is actually shown to occur using two essential assumptions:

1. The initial fine-grained density is a reasonably smooth function of its arguments, i.e., while it may have discontinuities, it is not a δ function in all its variables.
2. The linearized equations of motion are valid for a statistical calculation as long as the dependence of the Poincaré time on initial conditions is included in the approximation.

Assumption (1) implies that the present theory is a statistical one which refers to ensemble rather than time averages. It might be mentioned, however, that the initial distribution can be made as close to a δ function as we please. Assumption (2) is the key assumption made in the paper. For a single anharmonic oscillator, it can be proved. It is the suggestion of this paper that it may be true for more general systems.

The dependence of the Poincaré recurrence time on initial conditions is the essential source of irreversibility here. Because of this dependence some equilibrium distribution is approached whether or not the system is quasi-ergodic. Of course, if the equilibrium distribution is to depend only on the energy of the system, then the system or its representative ensemble must have a quasi-ergodic character.

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Quantum Theory of Surface Energy and Tension*

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The surface energy E_S of a system of interacting particles is $E_S=\int_{-\infty}^{\infty} dz\{\epsilon(z)-\epsilon_B[\rho(z)/\rho_B]\}$, where $\epsilon(z)$ and $\rho(z)$ are the energy and particle densities along the axis normal to the surface. ϵ_B and ρ_B are the corresponding quantities in the bulk. Alternatively one may formulate an exact expression for the surface tension defined as $\gamma=(\partial F/\partial S)_V$, with the result that

$$\gamma=\int_{-\infty}^{\infty} dz\left\{2[t_z(z)-t_\perp(z)]+\frac{1}{4}\int d\mathbf{r}(r^2-3r_z^2)\frac{1}{r}\frac{dv}{dr}\rho^{(2)}(z,z+r_z)\right\}.$$

$t_i(z)$ are the components of the average kinetic energy density and $\rho^{(2)}(r_1,r_2)$ is the pair distribution function. In the ground state $\gamma=E_S$. We have applied these formulas to liquid He^4 and He^3 assuming that $\rho^{(2)}=\rho(z)\times\rho(z+r_z)g_B(r)$. The bulk radial distribution $g_B(r)$ is obtained from x-ray data. Use of the thermodynamic data ϵ_B and $p=0$ gives t_B and checks $g_B(r)$. Further we assume a free-volume form of the kinetic energy density $t(z)=t_B[\rho(z)/\rho_B]^{5/3}$ and an exponential density fall-off $\rho(z)=\rho_B e^{-z/a}$. Calculated values of E_S show a minimum at $a=2.0$A. E_S and γ differ by 20% at this value, with γ being 0.38 erg/cm^2 for He^4. The experimental value of γ is 0.35 erg/cm^2.

I. INTRODUCTION

THE purpose of this paper is to describe a simple method of calculating the surface properties of a quantum mechanical fluid, when the bulk properties are theoretically or experimentally known. Several quantum-mechanical approaches have been used[1-3] to calculate the surface properties of the ground state of nuclear matter, whereas, for molecular fluids, the use of classical statistical mechanics has been found adequate.[4,5]

Starting with Swiatecki's expression for the surface energy of a system in a single quantum state, we derive an alternative expression, which gives the surface energy directly in terms of the anisotropic part of the pressure tensor. The canonical ensemble average then gives the surface tension, identical in form to the classical expression of Kirkwood and Buff.[4]

If approximate wave functions are used, these two expressions for the surface energy will give different estimates. A parameter δ, describing the skin depth, can thus be chosen at that value for which these expressions are closest. Moreover, if we consider the ground state, the surface energy should have a minimum as a function of δ, according to the variational principle. In all cases, it is, of course, required that the bulk data be adequately fitted.

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[1] C. F. von Weizsäcker, Z. Physik **96**, 431 (1935).

[2] W. J. Swiatecki, Proc. Phys. Soc. (London) **A64**, 226 (1951).

[3] R. Berg and L. Wilets, Phys. Rev. **101**, 201 (1956).

[4] J. G. Kirkwood and F. P. Buff, J. Chem. Phys. **17**, 338 (1949).

[5] F. P. Buff, Z. Elektrochem. **56**, 311 (1952).

