# Isobars of an ideal Bose gas within the grand canonical ensemble

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We investigate the isobar of an ideal Bose gas confined in a cubic box within the grand canonical ensemble for a large yet finite number of particles, $N$. After solving the equation of the spinodal curve, we derive precise formulas for the supercooling and the superheating temperatures that reveal an $N^{-1/3}$ or $N^{-1/4}$ power correction to the known Bose-Einstein condensation temperature in the thermodynamic limit. Numerical computations confirm the accuracy of our analytical approximation, and further show that the isobar zigzags on the temperature-volume plane if $N \geqslant 14\,393$. In particular, for the Avogadro's number of particles, the volume expands discretely about $10^5$ times. Our results quantitatively agree with a previous study on the canonical ensemble within 0.1% error.

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## I. INTRODUCTION

A classic paper written by Anderson in 1972 is titled "More is Different" [1], which characterizes the notion of "emergence," i.e., the way complex systems and patterns arise out of a multiplicity of relatively simple interactions. One relevant question is then, *How many is different?* To answer the question, we may consult quantum statistical physics where the key quantity is the partition function. Once we know the exact expression of the partition function, we can compute various physical quantities. For example, when the partition function in the grand canonical ensemble, $\mathcal{Z}(T,V,z)$, depends on three variables (temperature, volume, fugacity), the pressure and the average number of the particles are given by

$$P = k_B T \partial_V \ln \mathcal{Z}(T,V,z)\,, \quad N = z\partial_z \ln \mathcal{Z}(T,V,z)\,, \tag{1}$$

where $k_B$ denotes the Boltzmann constant. If the system is finite, due to the analytic property of the partition function, the physical quantities that are given as a fraction between the partition function and its derivatives, like (1), cannot feature any mathematical singularities. On the contrary, infinite systems may do so. In this way, it seems that, *More is the same; infinitely more is different* [2].

Viewing Avogadro's number, $N_A \simeq 6 \times 10^{23}$, as an enormous quantity might well suggest to take the infinity limit or the thermodynamic limit: the limit of the large volume and the large number of particles with the density held fixed [3]. Essentially due to the quantum commutation relation, $[\hat{x},\hat{p}] = i\hbar$, the reduced Planck's constant, $\hbar$, is positioned inside the expression of the partition function along with the volume, $V$, generically through the combination, $V/\hbar^3$, where the power of $\hbar$ corresponds to the dimension of space. This implies that the large volume limit may be traded with the classical limit $\hbar \to 0$, and hence special care should be taken while considering the thermodynamic limit in order to preserve any quantum nature [4–7]. Further, since taking the thermodynamic limit and taking the derivatives do not commute in general, it is safer and thus preferable to take the thermodynamic limit only at the end of computation.

Recently, two of the authors investigated the isobar of an ideal Bose gas confined in a box within the canonical ensemble, without assuming the thermodynamic limit [8]. Numerical computations based on the exact expression of the corresponding canonical partition function revealed that if the number of particles is equal to or greater than a certain critical value, which turns out to be 7616 for the "cubic" box, the isobar zigzags featuring an "$\mathcal{S}$ shape" on the $(T,V)$ plane (cf. Fig. 2 in the present paper). The two turning points on the $\mathcal{S}$-shaped isobar are naturally identified as the "supercooling" $(T^*,V^*)$ and the "superheating" $(T^{**},V^{**})$ points. Between the supercooling and the superheating temperatures, $T^* < T < T^{**}$, the volume becomes triple-valued. Since all the physical quantities are functions of the temperature and the volume, every physical quantity itself is triple-valued between the two temperatures and changes discontinuously on isobars as the temperature increases. In fact, any temperature derivative restricted on isobars diverges at the points with the universal singularity exponent, 1/2 [9]. In this way, imposing the "constant pressure constraint," a discrete phase transition was for the first time realized in a *finite* system, derived *ab initio* from the corresponding partition function.

However, due to the limitation in our computational power (supercomputer, SUN B6048), the numerical analyses performed in Refs. [8,9] were restricted to the particle numbers not greater than one million. In particular, the separation between the supercooling and the superheating temperatures gets wider as the number of particles increases within the range $7616 \leqslant N \leqslant 10^6$. Hence, it was not clear what would happen for a much larger number of particles, or closer to the thermodynamic limit.

