

## Statistical Mechanics of Ideal Fermions in a Thin Film

R. L. DEWAR AND N. E. FRANKEL

*School of Physics, University of Melbourne, Parkville, Victoria, Australia*

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Starting from the partition function for ideal fermions in a thin film with box boundary conditions, the influence of size effects on the specific heat is examined both numerically and analytically. For fairly thin films the specific heat is depressed at low temperatures and raised at high temperatures. In the very thin case, the behavior is that of a two-dimensional gas at low temperatures and that of a three-dimensional Boltzmann gas at high temperatures. The relevance to <sup>3</sup>He thin-film experiments is briefly discussed.

### 1. INTRODUCTION

BECAUSE of the widespread applicability of the ideal Fermi gas, or liquid,<sup>1</sup> as a model in physics, it is of interest to investigate the effect of finite geometry on the properties of such systems.

Although thin films of conducting materials may well be amenable to experiment, the investigation was primarily motivated by recent work on liquid helium,<sup>2,3</sup> for which reason the specific heat was chosen as the quantity for detailed investigation. We note that the corresponding case of ideal bosons has recently been studied numerically.<sup>4</sup>

### 2. THEORY

#### A. The Model

We take as our model a system of ideal fermions of mass  $m$  and spin  $S$  confined within a boxlike potential well of dimensions  $L \times L \times D$  and volume  $V$ .

Since  $L$  is allowed to approach infinity it is valid to use the grand canonical ensemble thus obtaining the partition function  $Z$  given by

$$\ln Z = \sum_{k,s} \ln(1 + ze^{-\beta \epsilon_{k,s}}). \quad (1)$$

We take the energy to be

$$\epsilon_{k,s} = (\hbar^2/2m)(k_1^2 + k_3^2), \quad (2)$$

where  $\mathbf{k}_1$  is any wave vector perpendicular to the normal to the film and  $k_3$  is given by

$$k_3 = n\pi/D, \quad n = 1, 2, 3, \dots \quad (3)$$

The partition function is now

$$\ln Z = \frac{(2S+1)V}{(2\pi)^2 D} \sum_{k_3} \int d^2 k_1 \times \ln \left\{ 1 + z \exp \left[ -\frac{\beta \hbar^2}{2m} (k_1^2 + k_3^2) \right] \right\}. \quad (4)$$

<sup>1</sup> For a collection of papers on Fermi liquid theory, see D. Pines, *The Many-Body Problem* (W. A. Benjamin, Inc., New York, 1962).

<sup>2</sup> D. F. Brewer, in *Superfluid Helium*, edited by J. F. Allen, (Academic Press Inc., New York, 1966), p. 159.

<sup>3</sup> D. F. Brewer, A. J. Symonds, and A. L. Thomson, in *Proceedings of the Ninth International Conference on Low Temperature Physics*, edited by J. G. Daunt *et al.* (Plenum Press, Inc., New York, 1965), p. 370.

<sup>4</sup> D. F. Goble and L. E. H. Trainer, *Phys. Rev.* **157**, 167 (1967).

The  $k_1$  integral may be done using the function  $f_s(z)$  defined in the Appendix, thus yielding

$$\ln Z = \frac{(2S+1)mV}{2\pi\beta\hbar^2 D} \sum_{k_3} f_2(ze^{-\beta\hbar^2 k_3^2/2m}). \quad (5)$$

To determine the thermodynamic functions of interest for the specific heat, namely, the number of particles  $N$  and the internal energy  $U$ , we use the standard relations

$$U = -\partial \ln Z / \partial \beta, \quad N = z \partial \ln Z / \partial z. \quad (6)$$

$z$  is to be eliminated by the requirement that  $N$  be a constant given by

$$N = n_0 V, \quad (7)$$

where  $n_0$  is the number density.

