}$. From Fig. 1 we see that for finite $N$, there exists a zero distribution that crosses the positive real axis, which does not correspond to the physical singularities of the canonical partition function. As $N\to\infty$, the zero distribution does not approach the positive real axis. Hence no phase transition arises, as it should.

### C. van der Waals gas

The equation of state of a van der Waals gas is given by

$$\left(P+\frac{N^2a}{V^2}\right)(V-Nb)=Nk_BT. \tag{34}$$

The critical point is given by

$$\left(\frac{\partial P}{\partial V}\right)_T=0,\quad \left(\frac{\partial^2 P}{\partial V^2}\right)_T=0, \tag{35}$$

giving

$$P_c=a/27b^2,\quad V_c=3Nb,\quad T_c=8a/27bk_B. \tag{36}$$

The equation of corresponding states is given by

$$\left(P'+\frac{3}{V'^2}\right)(3V'-1)=8T', \tag{37}$$

where $P'=P/P_c$, $V'=V/V_c$, and $T'=T/T_c$.

It is easy to show that the fugacity $z$ is given by

$$\frac{b}{\lambda^3}z=\frac{\theta}{1-\theta}\exp\left[\frac{\theta}{1-\theta}-\frac{27}{4T'}\theta\right], \tag{38}$$

where $\theta=Nb/V$. Expanding $\theta$ as a power series in $z$ and comparing with

$$\frac{N}{V}=\frac{1}{\lambda^3}\sum_{l=1}^{\infty}lb_l(T)z^l, \tag{39}$$

we obtain $b_l(T)$. $\mathcal{Q}_N$ is given by

$$\mathcal{Q}_N\left(\frac{V}{Nb}\right)=\left(\frac{b}{\lambda^3}\right)^N\sum_{n=1}^{N}D_n(N,T)\left(\frac{V}{Nb}\right)^n, \tag{40}$$

where $D_n(N,T)$ are coefficients.

We have obtained the zeros of $\mathcal{Q}_N$ for $T'=6.75$, $T'=1$, $T'=27/32$, and $T'=0.75$, as shown in Fig. 2. We have observed the following phenomena.