It is the purpose of the present paper first to verify the same feature of the ideal Bose gas within the grand canonical ensemble, both analytically and numerically, and second to address rigorously its thermodynamic limiting behavior.

Basically, we set to analyze the following equation [10], which shall be derived from the grand canonical partition function of the ideal Bose gas:

$$\left.\frac{dT}{dV}\right|_{P,N} = 0\,. \tag{2}$$

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This condition is equivalent to the usual definition of the spinodal curve [10–13],

$$\left.\frac{dP}{dV}\right|_{T,N} = 0\,, \tag{3}$$

and must be met at the supercooling and the superheating points on isobars.

## II. ANALYSIS

Essentially due to the nonrelativistic dispersion relation, $E = \vec{p}^{\,2}/(2m)$, where $m$ is the mass of the particle, the grand canonical partition function of the ideal Bose gas confined in a cubic box is a two-variable function depending on the fugacity, $z$, and the combination of temperature and volume, $TV^{2/3}$. Specifically, we set, as for the two fundamental variables in our analysis,

$$\varepsilon := \frac{\pi^2\hbar^2}{2mk_B}(TV^{2/3})^{-1}\,, \quad \sigma := -\ln z\,. \tag{4}$$

In terms of these, the grand canonical partition function reads

$$\ln \mathcal{Z}(\varepsilon,\sigma) = -\sum_{\vec{n}\in\mathbb{N}^3} \ln\left(1 - e^{-\varepsilon\vec{n}^2-\sigma}\right). \tag{5}$$

With the Dirichlet boundary condition that we deliberately impose, $\vec{n} = (n_1,n_2,n_3) \in \mathbb{N}^3$ is a *positive* integer-valued lattice vector, such that the lowest value of $\vec{n}^2$ is the spatial dimension, 3, and $\sigma$ is bounded from below,

$$\sigma > -3\varepsilon\,, \tag{6}$$

while $\varepsilon$ is positive. Searching for spinodal curves near to the thermodynamic limit, we shall be interested in the small-$\varepsilon$ region.

It is useful to note, for the computation of various physical quantities such as (1),

$$T\partial_T|_{V,z} = \tfrac{3}{2}V\partial_V|_{T,z} = -\varepsilon\partial_\varepsilon\,, \quad z\partial_z|_{T,V} = -\partial_\sigma\,. \tag{7}$$

It follows that the number of particles (1) reads

$$N(\varepsilon,\sigma) = -\partial_\sigma \ln \mathcal{Z}(\varepsilon,\sigma)\,, \tag{8}$$

and the formula of the pressure (1) is equivalent to

$$\mathcal{T}_P(\varepsilon,\sigma) := \left(\frac{2m}{\pi^2\hbar^2}\right)^{\frac{3}{5}} k_B T P^{-\frac{2}{5}} = \left[-\frac{2}{3}\varepsilon^{\frac{5}{2}}\partial_\varepsilon \ln \mathcal{Z}(\varepsilon,\sigma)\right]^{-\frac{2}{5}}. \tag{9}$$

Being a combination of $T$ and $P$, this dimensionless quantity, $\mathcal{T}_P$, can determine the physical temperature on an arbitrarily given isobar. Similarly, we may define a dimensionless "volume,"

$$\mathcal{V}_P(\varepsilon,\sigma) := \left(\frac{2m}{\pi^2\hbar^2}P\right)^{\frac{3}{5}} V = \left[-\frac{2}{3}\partial_\varepsilon \ln \mathcal{Z}(\varepsilon,\sigma)\right]^{\frac{3}{5}}, \tag{10}$$

and another dimensionless "temperature,"

$$\mathcal{T}_\rho(\varepsilon,\sigma) := \frac{2m}{\pi^2\hbar^2}k_B T\left(\frac{V}{N}\right)^{\frac{2}{3}} = \left[-\varepsilon^{\frac{3}{2}}\partial_\sigma \ln \mathcal{Z}(\varepsilon,\sigma)\right]^{-\frac{2}{3}}. \tag{11}$$