For convenience we define the specific heat to be dimensionless:

$$c_V = (1/N) \partial U / \partial (kT). \quad (8)$$

#### B. Calculations

To clarify the mathematics it is convenient to introduce the new temperature variable  $\theta$  defined by

$$\theta = 2mD^2 kT / \pi^2 \hbar^2. \quad (9)$$

This gives, using Eqs. (3) and (5),

$$\ln Z = \frac{(2S+1)\pi V}{4D^3} \theta \sum_{n=1}^{\infty} f_2(ze^{-n^2/\theta}) \quad (10)$$

or

$$\ln Z = [(2S+1)\pi V / 4D^3] \ln \mathfrak{z}, \quad (11)$$

where we have defined the new partition function  $\mathfrak{z}$  by

$$\ln \mathfrak{z} = \theta \sum_{n=1}^{\infty} f_2(ze^{-n^2/\theta}). \quad (12)$$

We also define parameters corresponding to  $U$  and  $N$  by

$$\mathfrak{u} = \theta^2 \partial \ln \mathfrak{z} / \partial \theta, \quad \mathfrak{N} = z \partial \ln \mathfrak{z} / \partial z. \quad (13)$$

From (6) and (7) it is easily seen that the physical value of  $\mathfrak{N}$ , which will later be seen to play the role of the principal size-effect parameter, is given by

$$\mathfrak{N} = [4 / (2S+1)\pi] n_0 D^2. \quad (14)$$

Thus  $\mathfrak{N}$  is roughly the number of particles in a box of side  $D$ . Equation (8) remains essentially unchanged;

$$c_V = (1/\mathfrak{N})\partial U/\partial\theta. \tag{15}$$

After the differentiations in Eq. (13) have been performed we get

$$\mathfrak{U} = \sum_{n=1}^{\infty} [n^2\theta \ln(1+ze^{-n^2/\theta}) + \theta^2 f_2(ze^{-n^2/\theta})], \tag{16}$$

$$\mathfrak{N} = \theta \sum_{n=1}^{\infty} \ln(1+ze^{-n^2/\theta}). \tag{17}$$

The foregoing functions were calculated numerically on an electronic computer for various values of  $\mathfrak{N}$  and  $\theta$ .  $z$  was eliminated numerically and  $c_V$  was calculated by numerical differentiation of  $\mathfrak{U}$ . Analytical results may also be obtained, as will be presented in Sec. 4.

### 3. NUMERICAL STUDY

#### A. Results for $\mathfrak{N} \gg 1$

It will be shown in Sec. 4 that in this case the size effects are small and  $c_V$  may be represented by the approximate formula, valid for  $\mathfrak{N}^{-1/3} \lesssim 0.3$ ,

$$c_V(\theta, \mathfrak{N}) \simeq c_V^{(0)}(\theta/\mathfrak{N}^{2/3}) + \Phi(\theta/\mathfrak{N}^{2/3})/\mathfrak{N}^{1/3}, \tag{18}$$

where  $c_V^{(0)}(\phi)$  is the bulk result.  $\Phi(\phi)$  is graphed in Fig. 1. To appreciate the order of magnitude of the effect, exact results for  $\mathfrak{N}^{-1/3} = 0, 0.5$ , and 1 are graphed in Fig. 2. Note that  $\theta/\mathfrak{N}^{2/3}$  is independent of  $D$ .

#### B. Results for $\mathfrak{N} \ll 1$

It is shown in Sec. 4 that in this case

$$c_V(\theta, \mathfrak{N}) \simeq c_{V2}(\theta/\mathfrak{N}) \text{ for } \theta \ll 1, \tag{19}$$

where  $c_{V2}(\psi)$  is the two-dimensional specific heat. In the nondegenerate region  $\theta \gg \mathfrak{N}$  it is shown that

$$c_V(\theta, \mathfrak{N}) \simeq c_{VB}(\theta), \tag{20}$$

where  $c_{VB}(\theta)$  is the specific heat of particles obeying Boltzmann statistics.

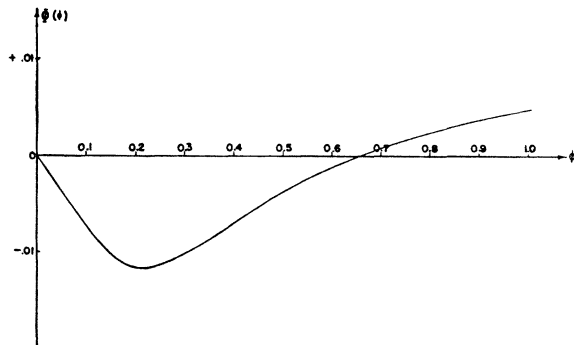


FIG. 1. The deviation function  $\Phi(\phi)$  for fairly thin films.

