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Density of electronic energy levels in disordered systems*

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The behavior of the density of electronic energy levels for a simple model of a disordered system is studied in the limit of very low energies. By reformulating the problem as one in Brownian motion, it proves possible to obtain the leading term and the first correction to it. The leading term is just the one already conjectured by Lifshitz.

I. INTRODUCTION

In recent years there has been considerable interest in the electronic structure of disordered systems.[1] Many interesting questions and conjectures have been formulated, although very little has actually been proved. In this paper we shall address ourselves to one of the simplest of these conjectures. It concerns the distribution of energy levels for a very idealized model of a disordered system. The model is the following: An electron is allowed to interact with fixed "impurities" of which a number N are distributed "at random" in a volume V. (The exact meaning of "at random" will be made clear below.) The interaction between an "impurity" located at the point $\vec{R}$ and the electron at the point $\vec{r}$ is represented by a short-range purely repulsive potential $v(\vec{r}-\vec{R})$. In the thermodynamic limit ($N\to\infty$, $V\to\infty$, but $N/V\to\rho$) it is not difficult to show that the density of energy levels per unit volume in the neighborhood of the energy ϵ [$g(\epsilon)$] is well defined and vanishes for $\epsilon<0$. We ask: How does $g(\epsilon)$ behave as ϵ approaches zero from above? This nontrivial question seems first to have been asked and answered by Lifshitz,[2] whose intuitively very appealing argument we give below. The purpose of our paper is to put the Lifshitz argument on a firmer mathematical basis and to obtain the first correction to it.

We may summarize Lifshitz's idea as follows: Electronic energy levels for arbitrarily small energy can only come from states with wave functions localized in very large regions which are empty of impurities. If the electronic wave function overlaps an impurity appreciably, there will be a finite potential energy of interaction, while the largeness of the region is necessary so that the kinetic energy can be made very small. Now, as is well known, the probability of a large region of volume Ω being free of impurities in a random system of impurities is proportional to $e^{-\rho\Omega}$. Since the volume Ω is very large, the low-lying levels for states localized in it will be insensitive to the exact conditions on the boundary ($\partial\Omega$) of Ω, and we may take the wave function to be zero on $\partial\Omega$. Now, clearly the main contribution to the probability of finding a low-level ϵ for the system will be proportional to the probability of finding a region Ω whose *lowest level* is ϵ. The probability of finding a region whose second level is ϵ will be exponentially smaller because of the exponential dependence of the probability on Ω. Further, because of this same exponential dependence, the regions whose shape is such that Ω is smallest for a given lowest level will make the main contribution. By a well-known "isoperimetric" inequality, this will mean spherical regions.[3] The lowest-level ϵ in an empty spherical volume of radius R_0 with the boundary condition that the wave function vanish on its surface is given by

$$\epsilon=\pi^2/2R_0^2 \quad \text{or} \quad R_0=(\pi^2/2\epsilon)^{1/2} \tag{1.1}$$

(units such that $m=\hbar=1$, which we use throughout this paper). The probability of such a region existing is proportional to $\exp[-\rho(4\pi/3)R_0^3]$, so that the density of low-lying levels will be given by

$$g(\epsilon)\sim\exp(-c_3/\epsilon^{3/2}) \quad (\epsilon\to 0)\,, \tag{1.2}$$

where

$$c_3=\tfrac{1}{3}4\pi(\tfrac{1}{2}\pi^2)^{3/2}\rho\,. \tag{1.3}$$

The expressions (1.2) and (1.3) constitute the Lifshitz conjecture. Although the intuitive reasoning involved is very physical and plausible, it has proven difficult to obtain this result directly from the Schrödinger equation for the problem.

The method which we shall describe in the following sections has the advantage of allowing us to introduce in a natural way an approximation scheme which corresponds closely to Lifshitz's physical idea and which yields Lifshitz's conjecture as its leading term. The method is based on a reformulation of the problem in terms of a problem in Brownian motion. This is done in Sec. II. For long times, the solution of this problem is equivalent to the knowledge of $g(\epsilon)$ for small ϵ. A variational method is then given for solving this problem, and

the solution is reduced to solving a certain nonlinear differential equation. In Sec. III, this equation is solved in the long-time limit and the leading two terms of $g(\epsilon)$ obtained from it. Finally, in Sec. IV the corrections to this variational method are estimated and shown to be smaller than the terms obtained in Sec. III.

II. FORMULATION OF THE PROBLEM

For the system described in the Introduction, the Hamiltonian is

$$H=\tfrac{1}{2}p^2+U(\{R\})\equiv H_0+U(\{R\}), \tag{2.1}$$

$$U(\{R\})=\sum_{j=1}^{N} v(\vec{r}-\vec{R}_j), \tag{2.2}$$

where the $\vec{R}_j$ are the positions of the impurities. To calculate the density of states, we consider first the "partition function" $Z_t(\{R\})$ defined by

$$Z_t(\{R\})=\mathrm{Tr}\, e^{-tH}, \tag{2.3}$$

where t is real and positive. Clearly, for a large system

$$Z_t(\{R\})=\int_0^\infty d\epsilon e^{-t\epsilon} Vg(\epsilon,(\{R\})), \tag{2.4}$$

since $Vg(\epsilon,(\{R\}))$ is the density of energy levels for the system. Now let the probability that $\vec{R}_1$ be in $d\vec{R}_1$, $\vec{R}_2$ be in $d\vec{R}_2$, etc., etc. be $d\vec{R}_1/V$, $d\vec{R}_2/V\cdots d\vec{R}_N/V$.[4] For each arrangement $Z_t(\{R\})$ will have a certain value, so that it is also a random variable with a certain probability distribution function. Now it is not difficult to show that in the thermodynamic limit, as would be expected on physical grounds, $Z_t\{R\}/V$ is certainly equal to its mean value $z(t)$ defined by

$$z(t)\equiv \lim_{\substack{V,N\to\infty\\ N/V\to\rho}} \int_V \frac{d\vec{R}_1}{V}\frac{d\vec{R}_2}{V}\cdots\frac{d\vec{R}_N}{V}\frac{Z_t(\{R\})}{V}, \tag{2.5}$$

so that there is a well-defined density of states per unit volume, $g(\epsilon)$, given by

$$\int_0^\infty g(\epsilon)e^{-\epsilon t}d\epsilon=z(t). \tag{2.6}$$

That is, to find $g(\epsilon)$ we need only find $z(t)$ and invert the Laplace transform.

To find $z(t)$ we proceed as follows. Define

$$I(t)=\frac{1}{Z_t^0}\int_V \frac{d\vec{R}_1}{V}\cdots\frac{d\vec{R}_N}{V} Z_t(\{R\}) \equiv\frac{\langle Z_t(\{R\})\rangle_{\mathrm{imp}}}{Z_t^0}, \tag{2.7}$$

where Z_t^0 is the partition function in the absence of impurities. Z_t^0 may be calculated easily and yields

$$Z_t^0=V/(2\pi t)^{3/2}, \tag{2.8}$$

$$I(t)=\frac{1}{Z_t^0}\left\langle\int_V d\vec{r}_0\langle\vec{r}_0|e^{-tH}|\vec{r}_0\rangle\right\rangle_{\mathrm{imp}} \tag{2.9}$$

in the coordinate representation. Now we interchange the impurity average and the $\vec{r}_0$ integration. Since after averaging over the positions of the impurities there is no preferred position[5] and $\langle\vec{r}_0|e^{-tH}|\vec{r}_0\rangle$ cannot depend on $\vec{r}_0$, we may write ($\vec{r}_0$ now some arbitrary point of V)

$$I(t)=\frac{1}{Z_t^0}V\langle\langle\vec{r}_0|e^{-tH}|\vec{r}_0\rangle\rangle_{\mathrm{imp}} =\frac{\langle\langle\vec{r}_0|e^{-tH}|\vec{r}_0\rangle\rangle_{\mathrm{imp}}}{\langle\langle\vec{r}_0|e^{-tH_0}|\vec{r}_0\rangle\rangle_{\mathrm{imp}}}. \tag{2.10}$$

The right-hand side of (2.10) may be written as a Wiener or path integral, according to the well-known Kac[6] formula. That is

$$I(t)=\left\langle\left\langle\exp\left(-\int_0^t U(\vec{r}_{t'})dt'\right)\middle|\vec{r}_0\right\rangle_t\right\rangle_{\mathrm{imp}} =\left\langle\left\langle\exp\left(-\int_0^t U(\vec{r}_{t'})dt'\right)\middle|\vec{r}_0\right\rangle_t\right\rangle_{\mathrm{imp}}, \tag{2.11}$$

where the inner angular bracket means the Wiener average over all paths $\vec{r}_{t'}$ beginning ($t'=0$) and ending ($t'=t$) at $\vec{r}_0$. For our purposes, we may take the definition of this average to be

$$\left\langle\exp\left(-\int_0^t U(\vec{r}_{t'})dt'\right)\middle|\vec{r}_0\right\rangle_t=\lim_{n\to\infty}\frac{\int d\vec{r}_1 d\vec{r}_2\cdots d\vec{r}_n P_{01}P_{12}\cdots P_{n0}\exp(-t\sum_{j=1}^n U(\vec{r}_j))}{\int d\vec{r}_1 d\vec{r}_2\cdots d\vec{r}_n P_{01}P_{12}\cdots P_{n0}}, \tag{2.12}$$

where

$$P_{ij}\equiv\frac{e^{-(\vec{r}_i-\vec{r}_j)^2/2\tau}}{(2\pi\tau)^{3/2}}, \tag{2.13}$$

$$\tau=t/(n+1). \tag{2.14}$$

Making use of (2.11) enables us to carry out the impurity average and thermodynamic limit rather simply,

$$\left\langle\exp\left(-\int_0^t U(\vec{r}_{t'})dt'\right)\right\rangle_{\mathrm{imp}}=\prod_{j=1}^N\int_V\exp\left(-\int_0^t v(\vec{r}_{t'}-\vec{R}_j)dt'\right)\frac{d\vec{R}_j}{V}$$

$$= \left[\frac{1}{V}\int_V d\vec{R}\exp\left(-\int_0^t v(\vec{r}_{t'}-\vec{R})dt'\right)\right]^N$$
$$= \left[1-\frac{1}{V}\int_V d\vec{R}\left(1-\exp\left(\int_0^t v(\vec{r}_{t'}-\vec{R})dt'\right)\right)\right]^N . \quad (2.15)$$