As we already wrote, $N$, $\mathcal{T}_P$, $\mathcal{V}_P$, and $\mathcal{T}_\rho$ are functions of the two variables $\varepsilon$, $\sigma$ only. They satisfy the identities

$$\varepsilon\mathcal{T}_P(\varepsilon,\sigma) = [\mathcal{V}_P(\varepsilon,\sigma)]^{-\frac{2}{3}}\,, \quad \varepsilon\mathcal{T}_\rho(\varepsilon,\sigma) = [N(\varepsilon,\sigma)]^{-\frac{2}{3}}\,. \tag{12}$$

Now the spinodal curve (2) is positioned on the $(\varepsilon,\sigma)$ plane to satisfy $dN(\varepsilon,\sigma) = 0$ and $d\mathcal{T}_P(\varepsilon,\sigma) = 0$, such that the following linear equation must admit a nontrivial solution:

$$\begin{pmatrix}0\\0\end{pmatrix} = \begin{pmatrix}\partial_\varepsilon\partial_\sigma \ln\mathcal{Z} & \partial_\sigma^2 \ln\mathcal{Z}\\ \left(\frac{5}{2}\varepsilon^{-1}\partial_\varepsilon + \partial_\varepsilon^2\right)\ln\mathcal{Z} & \partial_\varepsilon\partial_\sigma \ln\mathcal{Z}\end{pmatrix}\begin{pmatrix}d\varepsilon\\ d\sigma\end{pmatrix}. \tag{13}$$

It follows that the $2\times 2$ matrix in (13) must be singular,

$$\Phi := \det\begin{pmatrix}\partial_\varepsilon\partial_\sigma \ln\mathcal{Z} & \partial_\sigma^2 \ln\mathcal{Z}\\ \left(\frac{5}{2}\varepsilon^{-1}\partial_\varepsilon + \partial_\varepsilon^2\right)\ln\mathcal{Z} & \partial_\varepsilon\partial_\sigma \ln\mathcal{Z}\end{pmatrix} \equiv 0\,. \tag{14}$$

This algebraic equation determines the spinodal curve on the $(\varepsilon,\sigma)$ plane. Further, it is straightforward to show that the determinant is proportional to $\frac{d\mathcal{T}_P}{d\mathcal{V}_P}|_N$ as

$$\left.\frac{d\ln\mathcal{T}_P}{d\ln\mathcal{V}_P}\right|_N = \frac{2}{3\left(\partial_\sigma^2\ln\mathcal{Z}\right)^2 \mathrm{var}(\vec{n}^2)}\Phi\,, \tag{15}$$

where $\mathrm{var}(\vec{n}^2)$ is our shorthand notation for

$$\mathrm{var}(\vec{n}^2) := \frac{\partial_\varepsilon^2\ln\mathcal{Z}}{\partial_\sigma^2\ln\mathcal{Z}} - \left(\frac{\partial_\varepsilon\partial_\sigma\ln\mathcal{Z}}{\partial_\sigma^2\ln\mathcal{Z}}\right)^2, \tag{16}$$

which can be identified as the variance of $\vec{n}^2$ with respect to the probability distribution proportional to $\sinh^{-2}(\frac{1}{2}\varepsilon\vec{n}^2 + \frac{1}{2}\sigma)$ (in our convention, $\sinh^{-2}(x) = [\sinh(x)]^{-2}$, etc.). Hence, $\mathrm{var}(\vec{n}^2)$ is positive definite and the vanishing of the determinant is, as expected, equivalent to the vanishing of $\frac{d\mathcal{T}_P}{d\mathcal{V}_P}|_N$. Our main task is to solve (14) and express the solutions in terms of the more physical variables $N$, $\mathcal{T}_P$, $\mathcal{V}_P$, and $\mathcal{T}_\rho$ using (8), (9), (10), and (11). Our numerical solutions are depicted in Figs. 1 and 2, along with an analytic approximation that we discuss below.