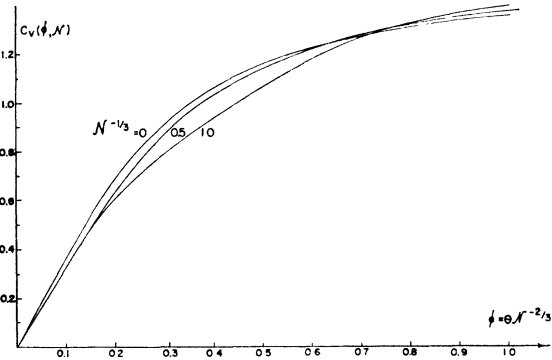


FIG. 2. Specific-heat curves for thick and thin films.

In Fig. 3 we show the curves for the cases  $\mathfrak{N} = 0.1$  and  $\mathfrak{N} = 0.01$ .

Note the two plateau regions corresponding to two- and three-dimensional Boltzmann gases. The physical explanation of this is that if we construct wave packets from the plane wave functions, the case  $\theta < 1$  corresponds to wave packets of greater width than the film which therefore constrains the particles to move only in the two transverse directions. For  $\theta > 1$  the thermal de Broglie wavelength is smaller than  $D$  and the particles behave as if in an infinite three-dimensional box.

### 4. ANALYTICAL STUDY

#### A. Zero Temperature

For  $z > 1$  we may write

$$z = e^{\nu^2/\theta}. \tag{21}$$

Using this substitution and the following result

$$f_2(x) = \frac{1}{2}(\ln x)^2 + \frac{1}{6}\pi^2 - f_2(1/x), \tag{22}$$

we get

$$\mathfrak{U} = \frac{1}{2} \sum_{n=1}^{[\nu]} (\nu^4 - n^4) + \frac{1}{6}\theta^2\pi^2[\nu] + \sum_{n=1}^{\infty} h_1(n), \tag{23}$$

$$\mathfrak{N} = \sum_{n=1}^{[\nu]} (\nu^2 - n^2) + \sum_{n=1}^{\infty} h_2(n),$$

where  $[\nu]$  is the largest integer  $\leq \nu$  and

$$h_1(n) = \theta n^2 \ln[1 + \exp(-|\nu^2 - n^2|/\theta)] + \theta^2 \operatorname{sgn}(n - \nu) f_2[\exp(-|\nu^2 - n^2|/\theta)], \tag{24}$$

$$h_2(n) = \theta \ln[1 + \exp(-|\nu^2 - n^2|/\theta)]. \tag{25}$$

These are actually the expressions on which the numerical calculations for low temperatures were performed. We here note simply that  $h_1$  and  $h_2$  vanish in the limit  $\theta \rightarrow 0$ . Thus

$$\mathfrak{U} = \frac{1}{2} \sum_{n=1}^{[\nu]} (\nu^4 - n^4) \text{ for } \theta = 0, \tag{26}$$

$$\mathfrak{N} = \sum_{n=1}^{[\nu]} (\nu^2 - n^2) \text{ for } \theta = 0. \tag{27}$$

The sum in (27) is well known;

$$\mathfrak{N} = \nu^2[\nu] - \frac{1}{6}[\nu]([\nu] + 1)(2[\nu] + 1). \quad (28)$$

For  $\mathfrak{N} \gg 1$  we get the familiar result

$$\nu \sim (\frac{3}{2}\mathfrak{N})^{1/2}. \quad (29)$$

For  $\mathfrak{N} \ll 1$  we get

$$\nu \simeq 1 + \frac{1}{2}\mathfrak{N}. \quad (30)$$

**B. Large  $\mathfrak{N}$**

In this case the region of most interest is  $\theta \gg 1$  and this is the basic approximation we make in this section.

