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# Bose-Einstein Condensation in Thin Films*

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An asymptotic evaluation of the specific heat of an ideal Bose gas confined to a thin-film geometry ($\infty \times \infty \times D$) is carried out, under a variety of boundary conditions, without converting summations into integrations. The theoretical results for the Dirichlet boundary conditions ($\psi_S = 0$) contain all the significant features of the numerical results obtained earlier by Goble and Trainor; in particular, we reproduce the characteristic length $D^*$ at which the specific heat of the system is at an absolute maximum. It turns out that $D^*$ is directly proportional to the mean interparticle distance $\bar{l}$, with a constant of proportionality $c(\approx 20-30)$. No such characteristic length appears if boundary conditions other than Dirichlet's are employed. The shift, and the rounding off, of the specific-heat maximum are also studied, and the distinguishing influence of the boundary conditions examined.

## I. INTRODUCTION

Following the work of Osborne[1] and Ziman,[2] several authors have investigated the phenomenon of Bose-Einstein condensation in thin helium films.[3–8] Most of these investigations are based on the ideal-gas model and are concerned with the dependence of the condensation temperature $T_0$ on the thickness $D$ of the film; in some cases, the varying influence of the boundary conditions (imposed on the wave functions of the system) has also been examined.[4,5] The relevance of the results thus obtained to the actual problem of helium films is indeed limited; nevertheless, these studies have served to elucidate the role played by the geometry of the system in determining its physical properties, especially in the neighborhood of a critical point such as $T_0$. It is clearly of interest to extend these investigations to study the behavior of the various thermodynamic functions of the system—in particular, the ones that possess singularities at the critical point—and examine the manner in which the "finiteness" of the geometry smooths out the singularities of these functions.

The corresponding problem for the Ising model has already been broached by Domb[9] and, at some length, analyzed by Fisher and Ferdinand.[10] In the case of Bose-Einstein systems, a numerical analysis has been carried out by Goble and Trainor[6] who have studied, among other things, the specific heat of an infinite slab of thickness $D$, in the neighborhood of the temperature $T_0(D)$, for different values of $D$. The results obtained by them reveal that the height $C_0(D)$ of the specific-heat maximum is itself a nonmonotonic function of $D$, being largest when the thickness of the slab is equal to a characteristic length $D^*$ ($\approx 70$ Å). This led Goble and Trainor to suggest that $D^*$ possibly represents some sort of a statistical *correlation length* which determines the stage at which the physical characteristics of the system change over from those of a three-dimensional one ($D \gg D^*$) to those of a two-dimensional one ($D \ll D^*$). However, because of the numerical character of their investigation, Goble and Trainor could not bring out the precise meaning of the length $D^*$ and its relationship, if any, with other parameters of the problem.

To elucidate these aspects, the present author has carried out an analytic study of the problem, in which the summations over states appearing in the various expressions pertaining to the system have been evaluated without having recourse to the customary procedure (of converting summations into integrations) which is liable to serious inaccuracies when applied to a finite system. This analysis is based on a technique developed by Krueger[7] which enables one not only to investigate the most significant features of the specific-heat behavior, as reported by Goble and Trainor, but also to bring out the sensitivity of these features to the boundary conditions employed. In particular, the peculiar features associated with the "existence" of the characteristic length $D^*$ appear only if one employs the Dirichlet boundary conditions ($\psi_S = 0$). With other boundary conditions, no such characteristic length appears. Moreover, when it appears, $D^*$ is found to be proportional to the mean interparticle distance $\bar{l}$, i.e., $D^* = c\bar{l}$, where the factor $c$ shows up quite naturally in the analysis and, within the approximation studied here, turns out to be about 30. The author, therefore, concludes that the length $D^*$ is of a purely statistical origin and is determined solely by the particle density in the system. Accordingly, it may not be regarded as a "correlation length" in the customary sense of the word.

The shift, and the rounding off, of the specific-heat maximum as a function of the thickness $D$ of the slab are also examined here. In passing, it is noted that, in view of the functional analogy between the ideal Bose gas and the spherical model of ferromagnetism,[11,12] the results obtained here should, in a sense, hold for the latter system as well.