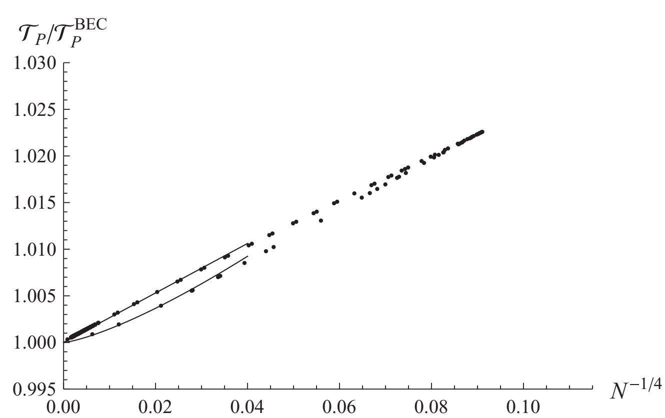


FIG. 1. The supercooling and the superheating spinodal curves on the $(N^{-1/4},\mathcal{T}_P/\mathcal{T}_P^{\rm BEC})$ plane (lower and upper curves, respectively). The dotted curves are from the numerical computations based on the exact formulas (8), (9), and (14). The solid lines correspond to our analytic approximation (31) and (32) for large $N$. A pair of spinodal curves starts to develop at $N = N_c \simeq 14\,392.4$ ($N_c^{-1/4} \simeq 0.091\,299\,1$), which is comparable to the critical number of the canonical ensemble, 7616 [8].

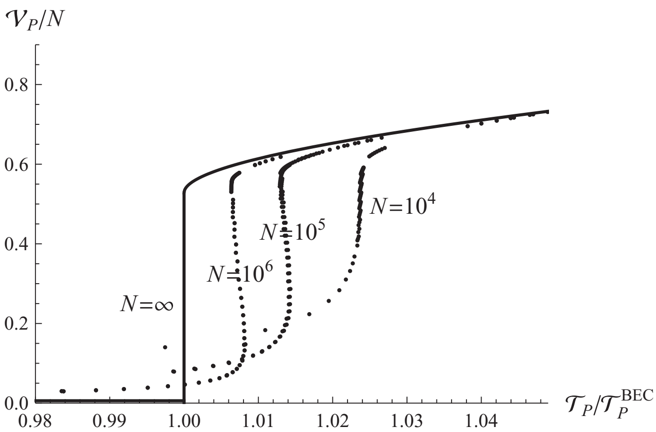


FIG. 2. Isobar curves on the $(\mathcal{T}_P/\mathcal{T}_P^{\text{BEC}},\mathcal{V}_P/N)$ plane. They zigzag featuring an "$\mathcal{S}$ shape" if $14\,393 \leqslant N < \infty$.

### A. Analytic approximation

Our analytic analysis starts with the following expression for the derivatives of the partition function, which holds for $k \geqslant \max(l,1)$:

$$(\partial_\varepsilon)^l(\partial_\sigma)^{k-l}\ln\mathcal{Z}(\varepsilon,\sigma) = \sum_{\vec{n}\in\mathbb{N}^3}\sum_{a=1}^{k}(\vec{n}^2)^l\frac{(-1)^k C_{k,a}}{(e^{\varepsilon\vec{n}^2+\sigma}-1)^a}$$
$$= \sum_{\vec{n}\in\mathbb{N}^3}\sum_{p=0}^{\infty}\sum_{b=1}^{k+p}(\vec{n}^2)^l\left(\frac{\sigma^p}{p!}\right)\frac{(-1)^{k+p}C_{k+p,b}}{(e^{\varepsilon\vec{n}^2}-1)^b}. \qquad (17)$$

Here $C_{k,a}$ are positive integers, determined by a recurrence relation,

$$C_{k+1,a} = aC_{k,a} + (a-1)C_{k,a-1}, \qquad (18)$$

with the initial value, $C_{1,1} = 1$. The recurrence relation comes from the expansion

$$\left(-\frac{d}{dx}\right)^k \ln(1-e^{-x}) = -\sum_{a=1}^{k}\frac{C_{k,a}}{(e^x-1)^a}. \qquad (19)$$

Taking an $x$ derivative of the right-hand side of (19) leads to (18).

Further, it is also useful to note

$$\partial_\sigma^2\ln\mathcal{Z}(\varepsilon,\sigma) = \sum_{\vec{n}\in\mathbb{N}^3}\left[\frac{1}{(\varepsilon\vec{n}^2+\sigma)^2} - \sum_{k=2}^{\infty}\left(\frac{1}{4}\right)^k \times \cosh^{-2}\left(\frac{\varepsilon\vec{n}^2+\sigma}{2^k}\right)\right]. \qquad (20)$$

This expression is due to an identity,

$$\sinh^{-2}(x) = \left(\frac{1}{4}\right)^p\sinh^{-2}\left(\frac{x}{2^p}\right) - \sum_{j=1}^{p}\left(\frac{1}{4}\right)^j\cosh^{-2}\left(\frac{x}{2^j}\right)$$
$$= x^{-2} - \sum_{j=1}^{\infty}\left(\frac{1}{4}\right)^j\cosh^{-2}\left(\frac{x}{2^j}\right), \qquad (21)$$

which holds for an arbitrary positive integer, $p$. Taking $p$ to infinity gives the second equality in (21).