We have applied this procedure to a calculation of the surface energy of liquid He^4 and He^3, where the interaction potential is well known and simple. In spite of the roughness of the approximation used, good agreement is found with the experimental value of the surface tension. In fact, our calculation yields a minimum in surface energy as a function of δ, despite the fact that we did not use an explicit wave function. We expect that this technique can also be applied successfully to the nuclear surface.

II. THEORY

We present a derivation of Swiatecki's expression for the case of a finite system of N identical particles each of mass m. We assume that the Hamiltonian can be written in the form

$$\mathcal{H}=\sum_{i=1}^{N}-\frac{\hbar^2}{2m}\nabla_i^2+U(\mathbf{r}_1\cdots\mathbf{r}_N). \tag{1}$$

Let $\psi(\mathbf{r}_1\cdots\mathbf{r}_N)$ be the normalized ground-state wave function of the system, and E the total binding energy. Then

$$\mathcal{H}\psi=E\psi. \tag{2}$$

Multiplying each side by $\psi^\dagger$ and integrating over all coordinates, we obtain

$$E=\int\epsilon(\mathbf{r})d^3r, \tag{3}$$

where

$$\epsilon(\mathbf{r})=N\int\psi^\dagger(\mathbf{r}\zeta)H\psi(\mathbf{r}\zeta)d\zeta, \tag{4}$$

$$H=-\frac{\hbar^2}{2m}\nabla_r^2+\frac{1}{N}U(\mathbf{r},\zeta). \tag{5}$$

ζ denotes the $N-1$ variables $\mathbf{r}_2\mathbf{r}_3\cdots\mathbf{r}_N$ and

$$d\zeta=d^3r_2\cdots d^3r_N.$$

$\epsilon(\mathbf{r})$ is the energy density of the system. We shall also need the particle density $\rho(\mathbf{r})$, given by

$$\rho(\mathbf{r})=N\int\psi^\dagger(\mathbf{r}\zeta)\psi(\mathbf{r}\zeta)d\zeta. \tag{6}$$

Over most of the volume occupied by the system we expect that $\epsilon(\mathbf{r})=\epsilon_B$ and $\rho(\mathbf{r})=\rho_B$, where ϵ_B and ρ_B are the constant energy and particle densities in the bulk. The volume contribution to the total energy per particle is therefore ϵ_B/ρ_B and consequently the surface contribution per particle must be $E/N-\epsilon_B/\rho_B$. Substituting Eqs. (3) and (6) we obtain for the total surface energy

$$E_S=\int\left[\epsilon(\mathbf{r})-\frac{\epsilon_B}{\rho_B}\rho(\mathbf{r})\right]d^3r. \tag{7}$$

It is clear that the integrand vanishes in the bulk. Swiatecki points out that whereas the surface energy and the bulk energy density are uniquely defined, this is not true for the energy density $\epsilon(\mathbf{r})$. Instead of Eq. (4) for $\epsilon(\mathbf{r})$, the form

$$\epsilon'(\mathbf{r})=N\int\frac{\hbar^2}{2m}\nabla\psi^\dagger\cdot\nabla\psi d\zeta+\int\psi^\dagger U\psi d\zeta \tag{8}$$

has also been used. Of course, this form still leads to the same value of E_s.

We proceed now to derive an expression for the surface energy of the ground state in terms of the anisotropic part of the pressure tensor. For this purpose we divide the skin region into cylinders normal to the surface which extend from the bulk to infinity (see Fig. 1).

For each cylinder we choose a frame of reference with the z axis along the axis of the cylinder. The origin is located so that the volume V enclosed by the x-y plane through the origin and the base of the cylinder contains the same number of particles at the bulk density ρ_B as the average number of particles in the cylinder, that is

$$\int_{-V/S}^{\infty}dz\int\int dxdy\,\rho(r)=\rho_BV. \tag{9}$$

The integration over x and y is confined to the area S of the base of the cylinder.