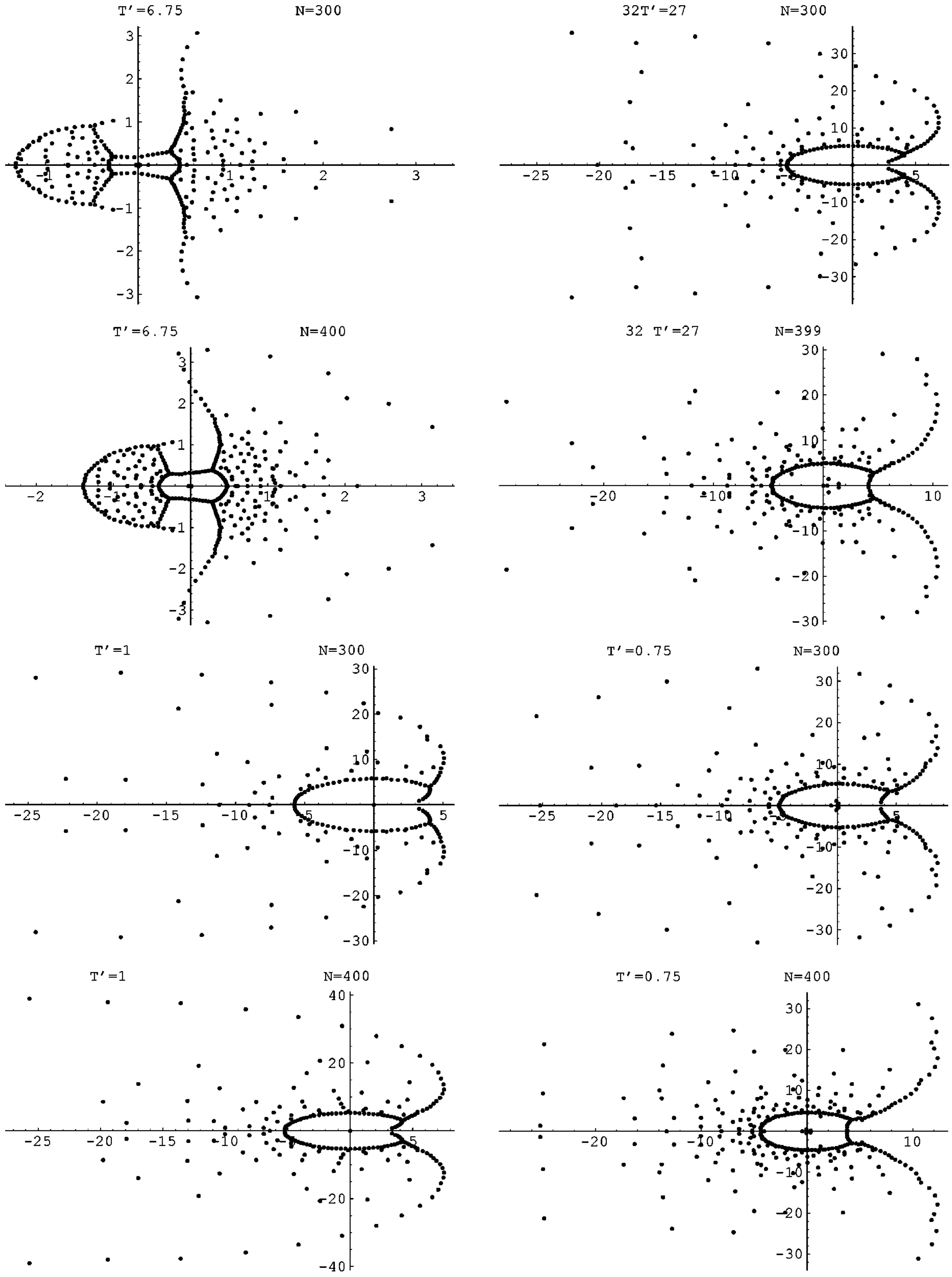

FIG. 2. The zeros of $\mathcal{Q}_N$ in variable $V/Nb$ for van der Waals gas with $T'=6.75$, $T'=1$, $T'=27/32$, and $T'=0.75$.

(1) For $T'=6.75$, $b_l(T)$ almost alternate in sign. For $N=300$ and $N=400$, there exist some zero distributions that cross the positive real axis, which does not correspond to the physical singularities of the canonical partition function. As $N$ increases, the zero distribution does not move towards the positive real axis. Hence no phase transition arises, as it should.

(2) For $T'\leqslant 1$, all $b_l(T)$ are positive. This means that the

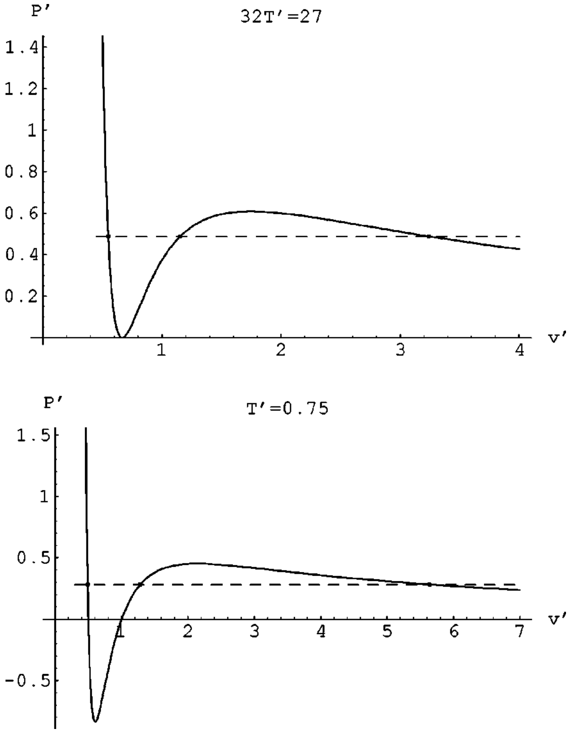

FIG. 3. The van der Waals loops and the Maxwell construction for $T'=27/32$ and $T'=0.75$.

coefficients of $\mathcal{Q}_N$ are positive and hence the zeros of $\mathcal{Q}_N$ are negative or complex.