## II. FORMULATION OF PROBLEM

Let us start with the expression for the internal energy of a Bose-Einstein system of noninteracting particles, viz.,

$$U=\sum_i \epsilon_i \langle n_i\rangle=\sum_i \epsilon_i (e^{(\epsilon_i-\mu)/kT}-1)^{-1}, \qquad (1)$$

where $\langle n_i\rangle$ is the mean occupation number of the state $i$, while the chemical potential $\mu$ of the system is determined by the condition

$$N=\sum_i \langle n_i\rangle=\sum_i (e^{(\epsilon_i-\mu)/kT}-1)^{-1}, \qquad (2)$$

the other symbols in (1) and (2) have their usual meanings. Eliminating $\mu$, we obtain $U$ as a function of $N$, $T$, and $L_j$, where $L_j$ ($j=1, 2, 3$) denote the linear dimensions of the container. It may be noted here that the dependence on $L_j$ comes through the eigenvalue spectrum $\epsilon_i$ and is influenced, quite naturally, by the boundary conditions imposed on the wave functions. The specific heat at constant volume is then given by

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_{N,L_j}=Nkf\left(\frac{\lambda}{\bar{l}}, \frac{L_j}{\bar{l}}\right), \qquad (3)$$

where $\lambda[=h/(2\pi MkT)^{1/2}]$ is the mean thermal wavelength of the particles (and is therefore a measure of the temperature of the system), while $\bar{l}[=(L_1L_2L_3/N)^{1/3}]$ is the mean interparticle distance (and is therefore a measure of the particle density in the system). In the case of infinite geometry ($L_1$, $L_2$, $L_3\to\infty$), the specific heat is known to possess a cusplike singularity at the critical temperature $T_0(\infty)$ such that[13,14]

$$\lambda_0(\infty)=\bar{l}\,[\zeta(\tfrac{3}{2})]^{1/3}, \qquad (4a)$$

while

$$C_0(\infty)=\tfrac{15}{4}Nk[\zeta(\tfrac{5}{2})/\zeta(\tfrac{3}{2})]; \qquad (4b)$$

here $\zeta(n)$ denotes the Riemann $\zeta$ function. In the case of a slab ($L_1$, $L_2\to\infty$, $L_3=\text{const}=D$, say), we expect that the specific heat would possess a nonsingular maximum at a temperature $T_0(D)$ such that

$$\lambda_0(D)=\bar{l}\,[\zeta(\tfrac{3}{2})]^{1/3}\,\phi_1(D/\bar{l}), \qquad (5a)$$

while

$$C_0(D)=\tfrac{15}{4}Nk[\zeta(\tfrac{5}{2})/\zeta(\tfrac{3}{2})]\,\varphi_2(D/\bar{l}), \qquad (5b)$$

where the functions $\phi_1$, $\phi_2\to 1$ as $D\to\infty$. It is now clear that if the quantity $C_0(D)$ possesses an extremum (at a value $D^*$, say), then we must have

$$D^*=c\bar{l}, \qquad (6)$$

where $c$ is a numerical factor that appears naturally in the analysis.

In order to determine the correct asymptotic form of the functions $\phi_1$ and $\phi_2$ and the corresponding value of the number $c$ (if it exists), we must not make the customary replacement of summations by integrations. It is better to work with the general formulas, which follow directly from Eqs. (1) and (2), viz.,

$$C_V=k(G_2-G_1^2/G_0), \qquad (7)$$

$$\left(\frac{\partial C_V}{\partial T}\right)_{N,L_j}=\frac{k}{T}\left\{-2\left(G_2-\frac{G_1^2}{G_0}\right)+\left[G_3'-3\left(\frac{G_1}{G_0}\right)G_2'+3\left(\frac{G_1}{G_0}\right)^2G_1'-\left(\frac{G_1}{G_0}\right)^3G_0'\right]\right\}, \qquad (8)$$

and

$$\left(\frac{\partial^2 C_V}{\partial T^2}\right)_{N,L_j}=\frac{k}{T^2}\left\{6\left(G_2-\frac{G_1^2}{G_0}\right)-\frac{3}{G_0}\left[G_2'-2\left(\frac{G_1}{G_0}\right)G_1'+\left(\frac{G_1}{G_0}\right)^2G_0'\right]^2\right.$$
$$\left.-6\left[G_3'-3\left(\frac{G_1}{G_0}\right)G_2'+3\left(\frac{G_1}{G_0}\right)^2G_1'-\left(\frac{G_1}{G_0}\right)^3G_0'\right]+\left[G_4''-4\left(\frac{G_1}{G_0}\right)G_3''+6\left(\frac{G_1}{G_0}\right)^2G_2''-4\left(\frac{G_1}{G_0}\right)^3G_1''+\left(\frac{G_1}{G_0}\right)^4G_0''\right]\right\}, \qquad (9)$$