For a $v(\vec{r})$ which goes to zero sufficiently rapidly as $|\vec{r}|$ does to infinity, the integral over $\vec{R}$ converges if extended over all space. Therefore, in the thermodynamic limit we may write

$$\lim_{\substack{N,V\to\infty \\ N/V\to\rho}} \left\langle \exp\left(-\int_0^t U(\vec{r}_{t'})dt'\right)\right\rangle_{\text{imp}} = \lim_{N\to\infty}\left\{1-\frac{\rho}{N}\int d\vec{R}\left[1-\exp\left(-\int_0^t v(\vec{r}_{t'}-\vec{R})dt'\right)\right]\right\}^N$$
$$= e^{-\rho W} , \quad (2.16)$$

where W is the functional

$$W = \int d\vec{R}\left[1-\exp\left(-\int_0^t v_{\vec{R}}(\vec{r}_{t'})dt'\right)\right] ,$$
$$v_{\vec{R}}(\vec{r}) \equiv v(\vec{r}-\vec{R}) , \quad (2.17)$$

and the $\vec{R}$ integration is extended over all space.

Putting all these results together, we have

$$z(t) = \frac{1}{(2\pi t)^{3/2}}\langle e^{-\rho W}|0\rangle_t , \quad (2.18)$$

where we have chosen the origin to be the point $\vec{r}_0$. This type of formula seems first to appear in the work of Edwards and Gulyaev.[7] The difficulty in using it lies in the fact that except for some very simple functionals, path integrals are extremely difficult to evaluate. We shall not be interested, however, in a general evaluation of $z(t)$, but only in its behavior as t approaches infinity. The reason for this is that from (2.6) the behavior of $z(t)$ for large t is, loosely speaking, determined by the behavior of $g(\epsilon)$ for small ϵ. More rigorously, such results may be formulated as Tauberian theorems. For example, the following theorem[8] will be sufficient to obtain the Lifshitz conjecture.

Suppose

$$\lim_{t\to\infty}\frac{1}{t^\beta}\ln z(t) = -B , \quad 0<B<\infty , \quad 0<B<1 ,$$

then

$$\lim_{\epsilon\to 0^+}\epsilon^\alpha \ln g(\epsilon) = -A , \quad (2.19)$$

where

$$\alpha = \frac{\beta}{1-\beta} , \quad A = (1-\beta)\beta^{\beta/(1-\beta)}B^{1/(1-\beta)} .$$

Therefore, if the Lifshitz conjecture is true, we would expect to find (2.19) with

$$\beta = \tfrac{3}{5} , \quad B = \tfrac{5}{6}(4\pi^4)^{2/5}\rho^{2/5} . \quad (2.20)$$

Now one of the principal advantages of the path-integral formulation as given by (2.18) is that it allows us in a rather natural way to formalize Lifshitz's argument in the Introduction. That is, the low-lying states, and therefore the large t behavior, come from electrons trapped in a potential well of large radius. Let us be a little more general and not specify the shape of the potential well for the moment but simply call it $\phi(\vec{r})$. If we only had such a well present, $z(t)$ would be, by the Kac formula, proportional to $\langle e^{-\Phi}|0\rangle_t$, where

$$\Phi = \int_0^t \phi(\vec{r}_{t'})dt' . \quad (2.21)$$

Therefore, we write

$$\langle e^{-\rho W}|0\rangle_t = \langle e^{-\Phi}|0\rangle_t \frac{\langle e^{-(\rho W-\Phi)}e^{-\Phi}|0\rangle_t}{\langle e^{-\Phi}|0\rangle_t}$$
$$\equiv \langle e^{-\Phi}|0\rangle_t \langle e^{-A}|0;\phi\rangle_t , \quad (2.22)$$

where

$$A = \rho W - \Phi . \quad (2.23)$$

The first factor in (2.22) may be thought of as giving the contribution to $z(t)$ when the electron is trapped in the potential ϕ, while the second factor represents the "probability" of finding such a potential. We shall determine the "best" ϕ by the following argument. Since the second factor is an average of the functional e^{-A}, we have, by Jensen's well-known theorem for convex functions,

$$\langle e^{-A}|0,\phi\rangle_t \geq e^{-\langle A|0,\phi\rangle_t} . \quad (2.24)$$

Therefore,

$$\langle e^{-\rho W}|0\rangle_t \geq \langle e^{-\Phi}|0\rangle_t e^{-\langle A|0,\phi\rangle_t} . \quad (2.25)$$

We choose ϕ such that the right-hand side of (2.25) is as large as possible, so that we will have the strongest possible inequality of this form. That is, we choose ϕ such that

$$\frac{\delta}{\delta\phi(\vec{r})}\langle e^{-\Phi}|0\rangle_t e^{-\langle A|0,\phi\rangle_t} = 0 , \quad (2.26)$$

where $\delta/\delta\phi(\vec{r})$ is the variational derivative of a functional of ϕ with respect to ϕ at the point $\vec{r}$.

So far all we have from this procedure is an inequality; so one may ask if any progress has been made towards an evaluation. However, (2.24) is actually the first term of the exact (assuming convergence) semi-invariant or cumulant expansion,[9]

$$\langle e^{-A}\rangle = \exp\left\{-\langle A\rangle + \frac{1}{2!}\left(\langle A^2\rangle - \langle A\rangle^2\right) - \frac{1}{3!}\left[\langle A^3\rangle - 3\langle A\rangle\left(\langle A^2\rangle - \langle A^2\rangle\right) - \langle A\rangle^3\right] + \cdots\right\}. \tag{2.27}$$

Therefore, if we can show that as $t\to\infty$ and ϕ is given from (2.26) $\langle A\rangle$ increases more rapidly with t than the other semi-invariants, then (2.25) will be an asymptotic evaluation rather than an inequality. This proves to be the case.

In order to carry out the procedure described above, we introduce some notation. Suppose we have a Hamiltonian $\tilde{H}$ given by

$$\tilde{H} = \tfrac{1}{2}p^2 + \tilde{\phi}(\vec{r}) . \tag{2.28}$$

Then in terms of the Green's function,

$$G_\tau(\vec{r}, \vec{r}' \,|\, \tilde{\phi}) \equiv \langle \vec{r}\,|e^{-\tau\tilde{H}}|\,\vec{r}'\rangle , \tag{2.29}$$

we have at once, making use of the Kac formula [(2.10) and (2.11)],

$$\langle e^{-\Phi}\,|0\rangle_t = (2\pi t)^{3/2} G_t(0, 0\,|\,\phi) , \tag{2.30}$$

$$\langle A\,|0, \phi\rangle_t = \rho\langle W\,|0, \phi\rangle_t - \langle \Phi\,|0, \phi\rangle_t , \tag{2.31}$$

$$\langle W\,|0, \phi\rangle_t = \frac{\int d\vec{R}\,\langle[1 - \exp(-\int_0^t v_{\vec{R}}(\vec{r}_{t'})dt')]\exp(-\int_0^t \phi(\vec{r}_{t'})dt')|0\rangle_t}{\langle\exp(-\int_0^t \phi(\vec{r}_{t'})dt')|0\rangle_t}$$

$$= \int d\vec{R}\,[G_t(0, 0\,|\,\phi) - G_t(0, 0\,|\,\phi + v_{\vec{R}})]/G_t(0, 0\,|\,\phi) , \tag{2.32}$$

$$\langle \Phi\,|0, \phi\rangle_t = \frac{\langle\int_0^t \phi(\vec{r}_{t'})dt' \exp(-\int_0^t \phi(\vec{r}_{t'})dt')|0\rangle_t}{\langle\exp(-\int_0^t \phi(\vec{r}_{t'})dt')|0\rangle}$$

$$= -\frac{\partial}{\partial\mu}\ln\left\langle\exp\left(-\int_0^t \mu\phi(\vec{r}_{t'})dt'\right)\middle|0\right\rangle_t\Big|_{\mu=1} = \frac{\partial \ln(2\pi t)^{3/2} G_t(0, 0\,|\,\mu\phi)}{\partial\mu}\Big|_{\mu=1}$$

$$= -\frac{\partial G_t(0, 0\,|\,\mu\phi)}{\partial\mu}\Big|_{\mu=1} \Big/ G_t(0, 0\,|\,\phi) . \tag{2.33}$$