From the inversion formula for Mellin transforms we have

$$\ln \bar{\delta} = \frac{1}{2\pi i} \int_{-i\infty+\sigma}^{i\infty+\sigma} \zeta(s)g(s) ds, \quad (31)$$

where  $\zeta(s)$  is the Riemann zeta function,  $\sigma > 1$ , and

$$g(s) = \theta \int_0^\infty f_2(ze^{-x^2/\theta})x^{s-1}dx. \quad (32)$$

Integration by parts allows us to evaluate  $g(s)$  in terms of  $f_s(z)$ , thus obtaining

$$\ln \bar{\delta} = \frac{1}{2\pi i} \int_{-i\infty+\sigma}^{i\infty+\sigma} \frac{2\theta^{1+s/2}\Gamma(2+\frac{1}{2}s)f_{2+s/2}(z)\zeta(s)}{s(s+2)} ds. \quad (33)$$

Because of the zeros of  $\zeta(s)$  at  $s = -2, -4, -6, \dots$ , the integrand is regular for all finite  $s$  save for two simple poles at  $s=0$  and  $s=1$ .

Displacing the contour of integration to the left as shown in Fig. 4 we find

$$\ln \bar{\delta} = \frac{1}{2}\pi^{1/2}\theta^{3/2}f_{5/2}(z) - \frac{1}{2}\theta f_2(z) + R, \quad (34)$$

where the remainder  $R$  is given by

$$R = \frac{1}{2\pi i} \int_c \frac{2\theta^{1+s/2}\Gamma(2+\frac{1}{2}s)f_{2+s/2}(z)\zeta(s)}{s(s+2)} ds. \quad (35)$$

Unfortunately, because of the behavior of the integrand at infinity,  $R$  is nonvanishing. However, when

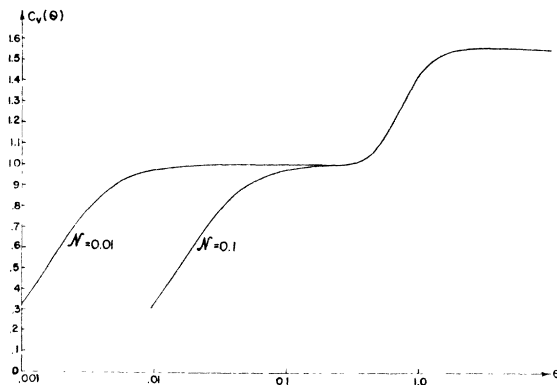


FIG. 3. Specific-heat curves for very thin films.

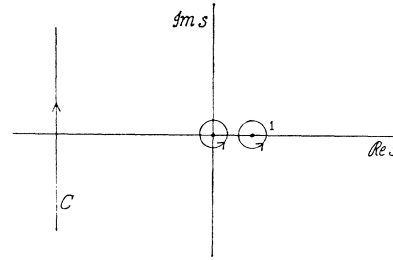


FIG. 4. The contour for the evaluation of the partition function.

$\theta \gg 1$  the  $\theta$  factor decays rapidly as  $\text{Re } s$  becomes increasingly negative, thus giving rise to low saddle points.  $R$  is always negligible in this case.

For instance, when  $z \sim 1$  we may show

$$|R| = O[\theta^{-1/2} \exp(-2\pi^{3/2}\theta^{1/2})]. \quad (36)$$

Assuming  $R$  is negligible we may now note that the leading term is  $O((\pi\theta)^{1/2})$  times the second term.

Accordingly, for  $\theta \gg 1$ , we may linearize with respect to the second term.

From (13) and (34) we get

$$\mathfrak{u} \simeq \frac{3}{4}\pi^{1/2}\theta^{5/2}f_{5/2}(z) - \frac{1}{2}\theta^2 f_2(z), \quad (37)$$

$$\mathfrak{N} \simeq \frac{1}{2}\pi^{1/2}\theta^{3/2}f_{3/2}(z) - \frac{1}{2}\theta f_1(z). \quad (38)$$

To linearize, write

$$z = z^{(0)} + z^{(1)}, \quad \mathfrak{u} = \mathfrak{u}^{(0)} + \mathfrak{u}^{(1)} \quad (39)$$

where  $z^{(0)}$  and  $\mathfrak{u}^{(0)}$  are defined by

$$\frac{1}{2}\pi^{1/2}\theta^{3/2}f_{3/2}(z^{(0)}) = \mathfrak{N}, \quad (40)$$

$$\mathfrak{u}^{(0)} = \frac{3}{4}\pi^{1/2}\theta^{5/2}f_{5/2}(z^{(0)}). \quad (41)$$

