# Phase-transition temperature in finite systems

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Pathria's approach has been used to deal with the properties of the finite cubic system of $^4$He under constant pressure. The analytic expressions for the total number of particles $N$ and the total pressure $p$ near the critical point are obtained for mixture, antiperiodic, Neumann, and periodic boundary conditions. Influences of various boundary conditions upon low-temperature and critical characters of finite systems are discussed. For five boundary conditions, the relationship between the superfluid transition temperature $T'$ and the size of the finite system $L_0$ has been obtained. The results of this paper can be used in the case of superconductivity. Besides, from this work and others, we have obtained the formula for the phase-transition temperature $T'$ in a finite system, $t=\sigma L_0^{-b}$; here $b$ is described as the finiteness constant, and $\sigma$ is determined by the boundary conditions, the properties of the system, and the interaction between the system and the walls of the container.

## I. INTRODUCTION

In the last 20 years, phase transitions in finite systems have been of interest. Some experimental research has been undertaken, and many problems were identified and awaited solutions by theoreticians. One such problem is how the size of finite systems affects the phase-transition temperature.[1] Fisher *et al.* advanced a finite-size scaling theory for first-order phase transitions.[2] According to this theory, one has

$$\Delta T = T_c(\infty) - T'(L) \sim L^{-1}, \quad L \to \infty . \tag{1}$$

Tell and Maris[3] showed that for a liquid in a Vycor glass tube of radius $r$ the melting temperature is lowered from the bulk melting temperature $T_3$ by an amount $\Delta T$ given by

$$\frac{\Delta T}{T_3} = \frac{2\alpha_{\rm LS} v_S \cos\theta}{l_{\rm LS} r} , \tag{2}$$

where $l_{\rm LS}$ is the latent heat of fusion per mole, $\alpha_{\rm LS}$ is the surface energy between the liquid and the solid, $\theta$ is the contact angle between the wall of the Vycor pore and the solid, and $v_S$ is the volume per mole in the solid phase. D. D. Awschalom *et al.* proved that[4]

$$\frac{\Delta T}{T_3} = \frac{2\Delta\sigma v}{\Delta h_f r} , \tag{3}$$

where $\Delta h_f$ is the heat of fusion, $\Delta\sigma$ is the difference between the solid-wall interfacial energy and the liquid-wall interfacial energy, and $v$ is the molar volume.

Ferdinand and Fisher advanced[5] the following relation for a continuous phase transition

$$t = \frac{T(L) - T_c(\infty)}{T_c(\infty)} \approx aL^{-b} , \quad b = 1/\nu , \quad L \to \infty , \tag{4}$$

where $\nu$ is the critical exponent pertaining to the correlation length and $a$ is a constant which depends on the details of the model and on the nature of the boundary conditions. With an exact solution method, for a $d=3$ Ising lattice $n_1 \times n_2 \times n_3$, Fisher *et al.* have computed[6] $t=-1/\langle n \rangle$ for free faces, $t=+1/\langle n \rangle$ for periodic boundary conditions, and $b \neq 1/\nu$.

All of the above discussion mainly relates to the influence of the finiteness of the size of systems in coordinate space. Gas-liquid and liquid-solid transitions all relate to the ordering of the molecular arrangement in coordinate space. The transitions of the Ising model and the transitions of ferromagnetics and antiferromagnetics relate to the ordering of spin arrangements in real space. For these ordering phenomena in coordinate space, the above theories are valid. Superfluidity and superconductivity are, however, regarded as "condensation in momentum space," so they are ordering phenomena in momentum space. We think that Pathria's method is appropriate for these problems.

Pathria and co-workers developed an analytical method to discuss the influences of the finiteness and boundary conditions of systems on Bose-Einstein (BE) condensation.[7–9] They introduced thermogeometric parameters $y_i$, and constructed an abstract thermogeometric space with a lattice structure whose lattice parameters are $y_i$. They regarded BE condensation as a collapse of the lattice points of the thermogeometric space towards its origin, and $y_i$ change form positive values to zero or imaginary values. Using a rigorous asymptotic analysis, they have studied Bose-Einstein condensation in a finite three-dimensional system at constant pressure, under Dirichlet boundary conditions. They have obtained the analytic expressions of the total particle number $N$ and the total pressure $p$ near the critical point and discussed influences of the finiteness of Dirichlet boundary conditions upon low-temperature and critical characters of the system. One of their results is that finiteness forces the transition temperature to be higher than the corresponding one in the bulk system. Obviously, this result contradicts the basic experimental facts of superfluidity in finite systems. In this paper, we shall explain and solve this contradiction. Using their method, we shall continue to discuss BE condensation in a finite three-dimensional system at constant pressure, under four other boundary conditions. We shall analyze and compare the different influences of these five boundary conditions. This helps us to understand the influences of finiteness on superfluidity and superconductivity. Besides, we shall obtain the general formula for the phase transition temperature $T'$ in a finite system.