The total energy $E(V,S)$ in the cylinder is given by

$$E(V,S)=\int_{-V/S}^{\infty}dz\int\int dxdy\,\epsilon(\mathbf{r}). \tag{10a}$$

Taking partial derivatives with respect to S at constant V and substituting Eq. (9) gives

$$\left(\frac{\partial E}{\partial S}\right)_V=\int_{-\infty}^{\infty}dz\left[\epsilon(z)-\frac{\epsilon_B}{\rho_B}\rho(z)\right]. \tag{11}$$

The lower limit of integration has been extended to $-\infty$ since the contribution comes only from the skin. It is assumed that S is sufficiently small so that variations of $\epsilon(\mathbf{r})$ and $\rho(\mathbf{r})$ along x and y can be neglected. Comparing this expression with Eq. (7) we find that $(\partial E/\partial S)_V$ is the contribution per unit area to the total surface energy, as expected.

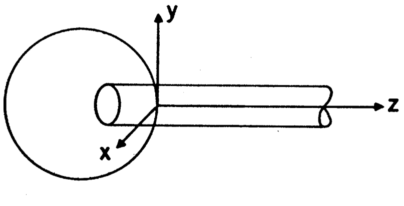

FIG. 1. Schematic diagram of the volume occupied by the system showing one of the cylinders referred to in the text, and the corresponding frame of reference.

All of these considerations apply equally well for any excited state ψ_n and corresponding energy E_n of the system. We may then form the statistical mechanical expression for the surface tension γ by noting that γ is the canonical ensemble average of $(\partial E_n/\partial S)_V$:

$$\gamma=\frac{\sum_n(\partial E_n/\partial S)_V e^{-E_n/kT}}{\sum_n e^{-E_n/kT}}. \tag{12}$$

Each $(\partial E_n/\partial S)_V$ is given by an expression of the form (11) where all averages are taken with ψ_n. It is understood that the unbound states are constrained to a fixed volume. At zero temperature the surface tension and surface energy are equal, a well-known fact in thermodynamics.

An alternative expression for $(\partial E/\partial S)_V$ may be developed by making the following change in the variables of integration[6]: $x'=x/\sqrt{S}$, $y'=y/\sqrt{S}$, $z'=Sz/V$, then

$$E(V,S)=V\int_1^\infty dz' \underset{\text{unit surface}}{\iint} dx'dy'\, \epsilon(S^{\frac{1}{2}}x', S^{\frac{1}{2}}y', Vz'/S), \tag{10b}$$

and

$$\left(\frac{\partial E}{\partial S}\right)_V=V\int_{-1}^\infty dz'\iint dx'dy'\frac{\partial \epsilon}{\partial S}. \tag{13}$$

Using Eqs. (4) and (5), we can write

$$\frac{\partial\epsilon}{\partial S}=N\int\left[\psi^\dagger\frac{\partial H}{\partial S}\psi+\frac{\partial\psi^\dagger}{\partial S}H\psi+\psi^\dagger H\frac{\partial\psi}{\partial S}\right]d\zeta, \tag{14}$$

$$\frac{\partial H}{\partial S}=\frac{\hbar^2}{2m}\frac{1}{S}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}-\frac{\partial^2}{\partial z^2}\right]+\frac{1}{SN}\left[\frac{1}{2}x\frac{\partial U}{\partial x}+\frac{1}{2}y\frac{\partial U}{\partial y}-z\frac{\partial U}{\partial z}\right], \tag{15}$$

and

$$\frac{\partial\psi}{\partial S}=\frac{1}{S}\left[\frac{1}{2}x\frac{\partial\psi}{\partial x}+\frac{1}{2}y\frac{\partial\psi}{\partial y}-z\frac{\partial\psi}{\partial z}\right]. \tag{16}$$

Returning to the original variables, we note that

$$\int_{-\infty}^\infty dz\iint dxdy\int\left[\frac{\partial\psi^\dagger}{\partial S}H\psi+\psi^\dagger H\frac{\partial\psi}{\partial S}\right]d\zeta=0. \tag{17}$$