where

$$G_s=\sum_i\left(\frac{\epsilon_i}{kT}\right)^s[\langle n_i\rangle+\langle n_i\rangle^2]=-\left\{\frac{\partial}{\partial\alpha}\left[\sum_i\left(\frac{\epsilon_i}{kT}\right)^s\langle n_i\rangle\right]\right\}_{T,L_j}, \qquad (10)$$

$$G_s'=-\left(\frac{\partial G_s}{\partial\alpha}\right)_{T,L_j}, \qquad G_s''=\left(\frac{\partial^2 G_s}{\partial\alpha^2}\right)_{T,L_j}, \qquad (11)$$

while $\alpha=-(\mu/kT)$. The problem, therefore, consists in evaluating the functions $G_s(\alpha, T, L_j)$. Once these functions are evaluated, the specific-heat maximum can be located by determining the temperature $T_0$ at which the derivative (8) vanishes, the value $C_0$ at the maximum can be obtained from (7) while the degree of rounding off of the maximum can be estimated from the magnitude of the derivative (9).

## III. ASYMPTOTIC ANALYSIS

We shall examine this problem under the following sets of boundary conditions:

(i) *Periodic boundary conditions* $[\psi(x_j+L_j)=\psi(x_j)]$, for which

$$\epsilon_{lmn}=\frac{h^2}{2M}\left(\frac{l^2}{L_1{}^2}+\frac{m^2}{L_2{}^2}+\frac{n^2}{L_3{}^2}\right), \quad l, m, n=0, \pm 1, \pm 2, \ldots \quad . \tag{12}$$

(ii) *Dirichlet boundary conditions* $[\psi_S=0]$, for which

$$\epsilon_{lmn}=\frac{h^2}{8M}\left(\frac{l^2}{L_1{}^2}+\frac{m^2}{L_2{}^2}+\frac{n^2}{L_3{}^2}\right), \quad l, m, n=1, 2, 3, \ldots \quad . \tag{13}$$

(iii) *Neumann boundary conditions* $[(\partial\psi/\partial\hat{n})_S=0]$, for which

$$\epsilon_{lmn}=\frac{h^2}{8M}\left(\frac{l^2}{L_1{}^2}+\frac{m^2}{L_2{}^2}+\frac{n^2}{L_3{}^2}\right), \quad l, m, n=0, 1, 2, \ldots \quad . \tag{14}$$

It is the spectral details of the eigenstates $\epsilon_{lmn}$ that cause a varying influence of the boundary conditions on the summations over states, such as the ones appearing in (10). To discern this influence, we note that if there is a variable $f(l, m, n)$, which is an *even* function of the quantum numbers $(l, m, n)$, then[15]

$$\sum_{l,m,n=\{^1_0\}}^{\infty} f(l,m,n)=\frac{1}{8}\left\{\sum_{l,m,n=-\infty}^{\infty} f(l,m,n)\mp\left[\sum_{l,m,0=-\infty}^{\infty} f(l,m,0)+\sum_{l,n=-\infty}^{\infty} f(l,0,n)+\sum_{m,n=-\infty}^{\infty} f(0,m,n)\right]\right.$$
$$\left.+\left[\sum_{l=-\infty}^{\infty} f(l,0,0)+\sum_{m=-\infty}^{\infty} f(0,m,0)+\sum_{n=-\infty}^{\infty} f(0,0,n)\right]\mp f(0,0,0)\right\} \tag{15}$$

or, alternatively,

$$S^{(3)}_{D/N}(L_1, L_2, L_3)=\tfrac{1}{8}\{S_P^{(3)}(2L_1, 2L_2, 2L_3)$$
$$+\theta[S_P^{(2)}(2L_1, 2L_2)+\cdots+\cdots]$$
$$+[S_P^{(1)}(2L_1)+\cdots+\cdots]+\theta f(0,0,0)\}, \tag{16}$$

where $S^{(m)}_{D/N}$ denotes an $m$-dimensional summation under Dirichlet boundary conditions $(\theta=-1)$ or under Neumann boundary conditions $(\theta=+1)$, while $S_P^{(m)}$ denotes an $m$-dimensional summation under periodic boundary conditions. For an asymptotic analysis of the infinite slab, Eq. (16) may be approximated by

$$S^{(3)}_{D/N}(L_1, L_2, L_3)$$
$$\simeq \tfrac{1}{8}[S_P^{(3)}(2L_1, 2L_2, 2L_3)+\theta S_P^{(2)}(2L_1, 2L_2)] \; . \tag{16$'$}$$