From these formulas it is not at all difficult to work out the criterion (2.26). Since the result is quite complicated and we are really only interested in the limit for large t, we shall only give the asymptotic evaluation for large t here. To do this, we need the following well-known representation of the Green's function [which follows at once from the definition (2.29)]:

$$G_\tau(\vec{r}, \vec{r}' \,|\, \tilde{\phi}) = \sum_j e^{-\tau E_j(\tilde{\phi})}\psi_j(\vec{r}\,|\,\tilde{\phi})\psi_j(\vec{r}'\,|\,\tilde{\phi}) , \tag{2.34}$$

where the $\psi_j(\vec{r}\,|\,\tilde{\phi})$ and the $E_j(\tilde{\phi})$ are the (real) normalized eigenfunctions and eigenvalues of $\tilde{H}$, i.e.,

$$\tilde{H}\psi_j(\vec{r}\,|\,\tilde{\phi}) = E_j(\tilde{\phi})\psi_j(\vec{r}\,|\,\tilde{\phi}) . \tag{2.35}$$

Now we expect from the Lifshitz picture (and will find) that ϕ is a large potential well in which the lower states form a discrete spectrum. Therefore, for large τ we expect the ground state ψ_0, E_0 to dominate (2.34) with an error which is exponentially small; so we may write

$$G_t(0, 0\,|\,\phi) \cong \psi_0^2(0\,|\,\phi)e^{-tE_0(\phi)} , \tag{2.36}$$

$$G_t(0, 0\,|\,\phi + v_R) = \psi_0^2(0\,|\,\phi + v_R)e^{-tE_0(\phi+v_R)} , \tag{2.37}$$

and

$$\frac{\partial}{\partial\mu}G_t(0, 0\,|\,\mu\phi)\Big|_{\mu=1}$$

$$= \frac{\partial}{\partial\mu}\psi^2(0\,|\,\mu\phi)e^{-tE_0(\mu\phi)}\Big|_{\mu=1}$$

$$= -t\psi^2(0\,|\,\phi)e^{-tE_0(\phi)}\frac{\partial E_0(\mu\phi)}{\partial\mu}\Big|_{\mu=1} + 2e^{-tE_0(\phi)}\psi_0(0\,|\,\phi)\frac{\partial\psi_0(0\,|\,\mu\phi)}{\partial\mu}\Big|_{\mu=1} . \tag{2.38}$$

The derivatives in (2.38) are directly calculable using perturbation theory ($\mu = 1+\epsilon$, $\epsilon\to 0$),

$$\frac{\partial E_0(\mu\phi)}{\partial\mu}\Big|_{\mu=1} = \int d\vec{r}\,\psi_0^2(\vec{r}\,|\,\phi)\,\phi(\vec{r}) , \tag{2.39}$$

$$\frac{\partial\psi_0(0\,|\,\mu\phi)}{\partial\mu}\Big|_{\mu=1} = \sum_{j=0}\frac{(\int\psi_0(\vec{r}\,|\,\phi)\,\phi(\vec{r})\psi_j(\vec{r}\,|\,\phi)d\vec{r})\psi_j(0\,|\,\phi)}{E_0(\phi) - E_j(\phi)} . \tag{2.40}$$

The leading term of (2.38) is the first term on the right-hand side (because of the factor of t). We shall drop the second term. (After the calculation is complete, we can go back and evaluate this correction term with the ϕ we have obtained. It is then found that this correction is smaller than the terms considered in this paper, though it is not exponentially small.) Therefore, we write to the accuracy considered,

$$\frac{1}{G_t(0, 0\,|\,\phi)}\frac{\partial G_t(0, 0\,|\,\mu\phi)}{\partial\mu}\Big|_{\mu=1} = -t\int d\vec{r}\,\psi_0^2(\vec{r}\,|\,\phi)\,\phi(\vec{r}) , \tag{2.41}$$

$$\langle A\,|0,\phi\rangle_t = \rho\int d\vec{R}\left(1-\frac{\psi_0^2(0\,|\,\phi+v_R)}{\psi_0^2(0\,|\,\phi)}\right.$$
$$\left.\times\exp\{-t[E_0(\phi+v_R)-E_0(\phi)]\}\right)$$
$$-t\int d\vec{r}\,\psi_0^2(\vec{r}\,|\,\phi)\,\phi(\vec{r})\,. \qquad (2.42)$$

Again, the factor $\psi_0^2(0\,|\,\phi+v_R)/\psi_0^2(0\,|\,\phi)$ may be replaced by unity in the limit of large t, to the order which interests us. The reason is essentially that because of the factor $\exp\{-t[E_0(\phi+v_R)-E_0(\phi)]\}$, only large R (of the order of the size of the well ϕ) where the wave function is small contributes. Since $v_{\vec{R}}=v(\vec{r}-\vec{R})$ is a short-range potential, this has little influence on the wave function at the origin. Thus we may write

$$\langle e^{-\Phi}\,|0\rangle_t e^{-\langle A|0,\phi\rangle_t}$$
$$= e^{-tQ+\ln\psi_0^2(0|\phi)+\ln(2\pi t)^{3/2}}, \qquad (2.43)$$

where

$$Q\equiv E_0(\phi)-\int\psi_0^2(\vec{r}\,|\,\phi)\,\phi(\vec{r})\,d\vec{r}$$
$$+\frac{\rho}{T}\int d\vec{R}(1-\exp\{-t[E_0(\phi+v_{\vec{R}})-E_0(\phi)]\})$$
$$=\int\psi_0(\vec{r}\,|\,\phi)\,\tfrac{1}{2}p^2\psi_0(\vec{r}\,|\,\phi)\,d\vec{r}$$
$$+\frac{\rho}{T}\int d\vec{R}(1-\exp\{-t[E_0(\phi+v_{\vec{R}})-E_0(\phi)]\})\,. \qquad (2.44)$$

We may neglect the term $\ln\psi_0^2(0\,|\,\phi)$ in the exponent since it is found from the same type of self-consistency argument as we have been using to be of order $\ln t$, which again is negligible compared to the terms we are retaining. Finally then, we may write

$$\ln\langle e^{-\Phi}\,|0\rangle_t e^{-\langle A|0,\phi\rangle_t}\cong -tQ\,. \qquad (2.44')$$

The stationarity condition (2.26) becomes

$$\delta Q/\delta\phi(\vec{r})=0\,. \qquad (2.45)$$

To proceed further in a simple manner, we must make some assumption about the potential $v_{\vec{R}}$, so as to be able to evaluate the energy shift in (2.44). The simplest assumption (which we shall make) is that the range of $v(\vec{r})$ is extremely short, shorter than any other length in the problem. This enables us to use the Fermi method of pseudopotentials.[10] A straightforward application of this method (see Appendix A) gives the following result: to calculate $E_0(\phi+v_{\vec{R}})-E_0(\phi)$, we may replace $v(\vec{r}-\vec{R})$ by $2\pi a\delta(\vec{r}-\vec{R})$ [where a is the scattering length for the potential $v(\vec{r})$] and use first-order perturbation theory. That is,

$$E_0(\phi+v_{\vec{R}})-E_0(\phi)=2\pi a\psi_0^2(\vec{R}\,|\,\phi)\,, \qquad (2.46)$$

so that

$$Q=\int\psi\frac{p^2}{2}\psi\,d\vec{r}+\frac{\rho}{t}\int d\vec{r}\,\{1-\exp[-2\pi at\psi^2(\vec{r})]\}\,. \qquad (2.47)$$

[We now use the simplified notation $\psi_0(\vec{r}\,|\,\phi)=\psi(\vec{r})$, $E_0(\phi)=E$.]

Since Q is a functional of ψ alone and ψ is normalized, the condition (2.45) is equivalent to

$$\frac{\delta}{\delta\psi(\vec{r})}\left(Q-\lambda\int\psi^2(\vec{r})\,d\vec{r}\right)=0\,, \qquad (2.48)$$

where λ is the Lagrange multiplier for the normalization constraint. This gives at once

$$\tfrac{1}{2}p^2\psi(\vec{r})+2\pi a\rho\,e^{-2\pi at\psi^2(\vec{r})}\psi(\vec{r})=\lambda\psi(\vec{r})\,, \qquad (2.49)$$

$$\int\psi^2(\vec{r})\,d\vec{r}=1\,. \qquad (2.50)$$

Comparing (2.49) with (2.35) when $\tilde{\phi}^2=\phi$ and $j=0$, we have[11]

$$\lambda=E\,, \qquad (2.51)$$

$$\phi(\vec{r})=2\pi a\rho\,e^{-2\pi at\psi^2(\vec{r})}\,. \qquad (2.52)$$

Informally, we may regard (2.52), together with the Schrödinger equation,

$$\tfrac{1}{2}p^2\psi(\vec{r})+\phi(\vec{r})\psi(\vec{r})=E\psi(\vec{r})\,, \qquad (2.53)$$

as a pair of relations by which the electron and the impurities influence each other in a "self-consistent" approximation. If the impurities were distributed uniformly, we might approximate their effect on the electron by a smoothed-out potential $2\pi a\rho$. But if the electronic state is chosen first, the impurity density ρ is multiplied by a Boltzmann factor $\exp[-2\pi at\psi^2(\vec{r})]$, leading to (2.52). Putting (2.52) and (2.53) together, we get (2.49) which describes the electron moving in the well from which impurities have been excluded by their interaction with that same electron.