The variational principle cannot be invoked to prove Eq. (17) since H is not the total Hamiltonian and the region of integration over the variable r is confined to the interior of the cylinder. A proof is given in Appendix I. Equation (13) then becomes

$$\left(\frac{\partial E}{\partial S}\right)_V=N\int_{-\infty}^\infty dz\left[\int\psi^\dagger(\mathbf{r}\zeta)S\frac{\partial H}{\partial S}\psi(\mathbf{r}\zeta)d\zeta\right] \tag{18a}$$

$$=\int_{-\infty}^\infty dz[p_{zz}-\tfrac{1}{2}(p_{xx}+p_{yy})]. \tag{18b}$$

p_{xx}, p_{yy}, and p_{zz} are the diagonal components of the pressure tensor, defined by

$$p_{xx}(\mathbf{r})=N\int\psi^\dagger(\mathbf{r}\zeta)\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}-\frac{x}{N}\frac{\partial U}{\partial x}\right]\psi(\mathbf{r}\zeta)d\zeta, \tag{19}$$

with similar expressions for p_{yy} and p_{zz}. Again the contribution of the integrand in (18) comes entirely from the skin region so that it is possible to extend the integration (18b) over the whole sphere for large radius of curvature, *viz.*,

$$(\partial E/\partial S)_V=\int[p_{nn}-p_{tt}]d(\mathbf{r}\cdot\mathbf{n}), \tag{18c}$$

where $\mathbf{n}$ is the unit vector normal to the surface. E and S are now the total energy and surface, respectively. p_{tt} and p_{nn} are the tangential and normal components of the pressure tensor.

Equation (18) is completely analogous to the classical expression for surface tension obtained by Kirkwood and Buff.[4]

If the potential U is of the form

$$U=\tfrac{1}{2}\sum_{ij}v(r_{ij}), \tag{20}$$

where $v(r)$ is spherically symmetric, we find that for a plane surface

$$\left(\frac{\partial E}{\partial S}\right)_V=\int_{-\infty}^\infty dz\left\{[2t_z(z)-t_x(z)-t_y(z)]+\frac{1}{4}\int d\mathbf{r}(r^2-3r_z)\frac{1}{r}\frac{dv}{dr}\rho^{(2)}(z, z+r_0)\right\}, \tag{21}$$

where

$$t_x(\mathbf{r})=N\int\psi^\dagger(\mathbf{r}\zeta)\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right]\psi(\mathbf{r}\zeta)d\zeta \tag{22}$$

is the x component of the kinetic energy density, with corresponding expressions for the y and z components, and

$$\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)=\tfrac{1}{2}N(N-1)\int|\psi(\mathbf{r}_1\cdots\mathbf{r}_N)|^2d\mathbf{r}_3\cdots d\mathbf{r}_N \tag{23}$$

is the pair correlation function. Equation (21) is valid only if the range of $v(r)$ is small compared to the radius of curvature of the system, since we have neglected contributions of the $N-1$ variables when any of these is outside the cylinder.

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[6] This change of variable was carried out on the classical partition function by F. P. Buff (reference 5).

Another interesting relation can be obtained in the following manner. Assume that the system occupies a sphere of radius R and volume V. Using Eq. (3) for the energy E and a coordinate transformation which reduces all variables by R, we find

$$R\frac{dE}{dR}=-\int_V[p_{xx}(\mathbf{r})+p_{yy}(\mathbf{r})+p_{zz}(\mathbf{r})]d\mathbf{r};\qquad(24)$$

also

$$R\frac{dE}{dR}=\left(\frac{\partial E}{\partial S}\right)_V R\frac{dS}{dR}+\left(\frac{\partial E}{\partial V}\right)_S R\frac{dV}{dR}=2\gamma S-3p_BV.$$

Using (24) in conjunction with (18b), we see immediately that

$$p_BV=\int p_{nn}d\mathbf{r},\qquad(25)$$

where the subscript indicates the direction normal to the surface. For the ground state $p_B=0$ and we find $\int p_{nn}d\mathbf{r}=0$. This condition could be used to determine a parameter in the theory if desired. We have not found this practical, since p_{nn} is an extremely sensitive function of the skin depth.

Equation (25) resembles the classical condition that $p_{nn}=p_B$. This is not so, however, owing to the definition of V, $V=\int[\rho(\mathbf{r})/\rho_B]d\mathbf{r}$. Apparently, the difference arises from the fact that we are constraining the "condensed" phase. The usual thermodynamic theory deals with the "condensed" phase in equilibrium with its vapor. We have not yet resolved this question. Of course, for the ground state $p_B=0$ in any case and this question is not of importance.