In the special case, when $f(l, m, n)=\langle n_\epsilon\rangle$, the summations $S^{(3)}(L_1, L_2, L_3)$ are identically equal to the total number of particles in the system. For such a sum, Krueger[7] obtained under the periodic boundary conditions

$$S_P^{(3)}(L_1, L_2, L_3)$$
$$\simeq \frac{L_1L_2L_3}{\lambda^3}g_{3/2}(\alpha)+\frac{2L_1L_2}{\lambda^2}\,g_1\!\left(2\pi^{1/2}\frac{L_3}{\lambda}\,\alpha^{1/2}\right), \tag{17}$$

where $g_n(\delta)$ are the familiar Bose-Einstein functions[13,14]

$$g_n(\delta)=\frac{1}{\Gamma(n)}\int_0^\infty \frac{x^{n-1}\,dx}{e^{x+\delta}-1}\;, \tag{18}$$

while

$$\lambda=h/(2\pi MkT)^{1/2}\;. \tag{19}$$

Combining (17) with the two-dimensional formula

$$S_P^{(2)}(L_1, L_2)\simeq\frac{L_1L_2}{\lambda^2}\,g_1(\alpha)\;, \tag{20}$$

we obtain for (16$'$)

$$S^{(3)}_{D/N}(L_1, L_2, L_3)\simeq\frac{L_1L_2L_3}{\lambda^3}\,g_{3/2}(\alpha)$$
$$+\frac{L_1L_2}{\lambda^2}\,g_1\!\left(4\pi^{1/2}\frac{L_3}{\lambda}\,\alpha^{1/2}\right)+\theta\frac{L_1L_2}{2\lambda^2}\,g_1(\alpha)\;. \tag{21}$$

Equations (17) and (21) might be represented by a single equation, viz.,

$$N(\alpha, T, L_j)\simeq\frac{V}{\lambda^3}\left[g_{3/2}(\alpha)+\frac{2}{(1+\theta^2)}\left(\frac{\lambda}{L_3}\right)g_1\!\left(2(1+\theta^2)\pi^{1/2}\frac{L_3}{\lambda}\,\alpha^{1/2}\right)+\tfrac{1}{2}\theta\left(\frac{\lambda}{L_3}\right)g_1(\alpha)\right], \tag{22}$$

where $\theta=0$ for periodic boundary conditions.

In the region of interest $(\alpha\ll 1)$, we may write

$$g_{3/2}(\alpha)=\sum_{l=1}^{\infty}\frac{e^{-l\alpha}}{l^{3/2}}\simeq\zeta(\tfrac{3}{2})-2\pi^{1/2}\alpha^{1/2} \tag{23}$$

and

$$g_1(\alpha)=-\ln(1-e^{-\alpha})\simeq-\ln\alpha\;. \tag{24}$$

Equation (22) then reduces to

$$N(\alpha, T, L_j) \simeq \frac{V}{\lambda^3}\left\{\zeta(\tfrac{3}{2}) - \frac{2}{(1+\theta^2)}\left(\frac{\lambda}{D}\right)\right.$$
$$\left.\times \ln\left[2\sinh\left((1+\theta^2)\pi^{1/2}\frac{D}{\lambda}\alpha^{1/2}\right)\right] - \tfrac{1}{2}\theta\left(\frac{\lambda}{D}\right)\ln\alpha\right\}, \quad (25)$$

where $L_3$ has been replaced by the more agreeable symbol $D$. To the same degree of approximation,

$$G_0 \equiv -\left(\frac{\partial N}{\partial \alpha}\right)_{T, L_j} \simeq \frac{VD}{\lambda^4}\pi(1+\theta^2)\left(\frac{\coth y}{y} + \frac{1}{2}\theta(1+\theta^2)\frac{1}{y^2}\right) \quad (26)$$

and

$$G_0' \equiv -\left(\frac{\partial G_0}{\partial \alpha}\right)_{T, L_j} \simeq \frac{VD^3}{2\lambda^6}\pi^2(1+\theta^2)^3 \times\left(\frac{\coth y}{y^3} + \frac{\operatorname{csch}^2 y}{y^2} + \theta(1+\theta^2)\frac{1}{y^4}\right), \quad (27)$$

where

$$y = (1+\theta^2)\pi^{1/2}(D/\lambda)\alpha^{1/2}. \quad (28)$$

Other summations can be evaluated in a similar manner.