In order to compute the sums in (17), we adopt the following scheme of analytic approximations:

(i) Introduce a cutoff, $\Lambda \geqslant 3$, for the lattice sum,

$$\sum_{\vec{n}\in\mathbb{N}^3} f(\varepsilon\vec{n}^2) = \sum_{\vec{n}^2\leqslant\Lambda} f(\varepsilon\vec{n}^2) + \sum_{\vec{n}^2>\Lambda} f(\varepsilon\vec{n}^2).$$

(ii) Approximate the last term by an integral,

$$\sum_{\vec{n}\in\mathbb{N}^3} f(\varepsilon\vec{n}^2) \simeq \sum_{\vec{n}^2\leqslant\Lambda} f(\varepsilon\vec{n}^2) + \int_{\varepsilon\Lambda}^{\infty}dx\left(\frac{\pi}{4}\varepsilon^{-\frac{3}{2}}x^{\frac{1}{2}} - \frac{3\pi}{8}\varepsilon^{-1}\right)f(x).$$

(iii) Put $\sigma = -\varepsilon\mu$ with a new variable, $\mu$. From (6), $\mu < 3$.

(iv) Keep only the dominant singular terms in the power-series expansion of (ii) in $\varepsilon$, which are manifestly cutoff-independent. Allow $\mu$ to be expandable in $\varepsilon$ with an arbitrary leading power.

The approximation (ii) can be traced back to an identity,

$$\sum_{\vec{n}\in\mathbb{N}^3} f(\varepsilon\vec{n}^2) = \frac{1}{8}\left[\sum_{\vec{n}\in\mathbb{Z}^3} f(\varepsilon\vec{n}^2)\right] - \frac{3}{8}\left[\sum_{\vec{n}\in\mathbb{Z}^2} f(\varepsilon\vec{n}^2)\right] + \frac{3}{8}\left[\sum_{n\in\mathbb{Z}} f(\varepsilon n^2)\right] - \frac{1}{8}f(0), \qquad (22)$$

where the first two sums on the right-hand side of the equality can be approximated by integrals in three- or two-dimensional spherical coordinates, and the remaining part may be neglected for small $\varepsilon$ (see [4] and references therein).

With the constants,

$$a_s := \int_0^\infty dx\,\frac{x^s}{e^x-1} = \Gamma(s+1)\zeta(s+1),$$
$$b := \int_0^\infty dx\,\sqrt{x}\cosh^{-2}(x), \qquad (23)$$

and the estimations [4],

$$\int_{\varepsilon\Lambda}^{\infty}dx\,\frac{1}{e^x-1} \simeq \int_{\varepsilon\Lambda}^{\infty}dx\,\frac{xe^x}{(e^x-1)^2} \simeq -\ln\varepsilon, \qquad (24)$$