III. CALCULATION OF THE SURFACE TENSION OF LIQUID He^4 AND He^3 AT $T=0$°K

To calculate the surface tension of liquid He^4 at zero temperature, we used the Slater-Kirkwood potential

$$v(r)=\left[770e^{-4.6r}-\frac{1.49}{r^6}\right]\times10^{-11}\text{ erg}\qquad(26)$$

between two helium atoms, and the bulk radial distribution function $g_B(r)$ obtained by Goldstein[7] from x-ray analysis.

The bulk energy density ϵ_B can be written in the form

$$\epsilon_B=t_B+v_B,\qquad(27)$$

where

$$t_B=\pi\rho_B{}^2\int_0^\infty g_B(r)\frac{dv}{dr}r^3dr,\qquad(28)$$

and

$$v_B=2\pi\rho_B\int_0^\infty g_B(r)v(r)r^2dr;\qquad(29)$$

t_B and v_B are the kinetic and potential energy densities in the bulk. To obtain Eq. (28) we used the virial theorem, noting that in the ground state the pressure is zero. By slight adjustments of $g_B(r)$ at small r where it is not well known and where dv/dr is very large, we were able to compute t_B and v_B so as to give approximately the observed value[8] of -14 cal/mole to ϵ_B. We find $t_B=28$ cal mole, $v_B=-40$ cal mole.

For preliminary calculations, of γ we have made several simplifying assumptions:

(*a*) We have assumed that the radial distribution function $g_B(r)$ is independent of the position of the pair with respect to the surface. In all probability the error introduced here is not serious as evidenced by the classical calculation of Kirkwood and Buff on liquid argon.

(*b*) We have assumed that the kinetic energy is isotropic, i.e., $t_x=t_y=t_z$. The assumption of isotropy is very poor if the surface turns out to be relatively sharp. However, on physical grounds alone one expects the surface region to be at least one interatomic distance in depth, which one hopes will be sufficient to smooth out anisotropy. A method which would allow for anisotropy in t would be to assume an independent-particle central potential of varying steepness related to δ in an obvious way in the manner of Swiatecki.

An alternative method, applicable at higher temperatures, has been worked out by Oppenheim[9] who estimated the anisotropic contribution of the kinetic energy to γ in liquid H$_2$ at about 20° K by using the first-order quantum corrections to the Wigner distribution function. He has found a very small effect of less than 10%. In view of the above results, one may hope that anisotropy in t will play a relatively unimportant role.

(*c*) The functional form we have used for t is $t(z)=t_B[\rho(z)/\rho_B]^{5/3}$. A more correct form is given by the free-volume expression $t(z)=\rho(z)A\{[\rho_0/\rho(z)]^{1/3}-1\}^{-2}$ which was found by Rosenbluth to give a density dependence in good agreement with the Monte Carlo calculation of the ground-state energy of a Bose gas of hard spheres.[10] After adjusting the constants A and ρ_0, to fit the bulk properties, this form did not yield results noticeably different from the more simple expression. It is of course understood that these functional forms only make sense for sufficiently diffuse surface regions.

(*d*) Finally we have assumed for analytical convenience that $\rho(z)$ drops off exponentially, assuming of course that $\int_{-L}^{\infty}\rho(z)dz=\rho_BL$.

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[7] L. Goldstein, Phys. Rev. 98, 857 (1955).

[8] W. H. Keesom, *Helium* (Elsevier Publishing Company, New York, 1942), p. 231.

[9] I. Oppenheim (private communication). We are grateful to Dr. Oppenheim for informing us of his results.

[10] M. Rosenbluth (unpublsihed). We thank Dr. R. Mazo for this communication.

Summarizing our assumptions below, we have set

$$\rho^{(2)}(z, z+r_z)=\rho(z)\rho(z+r_z)g_B(r),$$

$$t_x=t_y=t_z=\tfrac{1}{3}t=\tfrac{1}{3}t_B[\rho(z)/\rho_B]^{5/3},$$

$$\begin{aligned}\rho(z)&=\rho_B \quad \text{for} \quad z\leqslant\delta\\ &=\rho_B e^{-(z+\delta)/\delta} \text{ for } z\gg\delta.\end{aligned}$$

With these assumptions we have calculated the surface energy $E_S(\delta)$ from Eq. (11) and the surface tension $\gamma(\delta)$ from Eq. (21) as a function of the skin depth parameter δ. In the exact calculation, there will be a value of δ for which these are the same. The results are shown in Fig. 2.