Substituting the relevant expressions into (8) and retaining the most dominant terms, we obtain [again in the region of interest, where $\alpha = O(\lambda^2/D^2)$]

$$\frac{T}{Nk}\left(\frac{\partial C_V}{\partial T}\right)_{N, L_j} \simeq \left(\frac{\bar{l}}{\lambda}\right)^3\left[\tfrac{45}{8}\zeta(\tfrac{5}{2}) - \frac{27}{16\pi}\{\zeta(\tfrac{3}{2})\}^3 f(y)\right], \quad (29)$$

where

$$f(y) = \left(\frac{\coth y}{y^3} + \frac{\operatorname{csch}^2 y}{y^2} + \theta(1+\theta^2)\frac{1}{y^4}\right) \times\left(\frac{\coth y}{y} + \tfrac{1}{2}\theta(1+\theta^2)\frac{1}{y^2}\right)^{-3}. \quad (30)$$

For infinite $D$, the function $f(y)$ is identically zero for $T < T_0(\infty)$ and is equal to 1 for $T \gtrsim T_0(\infty)$; the derivative $(\partial C_V/\partial T)$, therefore, possesses a discontinuity at $T = T_0(\infty)$. For finite $D$, all physical quantities vary smoothly with $T$. In particular, the specific heat $C_V$ passes through a nonsingular maximum at a temperature $T_0(D)$ which satisfies the characteristic equation

$$f(y_0) = \tfrac{10}{3}\pi\,\zeta(\tfrac{5}{2})\{\zeta(\tfrac{3}{2})\}^{-3} \simeq 0.788. \quad (31)$$

The expression for $T_0(D)$, in terms of $\lambda_0(D)$, then follows from (25):

$$\left(\frac{\lambda_0}{\bar{l}}\right)^3 + \frac{2}{(1+\theta^2)}\left(\frac{\lambda_0}{D}\right)\ln(2\sinh y_0) - \theta\left(\frac{\lambda_0}{D}\right)\ln\left((1+\theta^2)\pi^{1/2}\frac{D}{\lambda_0}\frac{1}{y_0}\right) = \zeta(\tfrac{3}{2}), \quad (32)$$

while the value of the specific heat at $T_0(D)$ is given by (7):

$$\frac{C_0(D)}{Nk} = \left(\frac{\bar{l}}{\lambda_0}\right)^3\left\{\tfrac{15}{4}\zeta(\tfrac{5}{2}) + \theta\left(\frac{\lambda_0}{D}\right)\zeta(2) - \left(\frac{\lambda_0}{D}\right)\frac{9}{4\pi}[\zeta(\tfrac{3}{2})]^2 \times\left[(1+\theta^2)\left(\frac{\coth y_0}{y_0} + \frac{1}{2}\theta(1+\theta^2)\frac{1}{y_0^2}\right)\right]^{-1}\right\}. \quad (33)$$

## IV. RESULTS AND DISCUSSION

(i) In the case of periodic boundary conditions ($\theta = 0$), Eqs. (30) and (31) give $y_0 \simeq 0.854$. We then obtain from Eqs. (32) and (33)

$$\frac{T_0(D)}{T_0(\infty)} = \left(\frac{\lambda_0(\infty)}{\lambda_0(D)}\right)^2 \simeq 1 + \tfrac{4}{3}[\zeta(\tfrac{3}{2})]^{-2/3}\ln(2\sinh y_0)\left(\frac{\bar{l}}{D}\right) = 1 + 0.460\frac{\bar{l}}{D} \quad (34)$$

and

$$\frac{C_0(D)}{Nk} \simeq \frac{15}{4}\frac{\zeta(\frac{5}{2})}{\zeta(\frac{3}{2})} - \left\{\frac{9}{4\pi}[\zeta(\tfrac{3}{2})]^{4/3}(y_0\tanh y_0) - \tfrac{15}{2}\zeta(\tfrac{5}{2}) \times[\zeta(\tfrac{3}{2})]^{-5/3}\ln(2\sinh y_0)\right\}\left(\frac{\bar{l}}{D}\right) = 1.925 - 0.196\frac{\bar{l}}{D}. \quad (35)$$

These results are plotted in Figs. 1 and 2 (solid curves). We note that, under periodic boundary conditions, both $T_0(D)$ and $C_0(D)$ vary monotonically with $D$ and, as $D \to \infty$, approach the bulk values $T_0(\infty)$ and $C_0(\infty) \simeq 1.925\,Nk$, respectively.