(3) For $T'=1$, as $N$ increases, the zero distribution moves towards the positive real axis. As $N\rightarrow\infty$, the zero distribution approaches the positive real axis, giving the positive real zero $V_c/Nb=3$. For example, the zero $z_1$ closest to the positive real zero is $z_1=3.276\,74\pm0.888\,295i$ for $N=300$ and $z_1=3.3441\pm0.775\,72i$ for $N=400$. The zeros near the positive real axis are located on lines. For example, $|y|=-4.749\,31+1.716\,05x$ for $N=300$ and $|y|=-4.432\,95+1.554\,43x$ for $N=400$. It is estimated that $\delta=3$ and hence $(P-P_c)|_{T=T_c}\sim(V-V_c)^3$.

(4) For $T'<1$, as $N$ increases, the zero distribution moves towards the positive real axis at a right angle. The zeros near the positive real axis are located on lines. As $N\rightarrow\infty$, the zero distribution approaches the positive real axis, giving the positive real zero $z_r=V_r/Nb$. Here $V_l<V_r<V_g$. For example, $V_g=3.241\,11V_c$, $V_l=0.548\,266V_c$, $V_r\approx4.1V_c$ for $T'=27/32$ and $V_g=5.643\,09V_c$, $V_l=0.489\,631V_c$, $V_r\approx3.8V_c$ for $T'=0.75$ (see Fig. 3). For example, the zero $z_1$ closest to the positive real zero is $z_1=2.861\,92\pm0.948\,978i$ for $T'=27/32$, $N=300$ and $z_1=4.118\,52\pm0.426\,805i$ for $T'=27/32$, $N=399$; $z_1=3.696\,47\pm0.820\,717i$ for $T'=0.75$, $N=300$ and $z_1=3.792\,94\pm0.364\,11i$ for $T'=0.75$, $N=400$.

For $T'<1$, in the gas-liquid coexistence regime ($v_l\leqslant v\leqslant v_g$), the free energy is given by Eq. (26). In the single gas phase ($v>v_g$) or the single liquid phase ($v<v_l$), the free energy is given by Eq. (21).

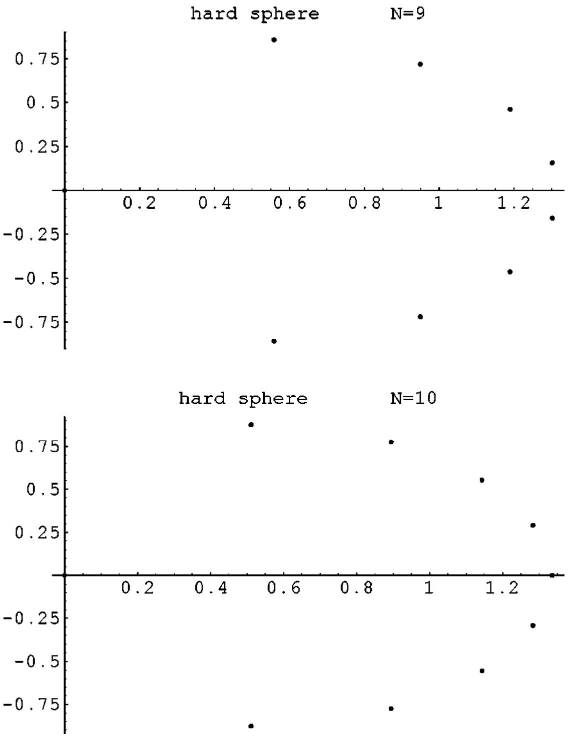

FIG. 4. The zeros of $\mathcal{Q}_9$ and $\mathcal{Q}_{10}$ in variable $V/4Nv_0$ for classical hard-sphere gas.