our scheme enables us to compute

$$\partial_\varepsilon\ln\mathcal{Z} \simeq -\left\langle\frac{3\varepsilon^{-1}}{3-\mu}\right\rangle_{-2} - \frac{\pi}{4}a_{\frac{3}{2}}\varepsilon^{-\frac{5}{2}} + \frac{3\pi}{8}a_1\varepsilon^{-2},$$
$$\partial_\sigma\ln\mathcal{Z} \simeq -\left\langle\frac{\varepsilon^{-1}}{3-\mu}\right\rangle_{-\frac{3}{2}} - \frac{\pi}{4}a_{\frac{1}{2}}\varepsilon^{-\frac{3}{2}} - \frac{3\pi}{8}\varepsilon^{-1}\ln\varepsilon,$$
$$\partial_\varepsilon^2\ln\mathcal{Z} \simeq \left\langle\frac{9\varepsilon^{-2}}{(3-\mu)^2}\right\rangle_{-3} + \frac{5\pi}{8}a_{\frac{3}{2}}\varepsilon^{-\frac{7}{2}} - \frac{3\pi}{4}a_1\varepsilon^{-3}, \qquad (25)$$
$$\partial_\varepsilon\partial_\sigma\ln\mathcal{Z} \simeq \left\langle\frac{3\varepsilon^{-2}}{(3-\mu)^2}\right\rangle_{-\frac{5}{2}} + \frac{3\pi}{8}a_{\frac{1}{2}}\varepsilon^{-\frac{5}{2}} + \frac{3\pi}{8}\varepsilon^{-2}\ln\varepsilon,$$
$$\partial_\sigma^2\ln\mathcal{Z} \simeq \frac{\varepsilon^{-2}}{(3-\mu)^2} + \left[\sum_{\vec{n}^2>3}\frac{1}{(\vec{n}^2-\mu)^2}\right]\varepsilon^{-2} - \frac{(2+\sqrt{2})\pi}{8}b\,\varepsilon^{-\frac{3}{2}},$$

where $\langle g(\varepsilon)\rangle_{-n}$ denotes a part of the series expansion of $g(\varepsilon)$ in $\varepsilon$, which is at least $(-n)$th-order singular, for example,

$$\langle \varepsilon^{-\frac{3}{2}}+\varepsilon^{-1}+1+\varepsilon\rangle_{-\frac{3}{2}}=\varepsilon^{-\frac{3}{2}}, \quad \langle \varepsilon^{-\frac{3}{2}}+\varepsilon^{-1}+1+\varepsilon\rangle_{-1}=\varepsilon^{-\frac{3}{2}}+\varepsilon^{-1}, \text{ etc.} \tag{26}$$

Especially for $\partial_\sigma^2 \ln \mathcal{Z}$, it is important to note that the sum, $\sum_{\vec{n}^2>3}(\vec{n}^2-\mu)^{-2}$, converges, since

$$\sum_{\vec{n}^2>\Lambda}\frac{1}{(\vec{n}^2-\mu)^2}\leqslant\sum_{\vec{n}^2>\Lambda}\frac{1}{(\vec{n}^2-|\mu|)^2}\simeq\int_\Lambda^\infty dx\,\frac{\frac{\pi}{4}x^{\frac{1}{2}}-\frac{3\pi}{8}}{(x-|\mu|)^2} = \frac{\pi}{8}\left[\frac{2\sqrt{\Lambda}-3}{\Lambda-|\mu|}+\frac{1}{\sqrt{|\mu|}}\ln\left(\frac{\sqrt{\Lambda}+\sqrt{|\mu|}}{\sqrt{\Lambda}-\sqrt{|\mu|}}\right)\right]. \tag{27}$$

The numerical values of the constants are

$$a_{\frac{1}{2}}=\frac{\sqrt{\pi}}{2}\zeta\left(\frac{3}{2}\right)\simeq 2.315\,16,\quad a_1=\frac{\pi^2}{6}\simeq 1.644\,93, \quad a_{\frac{3}{2}}=\frac{3\sqrt{\pi}}{4}\zeta\left(\frac{5}{2}\right)\simeq 1.783\,29,\quad b\simeq 0.758\,128. \tag{28}$$

Having the expressions (25), we now proceed to solve the spinodal curve condition (14). Since the indices $n$ of the symbol $\langle\cdot\rangle_{-n}$ appearing in (25) are various, letting the leading singular term of $\frac{\varepsilon^{-1}}{3-\mu}$ be order of $\varepsilon^{-h}$, we need to separately consider the following nine possible cases:

$$h<1,\quad h=1,\quad 1<h<\tfrac{5}{4},\quad h=\tfrac{5}{4},\quad \tfrac{5}{4}<h<\tfrac{3}{2},\quad h=\tfrac{3}{2},\quad \tfrac{3}{2}<h<2,\quad h=2,\quad 2<h\,.$$

Keeping only the two dominant terms in (25) for each case, it is straightforward to check that only the two cases, $h=1$ and 2, admit solutions, and hence there are two spinodal curves, as follows.

(i) *Curves on the* $(\varepsilon,\mu)$ *plane*.