It remains only to solve (2.49) and (2.50) in the limit of large t, which will be done in Sec. III.

III. SOLUTION OF THE SELF-CONSISTENT EQUATION IN THE LARGE-t LIMIT

In solving (2.49) and (2.50), we first remark that the solution ψ which minimizes Q may be taken to be spherically symmetric about some arbitrary point (which we choose as origin). In (2.47) we may use the well-known decomposition

$$p^2=p_r^2+L^2/r^2\,, \qquad (3.1)$$

where

$$p_r=\frac{1}{i}\left(\frac{\partial}{\partial r}+\frac{1}{r}\right), \qquad (3.2)$$

and L^2 is the square of the orbital-angular-momentum operator with respect to the origin. Clearly, because of the positivity of L^2/r^2, we have

$$Q \geq (\psi, p_r^2/r\psi) + \frac{\rho}{t}\int d\vec{r}(1 - e^{-2\pi a t \psi^2(r)}) \equiv Q_r \ . \quad (3.3)$$

Now the equation for minimizing Q_r is the same as (2.49) with p^2 replaced by p_r^2. It involves only differential operators with respect to r. As we shall see below, we obtain a unique solution to this equation which is therefore a function of r alone. Clearly, from (3.3) the minimum of Q is greater than or equal to the minimum of Q_r, but by taking ψ in (2.49) to be a function of r only, we attain the same value for Q as for $(Q_r)_{\min}$, and this is therefore the best we can do. Putting $\psi = \chi(r)/r$, we obtain

$$-\tfrac{1}{2}\chi''(r) + 2\pi a\rho \exp[-2\pi a t \chi^2(r)/r^2]\chi(r) = E\chi(r) \ , \quad (3.4)$$

$$4\pi\int_0^\infty dr\, \chi^2(r) = 1 \ , \quad (3.5)$$

with

$$\chi(0) = 0 \ . \quad (3.6)$$

To get an idea of what is involved in the solution of these equations, let us first take a "trial" wave function $\tilde{\chi}$ corresponding to the crudest Lifshitz picture. That is, take $\tilde{\chi}$ to correspond to a potential well which is zero until $r = b$ and then infinite. The b is then determined by the condition that the resultant $\tilde{Q}$ be minimized. The normalized wave function for such a well is

$$\tilde{\chi} = \sin\left(\frac{\pi}{b}r\right)\Big/\sqrt{2\pi b} \ , \quad (3.7)$$

and

$$\tilde{Q} = \frac{\pi^2}{2b^2} + \frac{4\pi\rho}{t}\int_0^b dr\, r^2\left[1 - \exp\left(-\frac{at\sin^2(\pi r/b)}{br^2}\right)\right] \quad (3.8)$$

$$= \frac{\pi^2}{2b^2} + \frac{4\pi\rho}{3t}b^3 + \tilde{Q}' \ , \quad (3.9)$$

where

$$\tilde{Q}' \equiv -\frac{4\pi\rho}{t}\int_0^b dr\, r^2 \exp\left(-\frac{at\sin^2(\pi r/b)}{br^2}\right) \ . \quad (3.10)$$

First, assume $\tilde{Q}'$ to be negligible (for large t). Then the best value of b (say b_0) is determined by

$$\frac{\partial}{\partial b}\left(\frac{\pi^2}{2b^2} + \frac{4\pi\rho}{3t}b^3\right) = 0 \ ,$$

or

$$b_0^5 = \pi t/4\rho \ . \quad (3.11)$$

The leading term of $\tilde{Q}(\tilde{Q}_0)$ is then given by

$$\tilde{Q}_0 = \frac{5}{3}\frac{\pi^2}{2b_0^2} = \tfrac{5}{6}(4\pi^4)^{2/5}\rho^{2/5}t^{-2/5} \ , \quad (3.12)$$

which is already accurante enough to give the Lifshitz conjecture [compare (2.20), remembering the exponent is tQ].

To verify that $\tilde{Q}'$ is negligible compared to the term we have calculated, we compute it as follows. Put $r = b_0(1-\xi)$, and replace t by (3.11) in the exponent,

$$\tilde{Q}' = -\frac{4\pi\rho b_0^3}{t}\int_0^1 d\xi(1-\xi)^2 \exp\left(-4\pi\rho a b_0^2 \frac{\sin^2\pi\xi}{(1-\xi)^2\pi^2}\right) \ . \quad (3.13)$$

Since $b_0 \to \infty$ as $t \to \infty$. the integral can easily be calculated by saddle-point methods, the main contribution coming from the neighborhood of $\xi = 0$. This yields

$$\tilde{Q}' = -\tilde{Q}_0 \tfrac{1}{5} 3\sqrt{\pi}\,\lambda_0/b_0 \ , \quad (3.14)$$

where λ_0 is the "skin depth" defined by

$$\lambda_0 \equiv (1/4\pi a\rho)^{1/2} \ . \quad (3.15)$$

This result suggests the following method of integrating (3.4) for large t: The potential term of (3.4) will be negligible till the exponent $2\pi a t\chi^2(r)/r^2$ is of order unity. Using the approximate trial function $\tilde{\chi}$ in ϕ as a first step in an iterative procedure, we see that this does not happen until $r - b_0$ is of order λ_0. Further, since $\tilde{\chi}$ equals zero for $r > b_0$, the potential quickly approaches $2\pi a\rho$. In this potential, the wave function will have an exponential decrease $e^{-(r-b_0)/\lambda_0}$. Therefore, we divide r into two ranges I and II. In I, $0 \leq r \leq b - \eta_0$, where $b \gg \eta_0 \gg \lambda_0$. In II $b - \eta_0 \leq r \leq \infty$. The exact value of the quantity b is somewhat arbitrary (as long as it is within about λ_0 of b_0). A very convenient choice proves to be such that the energy E is given by

$$E = \tfrac{1}{2}k^2 \ , \qquad k = \pi/b \ . \quad (3.16)$$

In region I, the wave function (χ_1) may be taken (with exponentially small error in t) to be that of a free particle,

$$\chi_1(r) = A\sin kr \ . \quad (3.17)$$

In region II, we must still satisfy (3.4). However, since the only region of r where the exponent can be of order unity is a little region of width $\sim\lambda_0$ about $r = b$, the leading term for the wave function (χ_2) in II satisfies

$$-\tfrac{1}{2}\chi_2'' + 2\pi a\rho \exp\left(-2\pi a t\frac{\chi_2^2}{b^2}\right)\chi_2 = \tfrac{1}{2}k^2\chi_2 \ . \quad (3.18)$$

Putting

$$r = b + \eta \quad (3.19)$$

and

$$\chi_2 = bg(\eta)/\sqrt{2\pi a t} \ , \quad (3.20)$$

Eq. (3.18) becomes

$$\frac{d^2g}{d\eta^2} + \frac{1}{\lambda_0^2}e^{-g^2}g = \left(\frac{\pi^2}{b^2}\right)g \ . \quad (3.21)$$

Since b will turn out to be approximately b_0, we can drop the right-hand side which yields a correction one order smaller than those considered here, and obtain for the leading contribution to g the equation

$$\frac{d^2g}{d\eta^2}+\frac{1}{\lambda_0^2}e^{-g^2}g=0\ . \tag{3.22}$$

Multiplying (3.22) by $2g'$ and integrating from η to ∞, we have at once

$$\left(\frac{dg}{d\eta}\right)^2=\left(\frac{1}{\lambda_0^2}\right)(1-e^{-g^2})\ . \tag{3.23}$$

Continuity of χ and χ' at $r=b-\eta_0$ gives

$$\frac{b}{\sqrt{2\pi at}}\,g(-\eta_0)=A\sin\frac{\pi}{b}(b-\eta_0)$$

$$=A\sin\left(\frac{\pi}{b}\eta_0\right)\cong A\frac{\pi}{b}\eta_0\ ,$$

$$\frac{b}{\sqrt{2\pi at}}\,g'(-\eta_0)=A\frac{\pi}{b}\cos\frac{\pi}{b}(b-\eta_0)$$

$$=-A\frac{\pi}{b}\cos\frac{\pi}{b}\eta_0\cong -A\frac{\pi}{b}\ ,$$

or

$$g(-\eta_0)=\frac{A\pi\sqrt{2\pi at}}{b^2}\eta_0\gg 1\ , \tag{3.24}$$

$$g'(-\eta_0)=-\frac{A\pi\sqrt{2\pi at}}{b^2}\ . \tag{3.25}$$

The normalization condition (3.5) becomes

$$1=4\pi\int_0^\infty dr\,\chi^2=4\pi\int_0^{b-\eta_0}dr\,\chi_1^2+4\pi\int_{b-\eta_0}^\infty dr\,\chi_2^2\equiv N_1+N_2\ , \tag{3.26}$$

$$N_1=4\pi\frac{A^2}{2}\left[b-\eta_0+\frac{\sin 2k\eta_0}{2k}\right]\cong 2\pi A^2(b-\tfrac{2}{3}k^2\eta_0^3), \tag{3.27}$$

$$N_2=4\pi\frac{b^2}{2\pi at}\int_{-\eta_0}^\infty d\eta\,g^2(\eta)$$

$$=4\pi\frac{b^2}{2\pi at}\int_0^{g(-\eta_0)}dg\,\frac{g^2}{|dg/d\eta|}$$

$$\cong\frac{2b^2\lambda_0}{at}\int_0^{g(-\eta_0)}dg\,\frac{g^2}{(1-e^{-g^2})^{1/2}}\ . \tag{3.28}$$

Since $g(-\eta_0)\gg 1$, the leading term of (3.28) is

$$N_2\cong\frac{2b^2\lambda_0}{at}\,\frac{g^3(-\eta_0)}{3}\sim O(\eta_0^3/b^3)\ . \tag{3.29}$$

Thus, neglecting corrections of order smaller than λ_0/b, we have

$$1=2\pi A^2 b\quad\text{or}\quad A=\frac{1}{\sqrt{2\pi b}}\ . \tag{3.30}$$

[Actually the η_0^3 term in (3.27) cancels N_2 to leading order, as it must since the result has to be independent of η_0.]