(ii) In the case of Dirichlet boundary conditions ($\theta = -1$), Eqs. (30) and (31) yield an imaginary value of $y_0$, namely, $2.687i$. This is not surprising because under these boundary conditions the zero-temperature limit of the chemical potential $\mu$ is $\epsilon_{111}$, which is equal to $h^2/(8MD^2)$; accordingly, the limiting value of $\alpha$ is $-h^2/(8MD^2kT) = -\frac{1}{4}\pi(\lambda/D)^2$ and, by (28), the corresponding value of $y$ is $\pi i$. Thus, an imaginary value of $y$, in particular, $y_0$, simply means that the corresponding value of $\alpha$, in particular, $\alpha(T_0)$, is negative.[16] Equations (32) and (33) now give, with $y_0 = y_0' i$,

$$\frac{T_0(D)}{T_0(\infty)} \simeq 1 + \tfrac{2}{3}[\zeta(\tfrac{3}{2})]^{-2/3}\ln\left(4\pi^{1/2}\frac{D}{\bar{l}[\zeta(\frac{3}{2})]^{1/3}}\frac{\sin y_0'}{y_0'}\right)\left(\frac{\bar{l}}{D}\right) = 1 + 0.352\left(\frac{\bar{l}}{D}\right)\left[\ln\left(\frac{D}{\bar{l}}\right) - 0.173\right] \quad (36)$$

and

$$\frac{C_0(D)}{Nk} \simeq \frac{15}{4}\frac{\zeta(\frac{5}{2})}{\zeta(\frac{3}{2})} - \left\{\left[\zeta(2) + \frac{9}{8\pi}[\zeta(\tfrac{3}{2})]^2\left(\frac{1}{y_0'^2} - \frac{\cot y_0'}{y_0'}\right)^{-1}\right][\zeta(\tfrac{3}{2})]^{-2/3} - \frac{15}{4}\frac{\zeta(\frac{5}{2})}{[\zeta(\frac{3}{2})]^{5/3}}\ln\left(4\pi^{1/2}\frac{D}{\bar{l}[\zeta(\frac{3}{2})]^{1/3}}\frac{\sin y_0'}{y_0'}\right)\right\}\left(\frac{\bar{l}}{D}\right)$$
$$= 1.925 + 1.015\left(\frac{\bar{l}}{D}\right)\left[\ln\left(\frac{D}{\bar{l}}\right) - 2.438\right]. \quad (37)$$

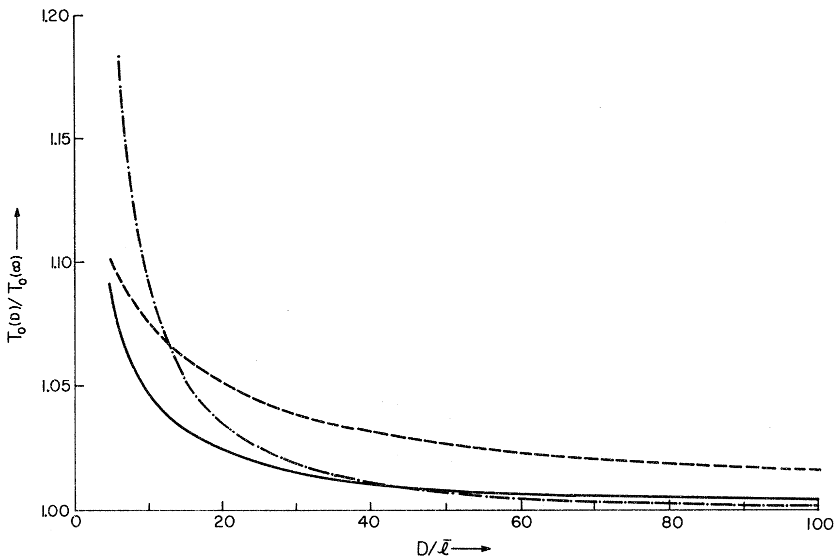


FIG. 1. Temperature $T_0(D)$ at which the specific heat of an infinite slab of thickness $D$ is maximum: $\theta = 0$, solid line; $\theta = -1$, dashed line; $\theta = +1$, dot-dashed line.

These results are also plotted in Figs. 1 and 2 (dashed curves). We note that while the variation of $T_0(D)$ is essentially monotonic, the variation of $C_0(D)$ is not. For large values of $D$, $C_0(D)$ increases as $D$ decreases but finally it passes through a maximum at $D = D^*$ which, in the present analysis, is given by

$$D^*/\bar{l} = c \simeq e^{3.438} \simeq 31 \ . \tag{38}$$

For $D < D^*$, $C_0(D)$ continually decreases with $D$.