(a) Constant $\mu\simeq\mu^*$ line with $h=1$, satisfying

$$\sum_{\vec{n}\in\mathbb{N}^3}\frac{1}{(\vec{n}^2-\mu^*)^2}=\frac{9}{8}\left[\zeta(\frac{3}{2})\right]^2. \tag{29}$$

Numerically, we get

$$\mu^*\simeq 2.618\,73.$$

(b) Linear line with $h=2$,

$$\mu\simeq\mu^{**}(\varepsilon)=3-\frac{240}{\pi^3}\,\varepsilon\,. \tag{30}$$

(ii) *Curves in terms of the physical variables,* $N$, $\mathcal{T}_P$, $\mathcal{V}_P$, $\mathcal{T}_\rho$.

(a) Supercooling spinodal curve, for $h=1$,

$$\mathcal{T}_P^*/\mathcal{T}_P^{\rm BEC}\simeq 1+\frac{\pi^3}{60}\left[\left(\mathcal{T}_P^{\rm BEC}\right)^5/\mathcal{T}_\rho^{\rm BEC}\right]^{\frac{1}{2}}N^{-\frac{1}{3}}, \quad \mathcal{V}_P^*\simeq\left(\mathcal{T}_\rho^{\rm BEC}/\mathcal{T}_P^{\rm BEC}\right)^{\frac{3}{2}}\left(N+\frac{\pi}{4}\mathcal{T}_\rho^{\rm BEC}N^{\frac{2}{3}}\ln N\right), \quad \mathcal{T}_\rho^*/\mathcal{T}_\rho^{\rm BEC}\simeq 1+\frac{\pi}{6}\mathcal{T}_\rho^{\rm BEC}N^{-\frac{1}{3}}\ln N. \tag{31}$$

(b) Superheating spinodal curve, for $h=2$,

$$\mathcal{T}_P^{**}/\mathcal{T}_P^{\rm BEC}\simeq 1+\frac{1}{150}\left(\frac{\pi^{15}}{15}\right)^{\frac{1}{4}}\left(\mathcal{T}_P^{\rm BEC}\right)^{\frac{5}{2}}N^{-\frac{1}{4}}, \quad \mathcal{V}_P^{**}\simeq 8\left(\frac{15}{\pi^3}\right)^{\frac{3}{4}}\left(\mathcal{T}_P^{\rm BEC}\right)^{-\frac{3}{2}}N^{\frac{3}{4}}, \quad \mathcal{T}_\rho^{**}\simeq 4\left(\frac{15}{\pi^3}\right)^{\frac{1}{2}}N^{-\frac{1}{6}}. \tag{32}$$

In the above, $\mathcal{T}_P^{\rm BEC}$ and $\mathcal{T}_\rho^{\rm BEC}$ denote two constants,

$$\mathcal{T}_P^{\rm BEC}=\left(\frac{64}{\pi^3}\right)^{\frac{1}{5}}\left[\zeta\left(\frac{5}{2}\right)\right]^{-\frac{2}{5}}\simeq 1.027\,81, \quad \mathcal{T}_\rho^{\rm BEC}=\frac{4}{\pi}\left[\zeta\left(\frac{3}{2}\right)\right]^{-\frac{2}{3}}\simeq 0.671\,253, \tag{33}$$

which correspond to the well-known Bose-Einstein condensation temperatures for the variables, $\mathcal{T}_P$ (9) and $\mathcal{T}_\rho$ (11), the definitions of which we recall here,

$$\mathcal{T}_P:=\left(\frac{2m}{\pi^2\hbar^2}\right)^{\frac{3}{5}}k_BTP^{-\frac{2}{5}},\quad \mathcal{T}_\rho:=\frac{2m}{\pi^2\hbar^2}k_BT\left(\frac{V}{N}\right)^{\frac{2}{3}}, \quad \mathcal{V}_P:=\left(\frac{2m}{\pi^2\hbar^2}P\right)^{\frac{3}{5}}V=N\left(\frac{\mathcal{T}_\rho}{\mathcal{T}_P}\right)^{\frac{3}{2}}. \tag{34}$$

## III. DISCUSSION

As computable from our analytic expressions, (31) and (32), the separation between the supercooling and the superheating temperatures becomes maximal if the number of particle is equal to

$$N_{\rm max}=\frac{5^{15}}{(27\pi)^3}\left[\zeta\left(\frac{3}{2}\right)\right]^4\simeq 2.328\,90\times 10^6. \tag{35}$$