Using (3.23), (3.24), and (3.30), (3.25) becomes

$$-\frac{1}{\lambda_0}=-\frac{A\pi\sqrt{2\pi at}}{b^2}=-\frac{\pi\sqrt{at}}{b^2\sqrt{b}}$$

or, by (3.15),

$$b^5=\frac{\pi t}{4\rho}=b_0^5\ ,$$

which is our previous result. To obtain the first correction to b by this method, we would have to carry the expansion of r around b (in the equation for g) one step further. This is not necessary, however, as is seen from the method which follows. Now let us compute Q,[12]

$$Q=K+D\ , \tag{3.31}$$

$$K\equiv 4\pi\left(\frac{1}{2}\int_0^{b-\eta_0}\chi_1^2\,dr+\frac{1}{2}\int_{b-\eta_0}^\infty\chi_2^2\,dr\right)\equiv K_1+K_2\ , \tag{3.32}$$

$$D=\frac{4\pi\rho}{t}\left(\int_0^{b-\eta_0}dr\,r^2(1-e^{-2\pi at\chi_1^2/r^2})+\int_{b-\eta_0}^\infty dr\,r^2(1-e^{-2\pi at\chi_2^2/r^2})\right)=D_1+D_2\ , \tag{3.33}$$

$$K_1=2\pi\int_0^{b-\eta_0}dr\,A^2k^2\cos^2kr=\pi k^2A^2\left(b-\eta_0-\frac{\sin 2k\eta_0}{2k}\right)=\frac{\pi^2}{2b^3}\left(b-2\eta_0+O(\eta_0^3)\right)\ . \tag{3.34}$$

$$K_2=2\pi\frac{b^2}{2\pi at}\int_0^{g(-\eta_0)}dg\,[g'(\eta)]=\frac{b^2}{at\lambda_0}\int_0^{g(-\eta_0)}dg\,(1-e^{-g^2})^{1/2}$$

$$=\frac{b^2}{at\lambda_0}\left(g(-\eta_0)-\int_0^{g(-\eta_0)}dg[1-(1-e^{-g^2})^{1/2}]\right)=\frac{b^2}{at\lambda_0}\,g(-\eta_0)-\frac{b^2c}{at\lambda_0}\ , \tag{3.35}$$

where

$$C\equiv\int_0^\infty dg[1-(1-e^{-g^2})^{1/2}]\cong 0.628\ , \tag{3.36}$$

[The limit may be extended to ∞, since $g(-\eta_0)\gg 1$ and the integral converges exponentially.] Using (3.24) and $b\cong b_0$, we see that the terms linear in η_0 in K cancel (as they must), and

$$K=\frac{1}{2}\frac{\pi^2}{b^2}-\frac{b^2c}{at\lambda_0}\ . \tag{3.37}$$

Similarly, with an exponentially small error,

$$D_1=\frac{4\pi\rho}{t}\int_0^{b-\eta_0}dr\,r^2=\frac{4\pi\rho(b-\eta_0)^3}{3t}\cong\frac{4\pi\rho(b^3-3b^2\eta_0)}{3t}\ , \tag{3.38}$$

and

$$\begin{aligned}D_2&\cong\frac{4\pi\rho}{t}\int_{-\eta_0}^{\infty}d\eta\,b^2(1-e^{-g^2})=\frac{4\pi\rho b^2}{t}\int_0^{g(-\eta_0)}\frac{dg}{|dg/d\eta|\,(1-e^{-g^2})}\\&=\frac{4\pi\rho\lambda_0 b^2}{t}\int_0^{g(-\eta_0)}dg(1-e^{-g^2})^{1/2}=\frac{4\pi\rho\lambda_0 b^2}{t}\,[g(-\eta_0)-c]\ .\end{aligned} \tag{3.39}$$

Again, the η_0 term in (3.38) cancels with the $g(-\eta_0)$ term in (3.39); so we obtain

$$D=\frac{4\pi\rho b^3}{3t}-\frac{4\pi\rho\lambda_0 b^2c}{t}=\frac{4\pi\rho b^3}{3t}-\frac{b^2c}{at\lambda_0}\ , \tag{3.40}$$

and

$$Q=\frac{1}{2}\frac{\pi^2}{b^2}+\frac{4\pi\rho b^3}{3t}-\frac{2b^2c}{at\lambda_0}\ . \tag{3.41}$$

Apart from the last terms (which are small corrections), (3.41) and (3.9) are the same, and therefore, $b=b_0$ plus a small correction, as we expected. If we write $b=b_0+b_1$, then b_1 does not actually contribute to (3.41) to the first order since the first two terms have their minimum value at $b=b_0$ and the last term is small. That is,

$$\begin{aligned}Q&=\frac{1}{2}\frac{\pi^2}{b_0^2}+\frac{4\pi\rho b_0^3}{3t}-\frac{2b_0^2c}{at\lambda_0}\ ,\\&=\frac{5}{3}\frac{\pi^2}{2b_0^2}\left(1-\frac{12c}{5}\frac{\lambda_0}{b_0}\right)\ .\end{aligned} \tag{3.42}$$

Although it is not necessary for our calculation, b may be obtained by finding the minimum of (3.41). This yields

$$b=b_0+\frac{4c}{5}\lambda_0\ , \tag{3.43}$$

which can also be obtained by a more careful integration of the equation for g, retaining first corrections to the approximation $r=b$.

Comparing (3.42) with (3.12) and (3.14), we see that the leading terms agree. All the more correct solution does is to replace the numerical coefficient $3\sqrt{\pi}/5=1.06$ of the correction term λ_0/b, by $12c/5=1.51$, which lowers Q as it must. Therefore to the order we are working, we find for large t,

$$z(t)\geq\exp-(d_3t^{3/5}+d_3't^{2/5}+\cdots)\ , \tag{3.44}$$

$$d_3\equiv\tfrac{5}{6}(4\pi^4)^{2/5}\rho^{2/5}\ , \tag{3.45}$$

$$d_3'=-2(\pi/4\rho)^{2/5}c\,1/a\lambda_0\ . \tag{3.46}$$

Assuming, as we shall show in Sec. IV, that the inequality may be replaced by an equality to the order in question, we can calculate the corresponding density of states per unit volume from (2.6) by inverting the Laplace transform and doing a straightforward saddle-point calculation. The result may be written (as ϵ approaches zero)

$$\ln g(\epsilon)=-(c_3/\epsilon^{3/2}+c_3'/\epsilon+\cdots)\ , \tag{3.47}$$

where

$$c_3=\tfrac{1}{3}4\pi\,\tfrac{1}{2}\pi^2\rho\ , \tag{3.48}$$

$$c_3'=-\pi^2c/a\lambda_0\ . \tag{3.49}$$

The first term of (3.47) is exactly Lifshitz's conjecture, and the second term is the first correction to it.

IV. ESTIMATE OF CONTRIBUTION OF HIGHER-ORDER SEMI-INVARIANTS

We have dropped the higher semi-invariant terms from (2.27), fixing the potential ϕ by the condition that this approximation be as close as possible to the correct $z(t)$. We shall now show that with this choice of ϕ, all the higher semi-invariants are of smaller order than $t^{2/5}$ [compare (3.44)], which suggests that for large t the inequality in (3.44) may be replaced by an equality.