These results are in good, qualitative agreement with the ones obtained numerically by Goble and Trainor.[6] Quantitatively, our value of $c$ is rather large in comparison with theirs, which is about 20. This need not be discouraging because the asymptotic analysis developed here is only a first-order approximation to the actual problem under investigation. In view of the fact that asymptotic expansions can be quite sensitive to the process of differentiation, it is fairly likely that a higher-order approximation would bring the value of $c$ closer to the one obtained numerically. At any rate, it is rewarding that a first-order treatment should simulate the results of numerical analysis so well and, at the same time, bring out the relationship between the quantities $D^*$ and $\bar{l}$.

(iii) In the case of Neumann boundary conditions ($\theta = +1$), Eqs. (30) and (31) give $y_0 \simeq 4.403$. It then

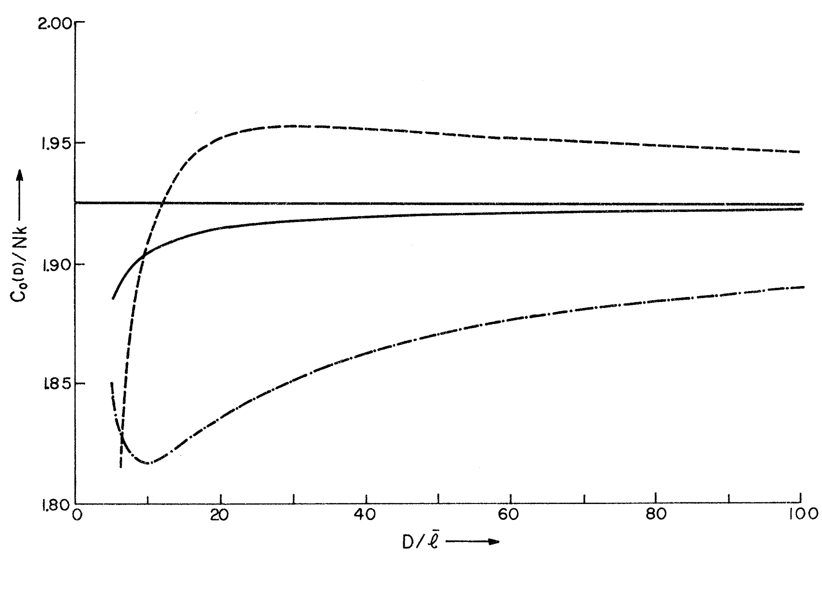


FIG. 2. Height $C_0(D)$ of the specific-heat maximum: $\theta = 0$, solid line; $\theta = -1$, dashed line; $\theta = +1$, dot-dashed line. Horizontal line corresponds to the bulk value $C_0(\infty)$.

follows that

$$\frac{T_0(D)}{T_0(\infty)} \simeq 1 + \tfrac{2}{3}[\zeta(\tfrac{3}{2})]^{-2/3} \ln\left(\frac{\bar{l}[\zeta(\frac{3}{2})]^{1/3}}{D\pi^{1/2}}(y_0 \sinh y_0)\right)\left(\frac{\bar{l}}{D}\right)$$

$$= 1 - 0.352\left(\frac{\bar{l}}{D}\right)\left[\ln\left(\frac{D}{\bar{l}}\right) - 4.940\right] \tag{39}$$

and

$$\frac{C_0(D)}{Nk} \simeq \frac{15}{4}\frac{\zeta(\frac{5}{2})}{\zeta(\frac{3}{2})} - \left\{\left[-\zeta(2) + \frac{9}{8\pi}[\zeta(\tfrac{3}{2})]^2\left(\frac{\coth y_0}{y_0} + \frac{1}{y_0^2}\right)^{-1}\right][\zeta(\tfrac{3}{2})]^{-2/3} - \frac{15}{4}\frac{\zeta(\frac{5}{2})}{[\zeta(\frac{3}{2})]^{5/3}} \ln\left(\frac{\bar{l}[\zeta(\frac{3}{2})]^{1/3}}{D\pi^{1/2}}(y_0 \sinh y_0)\right)\right\}\left(\frac{\bar{l}}{D}\right)$$

$$= 1.925 - 1.015\left(\frac{\bar{l}}{D}\right)\left[\ln\left(\frac{D}{\bar{l}}\right) - 1.242\right]. \tag{40}$$

In this case we find that for very large values of $D$, viz., $D > 140\,\bar{l}$, $T_0(D) < T_0(\infty)$. However, for those values of $D$ which are of practical interest, $T_0(D) > T_0(\infty)$; see again Figs. 1 and 2. We also find that, quite generally, the quantity $C_0(D)$ is less than $C_0(\infty)$ and decreases steadily with $D$. [At $D \simeq 9\bar{l}$, $C_0(D)$ passes through a minimum and for $D < 9\bar{l}$ it steadily increases as $D$ decreases. However, the validity of the asymptotic analysis at such low values of $D$ is rather questionable.]