## II. THE ANALYTIC EXPRESSIONS OF THE TOTAL PARTICLE NUMBER $N$ AND THE TOTAL PRESSURE $p$

We calculate and derive the results in the case of mixed boundary conditions. For the case of other boundary conditions, we give only the results of calculation and derivation.

The mixed boundary conditions are

$$\psi_{x=0}=\psi_{y=0}=\psi_{z=0}=0 , \tag{5a}$$

$$\left[\frac{\partial\psi}{\partial\hat{n}}\right]_{x=L}=\left[\frac{\partial\psi}{\partial\hat{n}}\right]_{y=L}=\left[\frac{\partial\psi}{\partial\hat{n}}\right]_{z=L}=0 . \tag{5b}$$

The energy spectrum of the system is

$$\epsilon_{l_1,l_2,l_3}=\frac{h^2}{8mL^2}[(l_1+\tfrac{1}{2})^2+(l_2+\tfrac{1}{2})^2+(l_3+\tfrac{1}{2})^2] , \tag{5c}$$

where $l_{1,2,3}=0, 1, 2,\ldots$.

In the system of noninteracting bosons, $\langle n_i\rangle$ is the mean occupation number on the single-particle state $\epsilon_i$, so the total particle number $N$ and the total pressure $p$ are, respectively,

$$N=\sum_i\langle n_i\rangle=\sum_i(e^{\alpha+\beta\epsilon_i}-1)^{-1} , \tag{6}$$

$$p=-\sum_i\langle n_i\rangle\frac{\partial\epsilon_i}{\partial V}=\frac{2}{3V}\sum_i\langle n_i\rangle\epsilon_i , \tag{7}$$

where $\alpha=-\mu/kT$ and $\mu$ is the chemical potential of the particle. $\lambda=(h^2/2\pi mkT)^{1/2}$ is the mean thermal wavelength of the particles, and we assume $\lambda\gg L$, so we have

$$N=\sum_i(e^{\alpha+\beta\epsilon_i}-1)^{-1}$$

$$=\sum_{j=1}^{\infty}e^{-j\alpha}\prod_{k=1}^{3}\sum_{l_k=0}^{\infty}\exp\left[-j\frac{\pi\lambda^2}{4L^2}\left[l_k+\frac{1}{2}\right]^2\right] . \tag{8}$$

According to Possion's summation formula

$$\sum_{l=-\infty}^{\infty}F(l)=\sum_{q=-\infty}^{\infty}F(q) , \tag{9}$$

where $F(q)$ is the Fourier transform of $F(l)$. We have

$$\sum_{1=0}^{\infty}\exp\left[-j\frac{\pi\lambda^2}{4L^2}\left[l_k+\frac{1}{2}\right]^2\right]=\exp\left[-j\frac{\pi\lambda^2}{16L^2}\right]\sum_{q=-\infty}^{\infty}\exp\left[-j\frac{\pi\lambda^2}{4L^2}l^2\right]\cosh\left[j\frac{\pi\lambda^2}{4L^2}\right]\cos(2\pi ql)dl$$

$$=\frac{L}{\lambda j^{1/2}}\left[1+2\sum_{q=1}^{\infty}(-1)^q\exp\left[-\frac{4\pi L^2q^2}{j\lambda^2}\right]\right] . \tag{10}$$

Setting $y=2\pi^{1/2}\alpha^{1/2}L/\lambda$, and substituting Eq. (10) in Eq. (8), we obtain

$$N=\frac{L^3}{j^{3/2}}\left[\sum_{j=1}^{\infty}\frac{e^{-j\alpha}}{j^{3/2}}+6\sum_{q_1=1}^{\infty}(-1)^{q_1}\sum_{j=1}^{\infty}\frac{e^{-j\alpha}}{j^{3/2}}\exp\left[-\frac{y^2q_1^2}{j\alpha}\right]+12\sum_{q_{1,2}=1}^{\infty}(-1)^{q_1+q_2}\sum_{j=1}^{\infty}\frac{e^{-j\alpha}}{j^{3/2}}\exp\left[-\frac{y^2}{j\alpha}(q_1^2+q_2^2)\right]\right.$$

$$\left.+8\sum_{q_{1,2,3}=1}^{\infty}(-1)^{q_1+q_2+q_3}\sum_{j=1}^{\infty}\frac{e^{-j\alpha}}{j^{3/2}}\exp\left[-\frac{y^2}{j\alpha}(q_1^2+q_2^2+q_3^2)\right]\right] , \tag{11}$$

$$\sum_{j=1}^{\infty}\frac{e^{-j\alpha}}{j^{3/2}}\exp\left[-\frac{y^2}{j\alpha}(q_1^2+q_2^2+q_3^2)\right]=\frac{\lambda}{2L}\frac{e^{-2y(q_1^2+q_2^2+q_3^2)^{1/2}}}{(q_1^2+q_2^2+q_3^2)^{1/2}} .$$