To calculate the higher-order semi-invariants, we proceed in the following way. What is needed is [see (2.27)]

$$e^{-F}=\langle e^{-A}|0,\phi\rangle_t=\frac{\langle e^{-\rho W+\Phi}e^{-\Phi}|0\rangle_t}{\langle e^{-\Phi}|0\rangle_t}\ . \tag{4.1}$$

We introduce the function $F(x)$ defined by

$$e^{-F(x)}=\langle e^{-xA}|0,\phi\rangle_t=\frac{\langle e^{-x\rho W}e^{-(1-x)\Phi}|0\rangle_t}{\langle e^{-\Phi}|0\rangle_t}\ , \tag{4.2}$$

so that

$$F=F(1)=\sum_1^{\infty}(-)^{n-1}F_n/n!\ , \tag{4.3}$$

where

$$F_n=(-)^{n-1}\frac{d^nF(x)}{dx^n}\bigg|_{x=1}\ . \tag{4.4}$$

It is easily seen that the F_n are precisely the desired semi-invariants. For if A is replaced by xA in (2.27), we obtain, using (4.2),

$$F(x)=x\langle A\rangle-(x^2/2!)(\langle A^2\rangle-\langle A\rangle^2)+\cdots . \quad (4.5)$$

To evaluate the F_n, we treat separately the two appearances of x in (4.2), as coefficient of W and of Φ. Thus we define $S(\mu,\alpha)$ by

$$e^{-S(\mu,\alpha)}=\langle e^{-\alpha W}e^{-\mu\Phi}|0\rangle_t/\langle e^{-\Phi}|0\rangle_t , \quad (4.6)$$

and expand S in powers of α for fixed μ,

$$S(\mu,\alpha)=\sum_0^\infty (-)^{n-1}S_n(\mu)\alpha^n/n! . \quad (4.7)$$

Clearly, if we take $\mu=1-x$, $\alpha=\rho x$, we have

$$F(x)=S(1-x,\rho x) ,$$

$$F'(x)=\left(\rho\frac{\partial}{\partial\alpha}-\frac{\partial}{\partial\mu}\right)S(\mu,\alpha) ,$$

$$\frac{d^nF(x)}{dx^n}=\left(\rho\frac{\partial}{\partial\alpha}-\frac{\partial}{\partial\mu}\right)^n S(\mu,\alpha)$$

and

$$F_n=(-)^{n-1}\left.\frac{\partial^nF(x)}{\partial x^n}\right|_{x=1}$$

$$=(-)^{n-1}\left(\rho\frac{\partial}{\partial\alpha}-\frac{\partial}{\partial\mu}\right)^n S(\mu,\alpha)\Big|_{\mu=1,\alpha=0} .$$

Then it follows immediately that

$$F_1=\left(\rho S_1+\frac{\partial}{\partial\mu}S_0\right)_{\mu=1} ,$$

$$F_2=\left(\rho^2S_2+2\rho\frac{\partial}{\partial\mu}S_1+\frac{\partial^2}{\partial\mu^2}S_0\right)_{\mu=1} ,$$

$$\cdots$$

$$F_n=\sum_0^\infty\binom{n}{l}\rho^l\left[\left(\frac{\partial}{\partial\mu}\right)^{n-l}S_l\right]_{\mu=1} . \quad (4.8)$$

Our next step is to express the S_l in terms of Green's functions. From (4.6), we obtain

$$S(\mu,\rho)=-\ln\frac{\langle e^{-\mu\Phi}|0\rangle_t}{\langle e^{-\Phi}|0\rangle_t}-\ln\langle e^{-\rho W}|0,\mu\phi\rangle_t . \quad (4.9)$$

The expansion of the second term in powers of ρ is formally identical to (4.5), so that on comparison with (4.7) we have

$$S_0=+\ln\langle e^{-\mu\Phi}|0\rangle_t/\langle e^{-\Phi}|0\rangle_t ,$$

$$S_1=\langle W|0,\mu\phi\rangle_t , \quad (4.10)$$

$$S_2=\langle W^2|0,\mu\phi\rangle_t-\langle W|0,\mu\phi\rangle^2 , \text{ etc.}$$

From (2.27), (4.3), and (4.7) we have

$$S_0=\ln G(\mu)/G(1) ,$$

$$S_1(\mu)=\langle W|0,\mu\phi\rangle_t\int d\vec{R}\left(1-\frac{G(\mu\phi+v_{\vec{R}})}{G(\mu\phi)}\right) ,$$

$$S_2(\mu)=\langle W^2|0,\mu\phi\rangle_t-\langle W|0,\mu\phi\rangle_t^2=\int d\vec{R}d\vec{R}'\left(\frac{G(\mu\phi+v_{\vec{R}}+v_{\vec{R}'})}{G(\mu\phi)}-\frac{G(\mu\phi+v_{\vec{R}})G(\mu\phi+v_{\vec{R}'})}{G^2(\mu\phi)}\right) ,$$

$$S_3(\mu)=\int d\vec{R}\,d\vec{R}'\,d\vec{R}''\left\{-\frac{G(\mu\phi+v_{\vec{R}}+v_{\vec{R}'}+v_{\vec{R}''})}{G(\mu\phi)}\right.$$

$$+\left[\left(\frac{G(\mu\phi+v_{\vec{R}}+v_{\vec{R}'})}{G(\mu\phi)}-\frac{G(\mu\phi+v_{\vec{R}})G(\mu\phi+v_{\vec{R}'})}{G^2(\mu\phi)}\right)\frac{G(\mu\phi+v_{\vec{R}''})}{G(\mu\phi)}+\text{cyclic}\right]$$

$$\left.+\frac{G(\mu\phi+v_{\vec{R}})G(\mu\phi+v_{\vec{R}'})G(\mu\phi+v_{\vec{R}''})}{G^3(\mu\phi)}\right\} , \text{ etc.} \quad (4.11)$$

Here

$$G(U)\equiv G_t(0,0|U) . \quad (4.12)$$

Evaluating these expressions for large t by (2.36), and remembering (that to the order of interest here) we can replace expressions like

$$\frac{\psi_0^2(0|\mu\phi+v_{\vec{R}})}{\psi_0^2(0|\mu\phi)} , \quad \frac{\psi_0^2(0|\mu\phi+v_{\vec{R}}+v_{\vec{R}'})}{\psi_0^2(0|\mu\phi)} , \text{ etc.,}$$

by unity, we find

$$S_0(\mu)=-t[E_0(\mu\phi)-E_0(\phi)] ,$$

$$S_1(\mu)=\int d\vec{R}(1-e^{-t\Delta_\mu(\vec{R})}),$$

$$S_2(\mu)=\int d\vec{R}_1\,d\vec{R}_2\,e^{-t[\Delta_\mu(\vec{R}_1)+\Delta_\mu(\vec{R}_2)]}D_{12}(\mu) ,$$

$$S_3(\mu)=\int d\vec{R}_1\,d\vec{R}_2\,d\vec{R}_3\,e^{-t[\Delta_\mu(\vec{R}_1)+\Delta_\mu(\vec{R}_2)+\Delta_\mu(\vec{R}_3)]}D_{123}(\mu) , \quad (4.13)$$

etc., where

$$D_{12}=e^{-t\Delta_\mu(\vec{R}_1,\vec{R}_2)}-1 , \quad (4.14)$$

$$D_{123}=-e^{-t\Delta_\mu(\vec{R}_1,\vec{R}_2,\vec{R}_3)}+(e^{-t\Delta_\mu(\vec{R}_1,\vec{R}_2)}+\text{cyclic})-2 , \quad (4.15)$$

etc., and the Δ_μ's are given by

$$\Delta_\mu(\vec{R})=E_0(\mu\phi+v_{\vec{R}})-E_0(\mu\phi) , \quad (4.16)$$

$$\Delta_\mu(\vec{R},\vec{R}') = E_0(\mu\phi + v_{\vec{R}} + v_{\vec{R}'}) - E_0(\mu\phi) - \Delta_\mu(\vec{R}) - \Delta_\mu(\vec{R}') , \tag{4.17}$$

$$\Delta_\mu(\vec{R},\vec{R}',\vec{R}'') = E_0(\mu\phi + v_{\vec{R}} + v_{\vec{R}'} + v_{\vec{R}''}) - E_0(\mu\phi) - [\Delta_\mu(\vec{R},\vec{R}') + \Delta_\mu(\vec{R}',\vec{R}'') + \Delta_\mu(\vec{R}'',\vec{R}')] - [\Delta_\mu(\vec{R}) + \Delta_\mu(\vec{R}') + \Delta_\mu(\vec{R}'')] , \tag{4.18}$$

$$\cdots \Delta_\mu(\vec{R},\vec{R}',\cdots,\vec{R}^{(n)}) = E_0(\mu\phi + v_{\vec{R}} + v_{\vec{R}^{(n)}}) - E_0(\mu\phi) - (\text{all lower-order } \Delta_\mu\text{'s}) . \tag{4.19}$$

Now the D's in the integrands of (4.13) can be expanded in products of Δ_μ's. For the exponential factor, $e^{-t\Delta_\mu(\vec{R}_i)}$ is practically zero unless $|\vec{R}_i| \gtrsim b_0 - \lambda_0$; that is because dropping even a single impurity into the *interior* of the well will raise E_0 drastically. So the integrals in (4.13) can just as well be restricted to the region where all the $|\vec{R}_i| \gtrsim b_0 - \lambda_0$. But if any $|\vec{R}_i| \gtrsim b_0 + \lambda_0$, all the Δ_μ's connected with it will vanish since the wave function is already excluded from that region. Therefore we need only evaluate the Δ_μ's in (4.14), (4.15), etc., for positions $\vec{R}_1$, $\vec{R}_2$, ..., on the "skin" of the well, $|\vec{R}| \approx b_0 \pm \lambda_0$. This problem is treated in Appendix B, with the result that

$$t\Delta_\mu^{12} \sim O(a\lambda_0/b_0^2) , \quad t\Delta_\mu^{123} \sim O((a\lambda_0/b_0^2)^2) , \text{ etc.,} \tag{4.20}$$

where

$$\Delta_\mu^{12\cdots n} \equiv \Delta_\mu(\vec{R}_1, \vec{R}_2, \cdots \vec{R}_n) . \tag{4.21}$$