The observed surface tension of the He^4 extrapolated to $T=0°$ K is 0.35 dyne/cm.[11] The two curves come closest at about $\delta_0=2$ A which corresponds also to the minimum of the surface energy $E_S(\delta)$. This is somewhat less than the range of the potential between helium atoms. For this value the calculated value of γ is 0.38 in good agreement with experiment. The calculated value of the $E_S(\delta)$ here is 0.5, indicating that γ is probably a more reliable function to calculate surface energy than is $E_S(\delta)$. We computed the binding energy and surface tension of He^3 by replacing the bulk particle density of He^4 by that of He^3, leaving all other quantities the same. We found $\epsilon_B=-5$ cal/mole and $\gamma=0.18$ dyne/cm. Experimentally $\epsilon_B=-5.05$,[12] and $\gamma=0.152$,[13] again indicating good agreement with experiment.

IV. CONCLUSION

The encouraging results of this paper indicate that a thorough knowledge of the bulk properties of a quantum fluid seems to be sufficient to estimate surface properties rather well. Rough guesses of the functional dependence of density and energy based on physical arguments, when employed in the formal expression developed here, seem to lead to fair quantitative estimates on surface energy and probably also on surface depth.

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We wish to thank Dr. E. E. Salpeter for some interesting discussions.

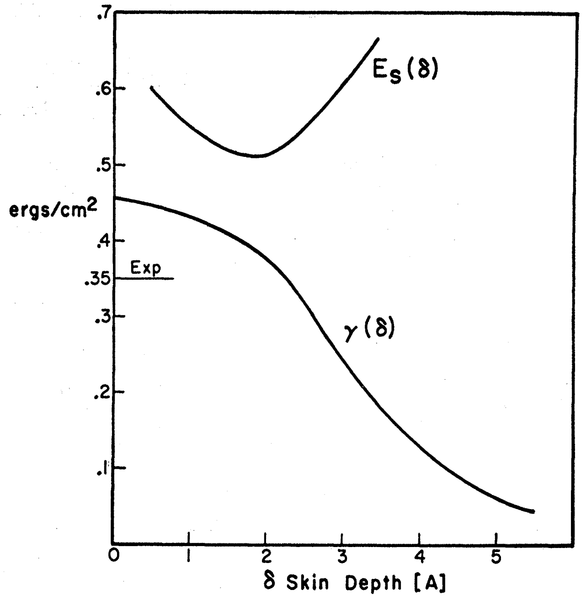

FIG. 2. Calculated values of the surface energy $E_S(\delta)$ and the surface tension $\gamma(\delta)$ for He^4 as a function of skin depth δ.

APPENDIX I

To prove Eq. (17) we sum the contributions of all cylinders into which the skin region was divided. Then

$$\sum\int_{-\infty}^{\infty}dz\int\int dxdy\int\left[\frac{\partial\psi^\dagger}{\partial S}H\psi+\psi^\dagger H\frac{\partial\psi}{\partial S}\right]d\zeta$$

$$=\int d^3r\int\left[\frac{\partial\psi^\dagger}{\partial S}H\psi+\psi^\dagger H\frac{\partial\psi}{\partial S}\right]d\zeta.$$

We can replace now the "one-particle" Hamiltonian H [Eq. (5)] by $1/N$ times the total Hamiltonian $\mathcal{H}$ [Eq. (1)]. Since $\mathcal{H}$ is Hermitian and ψ is an eigenstate, we obtain

$$E\sum\int_{-\infty}^{\infty}dz\int\int dxdy\int\frac{\partial}{\partial S}(\psi^\dagger\psi)d\zeta.$$

Using Eq. (16), we integrate by parts and find

$$\left[-V\rho_B+\int_{-V/S}^{\infty}dz\int\int dxdy\,\rho(\mathbf{r})\right]=0,$$

according to Eq. (9).

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[11] Reference 8, p. 263.

[12] *Progress of Low-Temperature Physics*, Vol. VI, p. 90.

[13] K. N. Zinov'eva, J. Exptl. Theoret. Phys. U.S.S.R. **29**, 899 (1955) [translation: Soviet Phys. JETP **2**, 774 (1956)].