For the case of the other two summations, substituting $q_1^2+q_2^2+q_3^2$ by $q_1^2$ and $q_1^2+q_2^2$, respectively, we obtain the results. From these results, we have

$$N=x\left[G_{3/2}(\alpha)+\frac{3\lambda}{L}\sum_{q_1=1}^{\infty}(-1)^{q_1}\frac{e^{-2yq_1}}{q_1}+\frac{6\lambda}{L}\sum_{q_{1,2}=1}^{\infty}\frac{e^{-2y(q_1^2+q_2^2)^{1/2}}}{(q_1^2+q_2^2)^{1/2}}+\frac{4\lambda}{L}\sum_{q_{1,2,3}=1}^{\infty}(-1)^{q_1+q_2+q_3}\frac{e^{-2y(q_1^2+q_2^2+q_3^2)^{1/2}}}{(q_1^2+q_2^2+q_3^2)^{1/2}}\right] , \tag{12}$$

where $x=L^3/\lambda^3$ is a quantity measuring the volume of the system.

Notice

$$\sum_{q_1=1}^{\infty}(-1)^{q_1}\frac{e^{-2yq_1}}{q_1}=y-\ln(2\cosh y)\ , \tag{13}$$

$$\sum_{q_{1,2}=1}^{\infty}(-1)^{q_1+q_2}\frac{e^{-2y(q_1^2+q_2^2)^{1/2}}}{(q_1^2+q_2^2)^{1/2}}=\ln(2\cosh y)-\frac{1}{2}y-\frac{c_1}{4}-\pi U_1^{(2)}(y^2)\ , \tag{14}$$

where

$$U_1^{(2)}(y^2)=\sum_{q_{1,2}=1}^{\infty}\{\sqrt{\pi^2[(q_1+\tfrac{1}{2})^2+(q_2+\tfrac{1}{2})^2]}-\sqrt{y^2+\pi^2[(q_1+\tfrac{1}{2})^2+(q_2+\tfrac{1}{2})^2]}\}\ ,$$

$$c_1=1.615\,534\ ,$$

$$\sum_{q_{1,2,3}=1}^{\infty}(-1)^{q_1+q_2+q_3}\frac{e^{-2y(q_1^2+q_2^2+q_3^2)^{1/2}}}{(q_1^2+q_2^2+q_3^2)^{1/2}}=\frac{1}{4}y-\frac{c_2}{8\pi}+\frac{3c_1}{8}-\frac{3}{4}\ln(2\cosh y)-\frac{y^2}{\pi}V_1^{(3)}(y^2)+3\frac{\pi}{2}U_1^{(2)}(y^2)\ , \tag{15}$$

$$V_1^{(3)}(y^2)=\sum_{q_{1,2,3}=0}^{\infty}\left[\left[q_1+\frac{1}{2}\right]^2+\left[q_2+\frac{1}{2}\right]^2+\left[q_3+\frac{1}{2}\right]^2\right]^{-1}\times\left\{y^2+\pi^2\left[\left[q_1+\frac{1}{2}\right]^2+\left[q_2+\frac{1}{2}\right]^2+\left[q_3+\frac{1}{2}\right]^2\right]\right\}^{-1}\ ,$$

$$c_2=5.49\,0136\ .$$

In the phase transition region discussed by us, $\alpha \ll 1$, so

$$G_{3/2}(\alpha)\approx\zeta(\tfrac{3}{2})-2\pi^{1/2}\alpha^{1/2}=\zeta(\tfrac{3}{2})-y/x^{1/3}\ . \tag{16}$$

Substituting Eqs. (13)–(16) in Eq. (12), we have

$$N=x\{\zeta(\tfrac{3}{2})-x^{-1/3}[D'+(4y^2/\pi)V_1^{(3)}(y^2)]\}\ , \tag{17}$$

where $D'=c_2/2\pi$.

Using an analogous method, we have calculated the expression for the total pressure

$$p=\left[\frac{2\pi m}{h^2}\right]^{3/2}(kT)^{5/2}\left[\zeta\left[\frac{5}{2}\right]-\frac{y^2\zeta(\frac{3}{2})}{12\pi x^{5/3}}-\frac{y^2N}{6\pi x^{5/3}}\right]\ . \tag{18}$$

The calculated results for the other four boundary conditions are given in the following equations. For Dirichlet boundary conditions (data from Ref. 1),

$$\psi_s=0\ ,$$
$$N/x=\zeta(\tfrac{3}{2})-x^{-1/3}[\ln x+D+(4y^2/\pi)S_1^{(3)}(y^2)]\ , \tag{19}$$

$$\frac{p}{(2\pi m/h^2)^{3/2}(kT)^{5/2}}=\zeta\left[\frac{5}{2}\right]-\frac{\pi^2}{6x^{1/3}}+\frac{\zeta(\frac{3}{2})}{12\pi x^{2/3}}(3\pi-y^2)-\frac{y^2N}{6\pi x^{5/3}}\ . \tag{20}$$