Since $a\lambda_0/b_0^2 \ll 1$, we may keep only its lowest power in (4.14), (4.15), etc. Thus we have

$$D_{12} \cong -t\Delta_\mu^{12} , \tag{4.22}$$

$$D_{123} \cong -t\Delta_\mu^{123} + t^2(\Delta_\mu^{12}\Delta_\mu^{23} + \text{cyclic}) , \text{ etc.} \tag{4.23}$$

We are now in a position to estimate the magnitude of F_2, F_3, etc. From the foregoing arguments, it follows that the m-fold integrals in (4.13) for $m \geq 2$ really cover only a volume of $O(\lambda_0 b_0^2)$, and that the integrand in S_m is $O((a\lambda_0/b_0^2)^{m-1})$, so that S_m itself is comparable to $\lambda_0 b_0^2 (a\lambda_0^2)^{m-1}$ or to $\lambda_0 b_0^2/\rho^{m-1}$. Differentiation by μ does not change this estimate, and hence, $\rho^m S_m$ contributes a quantity $O(\rho\lambda_0 b_0^2)$ to *each* F_n with $n \geq m$. The same reasoning applies to the second term of S_1 in (4.13) and to all derivatives of S_0. The first term of ρS_1 is obviously larger, approximately $\frac{4}{3}\pi\rho b_0^3$, but it is μ independent and therefore contributes only to F_1 [cf. the second term of (3.9)].

It follows that the F_n ($n \geq 2$) all contain leading terms comparable to $\rho\lambda_0 b_0^2$, which is just the order of the correction we have obtained to the Lifshitz conjecture. But if these terms are calculated in the pseudopotential approximation, we find that they cancel among themselves for each n. We shall exhibit this cancellation for $n = 2$ and $n = 3$ and leave the proof for general $n \geq 2$ to an appendix.

In the pseudopotential approximation, it is quite straightforward to work out the Δ_μ's (see Appendix A). The result may be stated very simply: The leading term is just what one would get from the first nonvanishing contribution of perturbation [the $v_{\vec{R}}$'s in (4.19) being treated by perturbation theory], with $v_{\vec{R}}$ then replaced by $2\pi a\delta(\vec{r} - \vec{R})$. That is

$$\Delta_\mu^1 \Rightarrow \int \frac{\delta E_0(\mu\phi)}{\delta[\mu\phi(\vec{r}_1)]} v(\vec{r}_1 - \vec{R}_1) d\vec{r}_1 = (2\pi a) K_\mu^1 , \tag{4.24}$$

$$\Delta_\mu^{12} \Rightarrow \int \frac{\delta^2 E_0(\mu\phi)}{\delta[\mu\phi(\vec{r}_1)]\,\delta[\mu\phi(\vec{r}_2)]} \times v(\vec{r}_1 - \vec{R}_1) v(\vec{r}_2 - \vec{R}_2) d\vec{r}_1 d\vec{r}_2 = (2\pi a)^2 K_\mu^{12} , \tag{4.25}$$

$$\Delta_\mu^{12\cdots n} = (2\pi a)^n K_\mu^{12\cdots n} , \tag{4.26}$$

where

$$K_\mu^{12\cdots n} = \frac{\delta^n E_0(\mu\phi)}{\delta[\mu\phi(\vec{R}_1)]\,\delta[\mu\phi(\vec{R}_2)]\cdots\delta[\mu\phi(\vec{R}_n)]} . \tag{4.27}$$

To calculate the derivatives of the S_n's (which are needed to calculate the F_n's), we use (4.26) and (4.27), obtaining

$$\begin{aligned} \frac{\partial^l \Delta_\mu^{12\cdots n}}{\partial\mu^l} &= (2\pi a)^n \frac{\partial^l}{\partial\mu^l} K_\mu^{12\cdots n} \\ &= (2\pi a)^n \int d\vec{R}_{n+1}\cdots d\vec{R}_{n+l} \\ &\quad \times \frac{\delta^l K^{12\cdots n}}{\delta[\mu\phi(\vec{R}_{n+1})]\cdots\delta[\mu\phi(R_{l+n})]} \\ &\quad \times \phi(\vec{R}_{1+n})\cdots\phi(R_{l+n}) \\ &= \rho^l (2\pi a)^{n+l} \int d\vec{R}_{n+1}\cdots d\vec{R}_{n+l} K_\mu^{12\cdots n\cdots n+l} \\ &\quad \times e^{-2\pi a t(K_\mu^{1+n} + \cdots + K_\mu^{l+n})} . \end{aligned} \tag{4.28}$$

In the last line of (4.28), we have substituted for the ϕ's from (2.52), thus using the fact that ϕ has been chosen to minimize F_1. Note that K_μ^i, with a single superscript, is just $\psi_0^2(\vec{R}_i)$ on account of (4.27).

Now consider F_2. Using the formulas we have just developed, we find

$$S_2 = 2\pi a\gamma \int d\vec{R}_1 d\vec{R}_2 A_{12} K^{12} , \tag{4.29}$$

$$\frac{\partial S_1}{\partial\mu} = -2\pi a\gamma\rho \int d\vec{R}_1 d\vec{R}_2 A_{12} K^{12} , \tag{4.30}$$

$$\frac{\partial^2 S_0}{\partial\mu^2} = 2\pi a\gamma\rho^2 \int d\vec{R}_1 d\vec{R}_2 A_{12} K^{12} , \tag{4.31}$$

where

$$\gamma = -2\pi a t \,, \tag{4.32}$$

$$A_{12\cdots n} = e^{\gamma(K^1+K^2+\cdots+K^n)} \,. \tag{4.33}$$

Using (4.8) we see at once that $F_2 = 0$.

Again, direct calculation gives

$$S_3 = -(2\pi a)^2\gamma \int d\vec{\mathrm{R}}_1 d\vec{\mathrm{R}}_2 d\vec{\mathrm{R}}_3 A_{123}(K^{123} + 3\gamma K^{12}K^{23}) \,, \tag{4.34}$$

$$\frac{\partial S_2}{\partial \mu} = (2\pi a)^2\gamma\rho \int d\vec{\mathrm{R}}_1 d\vec{\mathrm{R}}_2 d\vec{\mathrm{R}}_3 A_{123}(K^{123} + 2\gamma K^{12}K^{23}) \,, \tag{4.35}$$

$$\frac{\partial^2 S_1}{\partial \mu^2} = -(2\pi a)^2\gamma\rho^2 \int d\vec{\mathrm{R}}_1 d\vec{\mathrm{R}}_2 d\vec{\mathrm{R}}_3 A_{123} \times (K^{123} + \gamma K^{12}K^{23}) \,, \tag{4.36}$$

$$\frac{\partial^3 S_0}{\partial \mu^3} = +(2\pi a)^3\gamma\rho^3 \int d\vec{\mathrm{R}}_1 d\vec{\mathrm{R}}_2 d\vec{\mathrm{R}}_3 A_{123}(K^{123}) \,. \tag{4.37}$$

Using (4.8) again, we find $F_3 = 0$.

It is not difficult to extend this proof to any $n \geq 2$. This will be done in Appendix C. We conclude that our main result (3.47)–(3.49) gives the first two terms of $g(\epsilon)$ correctly, provided the semi-invariant expansion converges in a suitably uniform manner.

APPENDIX A: PSEUDOPOTENTIAL APPROXIMATION

We want to compute the "energy shifts" $\Delta^{12\cdots n}$ in the approximation where the range of $v(\vec{\mathrm{r}})$ is much smaller than any length in $\phi(\vec{\mathrm{r}})$ (pseudopotential approximation). For this we need the ground-state energy in the potential $\phi + u$ where

$$u \equiv \sum_{j=1}^{n} v(\vec{\mathrm{r}} - \vec{\mathrm{R}}_j) \,. \tag{A1}$$

Writing $H = p^2/2 + \phi$, $\tilde{H} = H + u$, we want the ground state $\tilde{\psi}$ of $\tilde{H}$, i.e.,

$$\tilde{H}\tilde{\psi}_0 = \tilde{E}_0\tilde{\psi}_0 \,. \tag{A2}$$

Equation (A2) is equivalent to the integral equation

$$\tilde{\psi}_0(\vec{\mathrm{r}}) = \psi_0(\vec{\mathrm{r}}) + \int d\vec{\mathrm{r}}'\, \theta(\vec{\mathrm{r}}, \vec{\mathrm{r}}' \,|\, \tilde{E}_0) u(\vec{\mathrm{r}}')\tilde{\psi}_0(\vec{\mathrm{r}}') \,, \tag{A3}$$

and

$$\tilde{E}_0 - E_0 = (\psi_0, u\tilde{\psi}_0) \,, \tag{A4}$$

where E_l, ψ_l $(l = 0, 1, \ldots)$ are the eigenvalues and eigenfunctions of H, and

$$\theta(\vec{\mathrm{r}}, \vec{\mathrm{r}}' \,|\, \tilde{E}_0) \equiv \sum_{l\neq 0} \frac{\psi_l(\vec{\mathrm{r}})\psi_l(\vec{\mathrm{r}}')}{\tilde{E}_0 - E_l} \,. \tag{A5}$$

[Equation (A3) may be verified at once by operating on both sides with $H - \tilde{E}_0$, (A4) by taking the scalar produce of (A2) with ψ_0. This is just the Brillouin-Wigner form of perturbation theory.]