### D. 3D classical hard-sphere gas

The known virial coefficients are [17] $a_2=c=4v_0/\lambda^3$, $a_3/c^2=0.625$, $a_4/c^3=0.286\,95$, $a_5/c^4=0.110\,25$, $a_6/c^5=0.0389$, $a_7/c^6=0.0137$, $a_8/c^7=0.004\,45$, $a_9/c^8=0.001\,50$, $a_{10}/c^9=0.000\,51$. From these virial coefficients, we obtain the infinite-volume cluster integrals $b_2/c=-1$, $b_3/c^2=1.6875$, $b_4/c^3=-3.553\,98$, $b_5/c^4=8.468\,76$, $b_6/c^5=-21.8381$, $b_7/c^6=59.4913$, $b_8/c^7=-168.75$, $b_9/c^8=493.735$, $b_{10}/c^9=-1480.48$. The canonical partition function is a polynomial in variable $V/Nv_0$. For $N=1$–10, $\mathcal{Q}_N=(4v_0/\lambda^3)^N q_N$ are given by

$$q_1=z,\quad q_2=2z-2z^2,\quad q_3=5.0625z-9z^2+4.5z^3,$$

$$q_4=-14.215\,92z+35z^2-32z^3+10.666\,67z^4,$$

$$q_5=42.3438z-131.037z^2+167.969z^3-104.167z^4+26.0417z^5,\quad q_6=-131.029z+484.078z^2-784.331z^3+688.5z^4-324z^5+64.8001z^6,$$

$$q_7=416.439z-1778.91z^2+3449.17z^3-3848.2z^4+2582.33z^5-980.408z^6+163.402z^7,\quad q_8=-1350z+6523.9z^2-14\,636z^3+19\,602.6z^4-16\,799z^5+9147.72z^6-2912.71z^7+416.102z^8,\quad q_9=4443.62z-23\,910.5z^2+60\,669.4z^3-9481.8z^4+97\,197z^5-67\,868.7z^6$$

$$+31\,139.1z^{7}-8541.03z^{8}+1067.63z^{9},$$

$$\begin{aligned} q_{10}=&-14\,804.8z+87\,634.9z^{2}-24\,7402z^{3}+434\,743z^{4}\\ &-521\,093z^{5}+439\,440z^{6}-259\,430z^{7}+102\,927z^{8}\\ &-24\,801.6z^{9}+2755.73z^{10}, \end{aligned} \tag{41}$$

where $z=V/4Nv_0$, $v_0$ is the volume of a hard sphere. The zeros of $\mathcal{Q}_9$ and $\mathcal{Q}_{10}$ are shown in Fig. 4.

### E. 1D classical hard rod gas

This problem is exactly solvable [18]. It is found that $Q_N$ is a polynomial of degree $N$ in variable $L/Na$,

$$Q_N=\frac{1}{N!}\left(\frac{Na}{\lambda}\right)^{N}\left(\frac{L}{Na}-\frac{N-1}{N}\right)^{N}, \tag{42}$$

where $L$ is the length of the system, $a$ is the length of a rod. Therefore, the zeros are $z_j=(N-1)/N$ and are positive. No phase transition arises.

## VII. CONCLUSION

Our observation is that for finite $N$ and $V$, the canonical partition function $Q_N$ of a classical or quantum fluid of $N$ particles may be expressed as a polynomial of degree $N$ in variable $V/N\lambda^3$, with coefficients that depend on only the cluster integrals $b_2(V,T), \ldots, b_N(V,T)$. The canonical partition function is determined completely by its zeros. In the infinite volume limit, the cluster integrals become volume independent. Using $b_l(T)$ to replace $b_l(V,T)$ in $Q_N$, we obtain the limiting canonical partition function $\mathcal{Q}_N$. For a tempered and stable potential, the thermodynamic limit exists. In the thermodynamic limit, $Q_N$ and $\mathcal{Q}_N$ are identical. Their asymptotic zero distributions are also identical. The thermodynamic limit guarantees the existence of the asymptotic zero distributions of $Q_N$ and $\mathcal{Q}_N$. In the thermodynamic limit, if the zero distribution approaches the positive real axis, a phase transition arises. The behavior of phase transition is determined solely by the zero distribution near the positive real axis. Below the critical temperature, the Maxwell's equal-area rule must be used to obtain the gas-liquid coexistence regime. Several examples are given. It is found that for 3D ideal Bose gas and van der Waals gas, as $N\to\infty$, the zero distribution of $\mathcal{Q}_N$ approaches the positive real axis and the zeros near the positive real axis are on lines, which determines the behaviors of phase transitions.

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