For Neumann boundary conditions,

$$\left[\frac{\partial\psi}{\partial\hat{n}}\right]_s=0\ ,$$
$$\frac{N}{x}=\zeta\left[\frac{3}{2}\right]+x^{-1/3}\left[\ln x+D'''-\frac{2\pi}{y^2}+\frac{6\pi\coth y}{y}-\frac{12y^2}{\pi}S_1^{(2)}(y^2)-\frac{4y^2}{\pi}S_1^{(3)}(y^2)\right]\ , \tag{21}$$

$$\frac{p}{(2\pi m/h^2)^{3/2}(kT)^{5/2}}=\zeta\left[\frac{5}{2}\right]+\frac{\pi^2}{6x^{2/3}}+\frac{\zeta(\frac{3}{2})}{12\pi x^{2/3}}(3\pi-y^2)-\frac{y^2N}{6\pi x^{5/3}}\ . \tag{22}$$

For periodic boundary conditions,

$$\psi_{x+L,y,z}=\psi_{x,y+L,z}=\psi_{x,y,z+L}=\psi_{x,y,z}\ ,$$
$$\frac{N}{x}=\zeta\left[\frac{3}{2}\right]+x^{-1/3}\left[D''-\frac{2\pi}{y^2}+\frac{3\pi\coth y}{y}-\frac{12y^2}{\pi}S_1^{(2)}(y^2)-\frac{8y^2}{\pi}S_1^{(3)}(y^2)\right]\ , \tag{23}$$

$$\frac{p}{(2\pi m/h^2)^{3/2}(kT)^{5/2}}=\zeta\left[\frac{5}{2}\right]-\frac{y^2\zeta(\frac{3}{2})}{3\pi x^{2/3}}-\frac{2y^2N}{3\pi x^{5/3}}\ . \tag{24}$$

For antiperiodic boundary conditions,

$$\psi_{x+L,y,z}=\psi_{x,y+L,z}=\psi_{x,y,z+L}=-\psi_{x,y,z}\ , \tag{25}$$

$$\frac{N}{x}=\zeta\left[\frac{3}{2}\right]-2x^{-1/3}\left[D'+\frac{4y^2}{\pi}V_1^{(3)}(y^2)\right],$$

$$\frac{p}{(2\pi m/h^2)^{3/2}(kT)^{5/2}}=\zeta\left[\frac{5}{2}\right]-\frac{y^2\zeta(\frac{3}{2})}{3\pi x^{2/3}}-\frac{2y^2N}{3\pi x^{5/3}}\ . \tag{26}$$

In the above expressions, $D=1.444\,437$,[1] $D'=0.873\,782$, $D''=-5.978\,893$, $D'''=-4.534\,453$,

$$S_1^{(2)}(y^2)=\sum_{q_{1,2}=1}^{\infty}(q_1^2+q_2^2)^{-1}[y^2+\pi^2(q_1^2+q_2^2)]^{-1}\ ,$$

$$S_1^{(3)}(y^2)=\sum_{q_{1,2,3}=1}^{\infty}(q_1^2+q_2^2+q_3^2)^{-1}\times[y^2+\pi^2(q_1^2+q_2^2+q_3^2)]^{-1}\ .$$

## III. LOW TEMPERATURE AND CRITICAL CHARACTERS

From the calculated results, we discuss the influences of finiteness on low-temperature and critical characters of systems.

For the bulk system, the chemical potential $\mu\le 0$. For Neumann and periodic boundary conditions, the finite system still keeps the character $\mu=0$ at low temperature. For the other boundary conditions, $y$ is an imaginary number and the chemical potential $\mu>0$ is at low temperature.

In these expressions for $p$, the first term represents the bulk behavior of the system. Under Dirichlet boundary conditions, the second term $-\pi^2/6x^{1/3}$ arises explicitly from the modification of the density of states of the system owing to its finite size. Under Neumann boundary conditions, the corresponding terms are $+\pi^2/6\pi^2/6x^{1/3}+1/12x$, and the algebraic symbols and values are both different from those of the Dirichlet case. This shows that the influences of boundary conditions on the terms are notable. Under the three other boundary conditions, no similar terms arise. This shows that the influences of the finite size of the system on the density of states of the system are not important in these cases.

Due to the finiteness of the system, the energy spectra change from continuous distributions to discrete distributions. In the region of low momentum, the effect of the change is more marked. The pressure $p_0$ contributed by condensed particles is not always zero. Substituting the limit value $y_0$ of $y$ in the last term in the expression for $p$, we can obtain $p_0$. For example, under mixed boundary conditions, $y_0^2=-3\pi^2/4$,

$$p_0=-\left[\frac{2\pi m}{h^2}\right]^{3/2}(kT)^{5/2}\frac{y_0^2N}{6\pi x^{5/3}}=\frac{2}{3}N\epsilon_0\frac{1}{V}\ . \tag{27}$$

The rightmost equation is suitable for every boundary condition. Under Neumann and periodic boundary conditions $\epsilon_0=0$ and, therefore, $p_0=0$.