We note from (40) that  $z^{(0)}$  is a function of  $\theta\mathfrak{N}^{-2/3}$  alone. Also note that the zeroth order specific heat  $c_V^{(0)}$  defined by

$$c_V^{(0)} = (1/\mathfrak{N})\partial\mathfrak{u}^{(0)}/\partial\theta \quad (42)$$

is simply the bulk specific heat and may be seen to be also a function of  $\theta\mathfrak{N}^{-2/3}$  alone.

The final result is

$$c_V \simeq c_V^{(0)} - \frac{2}{(\pi\theta)^{1/2}} \left\{ \frac{f_2}{f_{3/2}} - \frac{9}{8} \frac{1}{f_{1/2}} \right. \\ \left. \times \left[ f_1 - \frac{f_0 f_{3/2}}{f_{1/2}} + \frac{f_{-1/2} f_1 f_{3/2}}{(f_{1/2})^2} \right] \right\}, \quad (43)$$

where  $f_s$  denotes  $f_s(z^{(0)})$ . This is clearly of the form

$$c_V(\theta, \mathfrak{N}) \simeq c_V^{(0)}(\theta/\mathfrak{N}^{2/3}) + \Phi(\theta/\mathfrak{N}^{2/3})\mathfrak{N}^{-1/3}. \quad (44)$$

In the Boltzmann statistic limit we have

$$c_V \simeq \frac{3}{2} + 1/4(\pi\theta)^{1/2} \quad \text{for } \theta\mathfrak{N}^{-2/3} \gtrsim 5. \quad (45)$$

Thus

$$\Phi(\phi) \simeq 1/4(\pi\phi)^{1/2} \quad \text{for } \phi \gtrsim 5. \quad (46)$$

In the linear region we have

$$c_V \simeq \frac{1}{3}\pi^2 \left[ \left(\frac{3}{2}\right)^{1/3} - 1/4\mathfrak{N}^{1/3} \right] (\theta/\mathfrak{N}^{2/3}). \quad (47)$$

Thus

$$\Phi(\phi) \simeq -\frac{1}{12}\pi^2\phi \quad \text{for } \phi \lesssim 0.1. \quad (48)$$

### C. Small $\mathfrak{N}$

When  $\mathfrak{N} \ll 1$  it is advantageous to consider first the region  $\theta \ll 1$ . In this region we need retain only the first terms of the summations in Eqs. (16) and (17).

$$\mathfrak{U} \simeq \theta \ln(1+z') + \theta^2 f_2(z'), \quad (49)$$

$$\mathfrak{N} \simeq \theta \ln(1+z'), \quad (50)$$

where  $z' = ze^{-1/\theta}$ . This gives  $c_V(\theta, \mathfrak{N}) \simeq c_{V2}(\theta/\mathfrak{N})$ , where

$$c_{V2}(\psi) = 2\psi f_2(e^{1/\psi} - 1) - e^{1/\psi}/\psi(e^{1/\psi} - 1). \quad (51)$$

We may show that

$$c_{V2}(\psi) \simeq \frac{1}{3}\pi^2\psi \quad \text{for } \psi \ll 1 \quad (52)$$

$$c_{V2}(\psi) \simeq 1 \quad \text{for } \psi \gg 1. \quad (53)$$

To treat the rest of the  $\theta$  domain we observe that in the first plateau region  $\mathfrak{N} \ll \theta \ll 1$ ,  $z'$  has already become small and thus for all temperatures  $\theta \gg \mathfrak{N}$  we may apply Boltzmann statistics, that is, we may expand to first order in  $z$  in Eq. (12). Thus, for  $\theta \gg \mathfrak{N}$ ,

$$\ln \mathfrak{z} \simeq \theta \mathfrak{z} \sum_{n=1}^{\infty} e^{-n^2/\theta}. \quad (54)$$