This also agrees with the numerical result in Fig. 1, as $(N_{\rm max})^{-1/4}\simeq 0.025\,598\,4$. When the number of particles exceeds this critical value, the two temperatures $\mathcal{T}_P^*$ and $\mathcal{T}_P^{**}$—satisfying $\mathcal{T}_P^{\rm BEC}<\mathcal{T}_P^*<\mathcal{T}_P^{**}$—get closer, and eventually converge to the BEC temperature, $\mathcal{T}_P^{\rm BEC}$ (33), in the thermodynamic limit. That is to say, $N_{\rm max}$ is the critical number for the thermodynamic limit to start to work.

The ratio of the two volumes,

$$\mathcal{V}_P^*/\mathcal{V}_P^{**}\simeq\left(\frac{\pi}{15}\right)^{\frac{3}{4}}\left[\zeta\left(\frac{3}{2}\right)\right]^{-1}N^{\frac{1}{4}}\simeq 0.118\,511\times N^{\frac{1}{4}}, \tag{36}$$

enables us to estimate the discrete volume expansion rate at the liquid-gas-type phase transition. For Avogadro's number, $N_A\simeq 6.022\,14\times 10^{23}$, the volume expansion rate (36) gives $\mathcal{V}_P^*/\mathcal{V}_P^{**}\simeq 104\,399$. Thus, the ideal Bose gas made up of Avogadro's number of particles expands its volume discretely about $10^5$ times during the phase transition. This is a genuine *finite effect* of Avogadro's number, which cannot be seen directly in the thermodynamic limit where $\mathcal{V}_P^*/\mathcal{V}_P^{**}\to\infty$.

TABLE I. Quantitative agreement between the canonical and the grand canonical results, within 0.1% error.

| $(\mathcal{T}_P^{*},\mathcal{T}_P^{**})$ | Grand canonical | Canonical |
|---|---|---|
| $N = 10^5$ | (1.041,1.043) | (1.0410,1.0424) |
| $N = 10^6$ | (1.0348,1.0364) | (1.034,1.036) |

Our numerical computations based on the exact formulas agree quantitatively with the canonical ensemble results [8] for $N = 10^5$ and $10^6$ within 0.1% error (see Table I), though the minimum (natural) numbers required for the emergence of the spinodal curves are different, 14 393 versus 7616.

In this work, we have focused on the Dirichlet boundary condition. Alternatively imposing the periodic or Neumann boundary condition brings out a volume-independent ground-state energy that, as shown in [8], causes a thermodynamic instability at low temperature near absolute zero (see also [14]). This further implies that, under the alternative boundary conditions, periodic or Neumann, the isobar on the $(\mathcal{T}_P,\mathcal{V}_P/N)$ plane is of "$\mathcal{C}$ shape" rather than of the zigzagging "$\mathcal{S}$ shape," as in Fig. 2: That is, there is a nontrivial lower bound in $\mathcal{T}_P$ of the isobar, above which the volume is always double-valued. In the thermodynamic limit, the lower bound converges to $\mathcal{T}_P^{\mathrm{BEC}}$, and the isobar eventually becomes independent of the boundary conditions, identical to the case of $N = \infty$ in Fig. 2, except for $\mathcal{V}_P/N = 0$. When $\mathcal{V}_P/N = 0$, under the periodic or Neumann boundary condition, $\mathcal{T}_P$ may assume any value that is greater than or equal to $\mathcal{T}_P^{\mathrm{BEC}}$ (as anticipated in Fig. 12.8 of [3]), while under the Dirichlet boundary condition, it is quite the opposite, $0 \leqslant \mathcal{T}_P \leqslant \mathcal{T}_P^{\mathrm{BEC}}$, as depicted in Fig. 2.

In conclusion, we have shown, both numerically and analytically, that the isobar of the ideal Bose gas zigzags on the temperature-volume plane, qualitatively featuring the liquid-gas transition, if $N \geqslant 14\,393$. This is an emergent phenomenon of the finitely many bosonic identical particles. We have derived the precise formulas for the two turning points: supercooling (31) and superheating (32). Our formulas reveal an $N^{-1/3}$ or $N^{-1/4}$ power correction to the BEC temperature and enable us to estimate the volume expansion rate, (36).

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