Analyzing the expressions for Neumann and periodic boundary conditions, especially noticing that $p_0=0$, we discover that the systems are difficult to keep at constant pressure below the critical temperature $T_c$ under these two boundary conditions. Therefore, we will not discuss the low-temperature behaviors at constant pressure under these two boundary conditions.

The low-temperature characters under mixed and antiperiodic boundary conditions are analogous to the ones under Dirichlet boundary conditions.

Now we discuss the critical characters of the system. For example, we analyze the case of mixed boundary conditions. To do this, we must first of all determine the manner in which the parameters $x$ and $y^2$ vary as the system is cooled at constant $N$ and $p$. From (17) we obtain

$$\left[\frac{dy^2}{dx}\right]_N=\frac{x\zeta(\frac{3}{2})+2N}{12\pi x^{5/3}V_2^{(3)}(y^2)}>0\ , \tag{28}$$

where

$$V_2^{(3)}(y^2)=\frac{1}{\pi^2}\frac{d}{dy^2}[y^2V_1^{(3)}(y^2)]=\sum_{q_{1,2,3}=0}^{\infty}\left\{y^2+\pi\left[\left[q_1+\frac{1}{2}\right]^2+\left[q_2+\frac{1}{2}\right]^2+\left[q_3+\frac{1}{2}\right]^2\right]\right\}^{-2}\ .$$

Differentiating the expression for $p$ with respect to $T$, and using (28), we obtain

$$\left[\frac{\partial x}{\partial T}\right]_{N,p}=45\left[\frac{h^2}{2\pi m}\right]^{3/2}\frac{kp}{(kT)^{7/2}}\left[\frac{[x\zeta(\frac{3}{2})+2N]^2}{8\pi^2x^{10/3}V_2^{(3)}(y^2)}-\frac{y^2\zeta(\frac{3}{2})}{\pi x^{5/2}}-\frac{5y^2N}{\pi x^{8/3}}\right]^{-1}\ . \tag{29}$$

The specific heat at constant pressure is given by

$$C_p=\left[\frac{\partial}{\partial T}(U+pV)\right]_{N,p}=\frac{5}{2}p\left[\frac{\partial V}{\partial T}\right]_{N,p}=\frac{5}{2}p\lambda^3\left[\left[\frac{\partial x}{\partial T}\right]_{N,p}-\frac{3}{2}\frac{x}{T}\right]\ . \tag{30}$$

From (29), we know that $(\partial x/\partial T)_{N,p}$ is non-negative, so we have

$$[x\zeta(\tfrac{3}{2})+2N]^2\ge 8\pi x^{2/3}V_2^{(3)}(y^2)[\zeta(\tfrac{3}{2})y^2x+5y^2N]\ . \tag{31}$$

Then the expression for $C_p$ is given by

$$C_p=\frac{5}{2}\frac{p}{T}\lambda^3\left[45\zeta\left[\frac{5}{2}\right]-\frac{9}{4}\frac{y^2\zeta(\frac{3}{2})}{\pi x^{2/3}}-\frac{3[x\zeta(\frac{3}{2})+2N]^2}{16\pi^2x^{7/3}V_2^{(3)}(y^2)}\right][\Phi(x,y^2)]^{-1}\ , \quad (32)$$

where

$$\Phi(x,y^2)=\frac{[x\zeta(\frac{3}{2})+2N]^2}{8\pi^2x^{10/3}V_2^{(3)}(y^2)}-\frac{y^2\zeta(\frac{3}{2})}{\pi x^{5/3}}-\frac{5y^2N}{\pi x^{8/3}}\ .$$

When the temperature tends to $T_c$ from $T>T_c$, we can set $x\approx N/\zeta(\frac{3}{2})$. Substituting this value of $x$ into (31), we find the gradual approximate condition

$$V_2^{(3)}(y^2)\le\frac{3[\zeta(\frac{3}{2})]^{2/3}N^{1/3}}{16\pi y^2}\ . \quad (33)$$

In the case of equal sign, we have

$$y_1^2=-\tfrac{3}{4}\pi^2+C_4N^{-1/6}\ ,$$

where $C_6=8.0865i$. $y^2$ should be suitable for $\mathrm{Re}(y^2)\ge\mathrm{Re}(y_1^2)$. Substituting the values of $x$ and $y^2$ into the expression for $p$, we obtain

$$t\ge t_1=\frac{T_1-T_c(\infty)}{T_c(\infty)}\approx-\frac{3\pi}{40}\frac{[\zeta(\frac{3}{2})]^{5/3}}{\zeta(\frac{5}{2})}N^{-2/3}\ . \quad (34)$$

We have

$$N_0=\frac{1}{e^{\alpha+\beta\epsilon_0}-1}\approx\frac{1}{\alpha+\beta\epsilon_0}=\frac{4\pi x^{2/3}}{y^2+\frac{3}{4}\pi^2}\ .$$