From (13) we may show  $c_V(\theta, \mathfrak{N}) \simeq c_{VB}(\theta)$ , where

$$c_{VB}(\theta) = \frac{d}{d\theta} \left\{ \frac{d}{d\theta} \ln \left( \theta \sum_{n=1}^{\infty} e^{-n^2/\theta} \right) \right\}. \quad (55)$$

We have

$$c_{VB}(\theta) \simeq 1 \quad \text{for } \theta \ll 1, \quad (56)$$

$$c_{VB}(\theta) \simeq \frac{3}{2} + 1/4(\pi\theta)^{1/2} \quad \text{for } \theta \gg 1. \quad (57)$$

## 5. DISCUSSION

In the Secs. 1-4 we have presented a detailed analytical and numerical study of the specific heat of thin films of ideal fermions. We present, in this section, a physical discussion of the interesting behavior that we observed along with a discussion of possible experimental verifications of these anomalies.

There are three characteristic lengths of importance in this study:  $D$ , the film thickness;  $n_0^{-1/3}$ , the interparticle spacing; and the thermal de Broglie wavelength,  $\lambda = (2\pi\hbar^2/mKT)^{1/2}$ . This study was undertaken to see the interplay of the quantum size effects controlled by these lengths, and with them we can understand the general behavior of the results that we have obtained as depicted in Figs. 2 and 3.

When  $\mathfrak{N} \ll 1$ , we have the case where the thickness of the film is much less than the interparticle spacing and hence the film should behave essentially as a two-

dimensional gas of fermions at very low temperatures. In other words, one of the translational degrees of freedom should be frozen out at very low temperatures since the eigenvalues are proportional to  $D^{-2}$ ; at very low temperatures it should be impossible to excite this mode. This behavior is seen in Fig. 3. We also expect quantum size effects to become prevalent for  $D \approx \lambda$  ( $\theta \approx 1$ ), that is, when the size of the particle's wavepacket becomes comparable with the film thickness. We observed this effect in the specific heat reaching its maximum here with a value greater than the classical value of  $\frac{3}{2}$ . This is observed in Fig. 3. Lastly, for this case,  $\theta \approx 1$  and  $\mathfrak{N} \ll 1$ , we have  $n_0\lambda^3 \ll 1$ . Thus the system should be identical to a classical Boltzmann gas with quantum size effects. This is just the result discussed in Secs. 3 and 4 and seen in Fig. 3. We mention in passing that this general thermal behavior would also occur for thin films of bosons and was not observed<sup>4</sup> because such small values of  $\mathfrak{N}$  were not studied, the difference being that at very low temperatures the gas would resemble a two-dimensional Bose gas.

When  $\mathfrak{N} \gg 1$ , we have the effects of both three dimensionality and quantum size effects simultaneously occurring. For example, for temperatures such that  $\theta \approx 1$ , we still have a degenerate fermion situation as  $n_0\lambda^3 \gg 1$ , and thus we expect to see the degenerate three-dimensional fermion results modified by size effects. We see this in Fig. 2, where the specific-heat maximum anomaly is present along with a suppression of the specific heat at low temperatures below that of the bulk three-dimensional results.

It is interesting to see if any of these anomalies have experimental implications. The work of Landau has shown that at low temperatures, systems of interacting fermions can have ideal-gas behavior with an effective mass  $m^*$  instead of the free mass  $m$ . Thus we might expect thin films of liquid <sup>3</sup>He to manifest some of this behavior. That was our second primary objective in this study. It is hard to compare with Brewer *et al.*, because they present data for <sup>3</sup>He in Vycor porous glass (a narrow channel rather than thin-film geometry) and only for one thickness of approximately 30 Å. Nevertheless, a general suppression of the specific heat below the bulk results was observed. However, as our results in Fig. 2 indicate, we expect from an ideal-gas model to see the suppression take place in the very low temperature linear region and that the specific heat would rise above the bulk values as the temperature increases out of the linear region. If we assume this, then the difference between experiment and model is even further increased. It is hard to estimate what  $m^*$  might be and we had hoped that the results presented could be useful in a phenomenological sense to estimate  $m^*$ . Therefore, this might be an indication that further refinements in the theory may be in order, for example, to determine perhaps what the true quasiparticle spectrum (size-dependent) might look like.