In passing, we note that the results embodied in formulas (34), (36), and (39) are in complete agreement with the formal ones reported earlier.[17]

Finally we consider the question: How sharp is the specific-heat maximum? For this we observe that, in the vicinity of $T_0(D)$, the most dominant terms in the expression for $(\partial^2 C_V/\partial T^2)$, which determines the curvature of the specific-heat curve, are

$$\frac{k}{T^2}\left[-\frac{3}{G_0}\left(\frac{G_1}{G_0}\right)^4 (G_0')^2 + \left(\frac{G_1}{G_0}\right)^4 G_0''\right], \tag{41}$$

which vary as the *first* power of $D$. Accordingly, the curvature of the specific-heat curve at $T = T_0(D)$ is directly proportional to $D$. It then follows that (a) the larger the value of $D$ the sharper the specific-heat maximum and (b) a mathematical singularity occurs only if $D$ is infinite.

Combining the foregoing results we conclude that, apart from subtle differences in regard to the quantity $C_0(D)$, there is unanimity among the different sets of boundary conditions on the following points: For values of $D$, which are of practical interest, the specific-heat maximum shifts towards higher temperatures, becomes broader and essentially decreases in height as $D$ decreases. The only experimental data with which these results may be compared are those obtained by Frederikse[18] who measured the specific heat of unsaturated helium films of thickness $(1-8)\bar{l}$. He found that both $T_0(D)$ and $C_0(D)$ decrease monotonically as $D$ decreases. Although asymptotic formulas do not make much sense at such low values of $D$ it is plausible that the variation of $C_0(D)$ might be understandable in terms of a Bose-gas model restricted to a finite geometry. However, there still remains serious disagreement as regards the variation of $T_0(D)$. Possibly, interatomic interactions play an important role in determining the true influence of the finiteness of the geometry on the physical properties of the system.

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[1]M. F. M. Osborne, Phys. Rev. 76, 396 (1949).
[2]J. M. Ziman, Phil. Mag. 44, 548 (1953).
[3]M. Toda and F. Takano, J. Phys. Soc. Japan 9, 14 (1954).
[4]T. Tsuzuki, J. Yokohama Munic. Univ. 16, 1 (1957).
[5]A. D. Singh and R. K. Pathria, Nature 183, 668 (1959); Progr. Theoret. Phys. (Kyoto) 24, 229 (1960).
[6]D. F. Goble and L. E. H. Trainor, Phys. Rev. 157, 167 (1967); Can. J. Phys. 44, 27 (1966); 46, 1867 (1968).
[7]D. A. Krueger, Phys. Rev. Letters 19, 563 (1967); Phys. Rev. 172, 211 (1968).
[8]É. B. Sonin, Zh. Eksperim. i Teor. Fiz. 56, 963 (1969); 59, 1411 (1969) [Sov. Phys. JETP 29, 520 (1969); 30, 765 (1970)].
[9]C. Domb, Proc. Phys. Soc. (London) 86, 933 (1965).
[10]M. E. Fisher and A. E. Ferdinand, Phys. Rev. Letters 19, 169 (1967).
[11]J. D. Gunton and M. J. Buckingham, Phys. Rev. 166, 152 (1968).
[12]M. E. Fisher, G. A. T. Allan, and M. N. Barber, Proceedings of the IUPAP Conference on Statistical Mechanics, Chicago, 1971 (unpublished).
[13]K. Huang, *Statistical Mechanics* (Wiley, New York, 1963).
[14]R. K. Pathria, *Statistical Mechanics* (Pergamon, Oxford, to be published).
[15]R. K. Pathria, Nuovo Cimento Suppl. 4, 276 (1966).
[16]It will be noted that the function $f(y)$ appearing in the characteristic equations (30) and (31) is essentially a function of $y^2$. It is, therefore, valid for negative as well as positive values of $\alpha$; cf. Eq. (28).
[17]R. K. Pathria, Physics Letters 35A, 351 (1971), cf. Ref. 12.
[18]H. P. R. Frederikse, Physica 15, 860 (1949).