When the temperature tends to $T_c$ from $T<T_c$, we have $N\approx N_0$ and

$$y^2\approx-\frac{3}{4}\pi^2+\epsilon\ ,\quad \epsilon=\frac{4\pi x^{2/3}}{N}\ll 1\ . \quad (35)$$

Substituting (35) into (31), we know that the right-hand side of (31) is negative, so (31) can be satisfied at any value of $x$. But from (17), $x\le N/\zeta(\frac{3}{2})$. Substituting this and (35) into (18), we obtain $t\le t_1$. From this and (34), we obtain $t_c=t_1$. Obviously, at $t_1$, $y$ changes into an imaginary value, so a phase transition has already taken place. It is easy to prove that $t_c=t_1$ corresponds to the position $t_m$ that $C_p$ takes its maximum value. This case is similar to the bulk case, but different from the case of the film, in which $t_c\le t_m$. Reppy *et al.* have observed that $t_c$ corresponds to $t_m$ in aerogel.[10]

For Neumann boundary conditions,

$$t_c\approx-\frac{\pi^2}{15}\frac{[\zeta(\frac{3}{2})]^{1/3}}{\zeta(\frac{5}{2})}N^{-1/3}\ . \quad (36)$$

For antiperiodic boundary conditions,

$$t_c=-\frac{3}{10}\frac{\pi[\zeta(\frac{3}{2})]^{5/3}}{\zeta(\frac{5}{2})}N^{-2/3}\ . \quad (37)$$

For Dirichlet boundary conditions,

$$t_c\approx+\frac{4\pi^2}{75\zeta(\frac{5}{2})}\left[\frac{\pi}{15}\right]^{1/4}N^{-1/4}\ . \quad (38)$$

For periodic boundary conditions,

$$t_c\approx+\frac{8}{15}\frac{\zeta(\frac{3}{2})}{\zeta(\frac{5}{2})}N^{-1}\ . \quad (39)$$

From the results, we have come to the conclusion that Dirichlet and periodic boundary conditions make $T_c$ increase, but the other three boundary conditions all make $T_c$ decrease.

## IV. APPLICATIONS OF RESULTS

Now we apply the results to the liquid-helium system. In the case of the bulk system, the transition temperature $T_c$ of the noninteracting system is

$$T_c=\frac{2\pi\hbar^2}{mk_B}\left[\frac{N}{2.612V}\right]^{2/3}\ . \quad (40)$$

From (40), we obtain $T_c=3.1$ K, which is close to 2.17 K. Considering the attractive force between the atoms, we think that liquid-helium atoms are still regarded as free particles but their mass is the effective mass $m^*$ instead of $m$. If we take $m^*=1.43m$, we obtain $T_c=2.17$ K. Besides, the exponents in (4) possess some universalities being independent of the special properties of system. Therefore, we can use the noninteracting system in the discussion of the finite system, whose properties are analogous to those of the bulk liquid.

For comparing our results with data, we consider first of all the possibility of realizing these five boundary conditions in experimental systems of liquid helium. Because no periodic structure exists in the liquid, the periodic and antiperiodic boundary conditions are impossible to realize in liquid helium. In a general container, that fraction of helium particles close to the wall of the container has always been absorbed by the wall, so it is not to be regarded as bulklike. Our bulklike system is thus the inner part of the liquid helium. Therefore, we have $\psi|_s\neq 0$. But it is possible that $(\partial\psi/\partial n)|_s=0$. If $\psi|_s\neq 0$ and $(\partial\psi/\partial n)|_s\neq 0$, a macroscopic current with direction perpendicular to the boundary may appear. But, in both the equilibrium liquid helium in the normal state and in the superfluid helium, no such current exists; we therefore have $(\partial\psi/\partial n)|_s=0$. This is the case of Neumann boundary conditions. According to these considerations, Dirichlet boundary conditions are impossible to realize in any kind of containers. A drop of liquid helium in cosmic space can be regarded as the system which satisfies Dirichlet boundary conditions. The system comprising a film can be regarded as the system whose $x$ axis satisfies the mixed boundary conditions but whose $y$ and $z$ axes are close to the cases of bulk liquid.

From the above discussions, we know that Dirichlet and periodic boundary conditions do not fit real experimental systems of liquid helium. Therefore, Pathria's conclusion that Dirichlet boundary conditions increase the transition temperature does not contradict the experimental data. In fact, in liquid helium only Neumann and mixed boundary conditions fit real experimental cases. The transition temperature can relate to the shape of the boundary. Our results for cubic boundaries cannot exactly describe the cases of differently shaped boundaries, but as a qualitative analysis, our results are available.