Furthermore, it is interesting to see if the results depicted in Fig. 3 could be observed. For the density of liquid  $^3\text{He}$ , it would most likely require film thicknesses less than an interparticle spacing. Thus to see these phenomena, we would need an experimental situation of a dilute concentration of  $^3\text{He}$  atoms; it is also quite possible that this situation would allow for better agreement with these ideal-gas results. We therefore believe that thin films of liquid  $^4\text{He}$  and  $^3\text{He}$  mixtures with a dilute concentration of  $^3\text{He}$  would be a most interesting experimental situation. If the mixture can be treated to some extent as a mixture of ideal systems of  $^4\text{He}$  and  $^3\text{He}$ , then the  $^3\text{He}$  would behave as a size-modified classical Boltzmann gas, and there should be a good chance of seeing the specific-heat maximum anomaly as well as the long flat two-dimensional behavior after the  $^4\text{He}$  contribution is subtracted. It would also be interesting to study such films to observe the effect of the  $^3\text{He}$  impurity on the already interesting anomalous behavior of thin superfluid  $^4\text{He}$  films.<sup>2</sup> It might also be possible to see these effects in the thermal response of thin films of charged carriers, such as electrons in metals under suitable conditions.

The role of boundary conditions might be questioned, and we note that no qualitative change in the results is expected. We have investigated the role of boundary conditions for convenience in the size-modified classical Boltzmann region and find no qualitative change. Finally, in summarizing, we remark that the results of this study should provide a sensitive test of quantum size effects in systems which can be treated to a good approximation as thin films of ideal fermions.

#### ACKNOWLEDGMENTS

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#### APPENDIX

The preceding calculations have relied heavily on the properties of the function  $f_s(z)$ , defined by

$$f_s(z) = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{z^n}{n^s} \quad \text{for } |z| < 1 \quad (\text{A1})$$

and by analytic continuation for  $|z| \geq 1$ .

This is a special case of the function studied.<sup>5</sup> The numerical evaluation of the function has been extensively discussed,<sup>6</sup> where tables may be found for the cases  $s = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$ . In the numerical calculation of  $c_V$ ,  $f_2(z)$  was calculated by using Eq. (22) to restrict  $z$  to the range  $0 < z < 1$  and Euler's transformation was used to hasten convergence.

We shall now give a compendium of the properties used in the calculations.

For  $\text{Re } s > 0$  we have the integral representation

$$f_s(z) = \frac{z}{\Gamma(s)} \int_0^{\infty} \frac{t^{s-1} e^{-t}}{1 + z e^{-t}} dt. \quad (\text{A2})$$

By using a contour integral representation similar to that used for the Riemann zeta function<sup>7</sup> we may show  $f_s(z)$  to be regular in the  $s$  plane except for the point at infinity.

For  $z > 1$  the behavior of  $f_s(z)$  for negative  $\text{Re } s$  may be studied via Lerch's transformation

$$f_s(z) = i(2\pi)^{s-1} \Gamma(1-s) \{ e^{i\pi s/2} \zeta[1-s, \frac{1}{2} - (\ln z)/2\pi i] - e^{-i\pi s/2} \zeta[1-s, \frac{1}{2} + (\ln z)/2\pi i] \}. \quad (\text{A3})$$

Equation (22) may be deduced from (A3) but may more easily be verified by differentiation using the useful result

$$f_s'(z) = f_{s-1}(z)/z. \quad (\text{A4})$$

Finally, we give the first two terms of the asymptotic expansion for large  $z$ ;

$$f_s(z) \sim \frac{(\ln z)^s}{\Gamma(s+1)} + \frac{1}{6}\pi^2 \frac{(\ln z)^{s-2}}{\Gamma(s-1)} \quad \text{for } |z| \gg 1. \quad (\text{A5})$$

<sup>5</sup> *Higher Transcendental Functions*, edited by A. Erdelyi (McGraw-Hill Book Co., Inc., New York, 1953), Vol. 1, p. 27.

<sup>6</sup> J. McDougall and E. Stoner, *Trans. Roy. Soc. (London)* **A237**, 67 (1938).

<sup>7</sup> E. T. Whittaker and G. N. Watson, *A Course in Modern Analysis* (Cambridge University Press, New York, 1965), p. 266.