Lauter *et al.* pointed out that the formation of 1 or 2 solid layers next to the substrates is due to van der Waals interaction, and a film with a thickness larger than about four or five atomic layers would have essentially the structure and the excitation of bulk liquid.[11] Therefore, under Neumann boundary conditions, the volume of our bulklike system is $L^3 < L_0^3$, where $L_0^3$ is the volume of container. Setting $L^3 = L_0^3/\gamma_1^3$, $\gamma_1 > 1$, and noticing $N = L^3 n_0$, where $n_0$ is the number density of particles, and substituting this into (36), we find

$$t_c = -\frac{\pi^2}{15}\frac{[\zeta(\frac{3}{2})]^{1/3}}{\zeta(\frac{5}{2})}\frac{1}{n_0^{1/3}}\gamma_1 L_0^{-1} . \tag{41}$$

If the thickness of layers whose properties are different from the bulklike system is $d_c$, we have

$$\gamma_1 = \frac{L_0}{L_0 - 2d_c} = \frac{1}{1 - 2d_c/L_0} . \tag{42}$$

For mixed boundary conditions, since half of the surfaces are free surfaces, we have

$$\gamma_2 = \frac{L_0}{L_0 - d_c} = \frac{1}{1 - d_c/L_0} . \tag{42a}$$

From (42) and (42a), we know that $\gamma_1$ and $\gamma_2$ increase as $L_0$ decreases. For the other three boundary conditions, no inert layer exists at the boundaries, so $L^3 = L_0^3$.

Taking the $nm^3$ as the unit of volume and noticing the density of liquid helium $\delta = 0.145$ g/cm$^3$ near $T = 2$ K, we find $n_0 = 21.8/nm^3$. Substituting this into (41), we obtain

$$t_c \approx -0.242\gamma_1 L_0^{-1} . \tag{41a}$$

Generally, we can write $t_c$ in the following form

$$t_c = \frac{T' - T_c(\infty)}{T_c(\infty)} = \sigma L_0^{-b} , \tag{43}$$

where $L_0$ is in units of nm.

In Table I, $b (\neq 1/\nu)$ depends on the boundary conditions, and under Neumann and mixed boundary conditions, $\sigma$ depends on the media through $\gamma_1$ and $\gamma_2$. These points are different from (4).

Now we compare our results with experimental data, which are shown in Table II. From Ref. 11, because the irregularity of the surfaces of the walls can increase $d_c$, we take $d_c = 6$ layers $\times 0.36$ nm/layer$= 2.16$ nm. Therefore, we obtain the theoretical values of $\gamma_1$ from (42). The values of $\gamma_1$ in round brackets are experimental values of $\gamma_1$.

The relation of $t_c$ on $L_0^{-1}$ is shown in Fig. 1. In Fig. 1, the theoretical line is close to experimental data. $\gamma_1$ of some media, for example, aerogel, are greater because there are lots of small pores in the medium.

Some experiments have proven that the films in porous glasses possess some behaviors of three dimension.[14,15,16] There are many peaks and valleys on the surfaces of the media. We think that the films in valley will be restricted further by the inert layers on neighboring peaks, so almost half of the surfaces of the film system is inert layers and the other half is free surfaces. The system is approximately suitable to mixed boundary conditions in the 3D case. From (43) and (42a), we obtain

$$t_c = -\frac{0.112}{(L_0 - d_c)^2} . \tag{44}$$

Brewer *et al.* obtained the experimental rule for Vycor glass,[17]

$$\Delta T = -\frac{0.42}{(L_0 - 0.32)^2} , \quad t_m = -\frac{0.111}{(L_0 - 0.32)^2} . \tag{45}$$

Here $t_m$ expresses the position of specific-heat maxima. Obviously, (45) and (44) are coincident.

In superconductors, Dirichlet and periodic boundary conditions are easy to be satisfied. In these cases, finiteness increases the transition temperature $T'$. Although we do not have sufficient data to prove our results, we often encounter the case that a bulk superconductor sample can show the Meissner effect, but it is not a superconductor as a whole. This shows that many small parts of the bulk sample have already moved into the superconductive state but the whole one will not until the temperature decreases to a certain value. The fact is suitable for our results.

About Ising 3D lattices, Fisher *et al.* have proved[6] that finiteness decreases $T'$ for free surfaces but increases $T'$ for periodic boundary conditions, and $b = 1$ for both cases.

TABLE I. $\sigma$ and $b$ under five boundary conditions.

| | Neumann | Mixture | Periodic | Antiperiodic | Dirichlet |
|---|---|---|---|---|---|
| $\sigma$ | $-0.242\gamma_1$ | $-0.112\gamma_2^2$ | $+0.048$ | $-0.446$ | $+0.123$ |
| $b$ | 1 | 2 | 3 | 2 | $\frac{3}{4}$ |

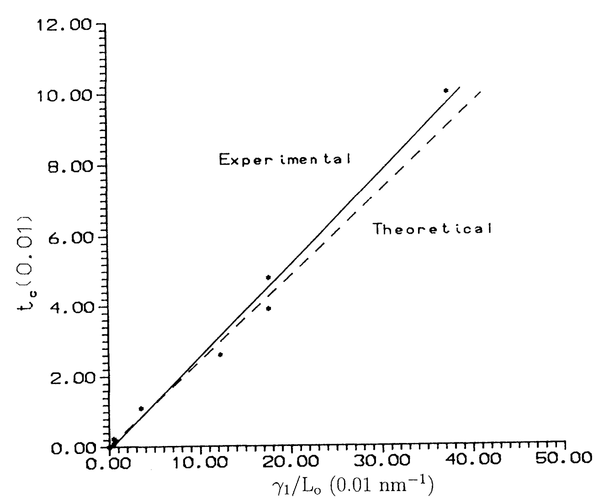


FIG. 1. The relation between $t_c$ and $\gamma_1/L_0$.

TABLE II. The temperature of superfluid transition of various media.

| Medium | $L_0$ (nm) | $T'$ (K) | $t_c$ | $\gamma_1$ |
|---|---|---|---|---|
| Bulk | $\infty$ | 2.172 | 0 | 1 |
| Aerogel[a] | 5–500 | 2.167 | $0.23\times10^{-3}$ | 1.02 (1.90[b]) |
| Xerogel[a] | 10 | 2.088 | $3.9\times10^{-2}$ | 1.76 (1.61) |
| Vyco[a] | 7 | 1.952 | 0.1 | 2.61 (2.89) |
| $Fe_2O_3$[c] | 300 | 2.17 | $9.2\times10^{-4}$ | 1.02 (1.14) |
| Linde B[c] $Al_2O_3$ | 32.5 | 2.148 | $1.1\times10^{-2}$ | 1.15 (1.47) |
| Carbolac 2[c] Carbon black | 12.5 | 2.139 | $2.6\times10^{-2}$ | 1.53 (1.34) |
| Carbolac 1[c] Carbon black | 10 | 2.068 | $4.8\times10^{-2}$ | 1.76 (1.98) |

[a]Reference 12.
[b]We take effective $L_0^*=200$ nm.
[c]Reference 13.

## V. A COMPARISON BETWEEN RESULTS OF THE SCALING THEORY AND THE EXACT ANALYTICAL METHODS

Recently the finite-size scaling theory on first-order transitions has been developed perfectly by Fisher and Privman.[18] Their results have been proven by exact analytical and numerical results, and by other phenomenological theories.[19,20,21,3] In 1985, the Privman-Fisher hypothesis on the singular part of the free-energy density of a finite system had been examined in the spherical model of ferromagnetism by Singh and Pathria.[22] About the Ising model, the finite-size scaling theory was a considerable success.[23]

About the Bose condensate in finite system, the scaling theory pointed to[2,6]

$$t_m=aL_0^{-b} , \tag{4a}$$

$$\delta t=a_1L_0^{-\theta} , \tag{4b}$$

$$\frac{1}{b}>\frac{1}{\theta}=\nu \quad\text{or}\quad \frac{1}{b}=\frac{1}{\theta}=\nu , \tag{4c}$$

where $\delta t$ is the region of rounding. For helium, $\nu=0.675\pm0.001$.[24] For samples confined to a cylindrical geometry of up to 200 nm in diameter, Chen and Gasparini,[25] have measured $1/b=0.583\pm0.046$ and $1/\theta=0.598\pm0.008$; therefore $1/b<1/\theta<\nu$, which disagrees with (4c). For Dirichlet and periodic boundary conditions (BC), using the finite-size scaling theory in helium, Huhn and Dohm have obtained[26] $1/b=0.5$, which also disagrees with (4c). Following the approach of Barber and Fisher, Pathria *et al.* have formulated a finite-size theory for the Bose condensate. They have proved that the predictions of the scaling formulation are agreeable to the analytical results in finite system in three dimensions with constant density under periodic, antiperiodic, Neumann, and Dirichlet BC. Our results are for the cases with constant pressure, so they are different from the ones for the cases with constant density. From the results of cases with constant pressure, under Dirichlet and Neumann BC, $b=\frac{3}{4}$ and 1, respectively, and they are in agreement with (4c). But, under mixed antiperiodic and periodic BC, $b=2$, 2, and 3, respectively, and they disagree with (4c), like the results of Chen and Gasparini[25] and Huhn and Dohm.[26] Then, from the cases with constant density to the ones with constant pressure, values of $b$ have changed obviously. From the two points, as mentioned above, it is necessary to find a suitable scaling formulation of the Bose condensate which can agree with the results of the cases with constant pressure.

## VI. CONCLUSION

For phase transition in a finite system, we can express the relation between $t_c$ and $L_0$ in the following formula:

$$t_c=\frac{T'-T_c(\infty)}{T_c(\infty)}=\sigma L_0^{-b} . \tag{46}$$

$b>0$ depends on the boundary conditions and these kinds of phase transitions. $b$ is a new constant, which can equal $1/\nu$ or other values, so we call it the finiteness exponent. Under Neumann and mixed boundary conditions $\sigma<0$, but under periodic boundary conditions $\sigma>0$. Under Neumann and mixed boundary conditions, $\sigma$ depends on the variety of media, but under the others, $\sigma$ does not relate to the variety of media. For the first-order phase transition, $b=1$, $\sigma<0$, and $\sigma$ depends on the variety of media.

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