Now according to Blatt and Weisskopf, [10] in the pseudopotential approximation we may make the replacement

$$u(r')\tilde{\psi}_0(r') \to 2\pi a \sum_{j=1}^{n} B_j \delta(\vec{\mathrm{r}}' - \vec{\mathrm{R}}_j) \,, \tag{A6}$$

where

$$B_j \equiv \lim_{\vec{\mathrm{r}}\to\vec{\mathrm{R}}_j} \frac{\partial[\,|\vec{\mathrm{r}} - \vec{\mathrm{R}}_j|\tilde{\psi}_0(\vec{\mathrm{r}})]}{\partial|\vec{\mathrm{r}} - \vec{\mathrm{R}}_j|} \,. \tag{A7}$$

Therefore,

$$\tilde{\psi}_0(\vec{\mathrm{r}}) = \psi_0(\vec{\mathrm{r}}) + (2\pi a)\sum_{j=1}^{n} \theta(\vec{\mathrm{r}}, \vec{\mathrm{R}}_j \,|\, \tilde{E}_0)B_j \,. \tag{A8}$$

Clearly, when $\vec{\mathrm{r}} \to \vec{\mathrm{R}}_i$, we must have

$$\theta(\vec{\mathrm{r}}, \vec{\mathrm{R}}_i \,|\, \tilde{E}_0) = -\frac{1}{2\pi(\vec{\mathrm{r}} - \vec{\mathrm{R}}_i)} + \tilde{\theta}_{ii} \,, \tag{A9}$$

where $\tilde{\theta}_{ii}$ is a well-defined function of $\vec{\mathrm{R}}_i$ and $\tilde{E}_0$. This follows from the fact that $\tilde{\psi}_0(r)$ has to be proportional to $1 - a/(\vec{\mathrm{r}} - \vec{\mathrm{R}}_i)$ for $\vec{\mathrm{r}} \to \vec{\mathrm{R}}_i$, from scattering theory. [We may also verify (A9) directly, since when $\vec{\mathrm{r}}$ is very close to $\vec{\mathrm{r}}'$, (A5) is dominated by the very highly excited states (plane waves), and $|\tilde{E}_0 - E_0|$ is negligible.] Therefore, for $\vec{\mathrm{r}}$ near $\vec{\mathrm{R}}_i$ we may write

$$\tilde{\psi}_0(\vec{\mathrm{r}}) = \psi_i - \frac{a}{(\vec{\mathrm{r}} - \vec{\mathrm{R}}_i)} B_i + 2\pi a \sum_{j=1}^{n} \tilde{\theta}_{ij}B_j \,, \tag{A10}$$

where

$$\psi_i = \psi_0(\vec{\mathrm{R}}_i) \,, \tag{A11}$$

$$\tilde{\theta}_{ij} = \theta(\vec{\mathrm{R}}_i, \vec{\mathrm{R}}_j \,|\, \tilde{E}_0) \quad (i \neq j) \,. \tag{A12}$$

Calculating B_i from (A7) we see that the second term on the right-hand side contributes nothing, and

$$B_i = \psi_i + 2\pi a \sum_j \tilde{\theta}_{ij}B_j \,, \tag{A13}$$

or

$$B_i = \psi_i + 2\pi a \sum_j \tilde{\theta}_{ij}\psi_j + (2\pi a)^2 \sum_{j,j'} \tilde{\theta}_{ij}\theta_{jj'}\psi_{j'} + \cdots \,. \tag{A14}$$

Using (A6), (A14) becomes

$$\tilde{E}_0 - E_0 = 2\pi a \sum_j \psi_j B_j = 2\pi a \sum_j \psi_j^2 + (2\pi a)^2 \sum_{j,j'} \psi_j\tilde{\theta}_{jj'}\psi_{j'} + (2\pi a)^3 \times \sum_{j,j',j''} \psi_j\tilde{\theta}_{jj'}\tilde{\theta}_{j'j''}\psi_{j''} + \cdots \,. \tag{A15}$$

This is an implicit equation for $\tilde{E}_0$, since $\tilde{\theta}_{ij}$ depends on $\tilde{E}_0$.

Before we discuss the general case, we consider some low orders. For $n = 1$ we have, writing $\tilde{E}_0 = E_0(1)$,

$$\tilde{E}_0 - E_0 = \Delta(\vec{R}_1) \equiv \Delta^1$$
$$= (2\pi a)\psi_1^2 + (2\pi a)^2 \tilde{\theta}_{11}^{(1)} \psi_1^2 + (2\pi a)^3 (\theta_{11}^{2(1)})^2 \psi_1^2 + \cdots$$
$$= 2\pi a \psi_1^2 [1 + 2\pi a \tilde{\theta}_{11}^{(1)} + (2\pi a \tilde{\theta}_{11}^{(1)})^2 + \cdots] , \quad \text{(A16)}$$

where $\tilde{\theta}_{ij}^{(1)}$ is $\tilde{\theta}_{ij}$ for $\tilde{E}_0(1)$. Now $\tilde{\theta}_{11}$ is a function of $\tilde{E}_0$, independent of the scattering potential v and with the dimensions of an inverse length. Similarly, ψ_1^2 is independent of the scattering potential and has the dimensions of an inverse length cubed, and E_0 is independent of v and has the dimensions of an inverse length squared. Therefore, since by definition $a \ll$ any length in the unperturbed problem, $2\pi a \psi_1^2 \ll E_0$, and $E_0(1) = E_0 +$ small correction.

$$\Delta^1 = 2\pi a \psi_1^2 . \quad \text{(A17)}$$

For $n = 2$ we have, in an obvious notation,

$$E_0(12) - E_0 = 2\pi a \{\psi_1^2 + \psi_2^2 + 2\pi a (\tilde{\theta}_{11}^{(12)} \psi_1^2 + \tilde{\theta}_{22}^{(12)} \psi_2^2 + 2\tilde{\theta}_{12}^{(12)} \psi_1 \psi_2) + (2\pi a)^2 [(\tilde{\theta}_{11}^{(12)})^2 \psi_1^2 + (\tilde{\theta}_{22}^{(12)})^2 \psi_2^2 + \cdots] + \cdots\} . \quad \text{(A18)}$$

Since

$$\Delta(\vec{R}_1, \vec{R}_2) = \Delta^{12} = E_0(12) - E_0 - \Delta^1 - \Delta^2 , \quad \text{(A19)}$$

we find, using (A16),

$$\Delta^{12} = (2\pi a)^2 [(\tilde{\theta}_{11}^{(12)} - \tilde{\theta}_{11}^{1}) \psi_1^2 + (\tilde{\theta}_{22}^{(12)} - \tilde{\theta}_{22}^{2}) \psi_2^2 + 2\tilde{\theta}_{12}^{(12)} \psi_1 \psi_2] + \cdots . \quad \text{(A20)}$$

Now recalling that $\tilde{\theta}_{11}$ is a smooth function of $\tilde{E}_0$, we have $\tilde{\theta}_{11}^{(12)} = \tilde{\theta}_{11}(\tilde{E}_0(12))$, $\tilde{\theta}_{11}^{1} = \tilde{\theta}_{11}(E_0(1))$. Hence $\tilde{\theta}_{11}^{(12)} - \tilde{\theta}_{11}^{(1)}$ is small if $\tilde{E}_0(12) - \tilde{E}_0(1) = \Delta^{12} + \Delta^2$ is small. But from (A20) and (A17) we see that Δ^{12} is second order (by order we mean power of a divided by a characteristic length of ϕ), Δ^1 is of first order, and therefore, $\tilde{\theta}_{11}^{(12)} - \tilde{\theta}_{11}^{(1)}$ is first order. The leading term of Δ^{12} is thus

$$\Delta^{12} = (2\pi a)^2 2\theta_{12} \psi_1 \psi_2 , \quad \text{(A21)}$$

where

$$\theta_{ij} = \theta(\vec{R}_i, \vec{R}_j | E_0) \quad (i \neq j) . \quad \text{(A22)}$$

It is not difficult to continue this process and obtain an explicit formula for $\Delta^{12\cdots n}$. However, for our purposes it is convenient to express the result in a different form. We notice first that in (A17) and (A21) the diagonal elements θ_{ii} do not contribute in the leading term. It is elementary (but a little tedious) to show by induction that this is also true for $\Delta^{12\cdots n}$. Now consider for a moment the case where v is a weak potential. Equation (A3) becomes

$$\tilde{\psi}_0(\vec{r}) = \psi_0(\vec{r}) + \sum_j \int d\vec{r}' \, \theta(\vec{r}, \vec{r}' | \tilde{E}_0) v_j(\vec{r}') \tilde{\psi}_0(r') . \quad \text{(A23)}$$

We want to calculate the first nonvanishing term of $\Delta^{12\cdots n}$ in perturbation theory. We assert that if this is done and then v_j is replaced by $2\pi a \delta(\vec{r} - \vec{R}_j)$, the answer will be the same as the leading term of the pseudopotential approximation. To see this, write (A23) at the point $\vec{r} = \vec{R}_i$,

$$\tilde{\psi}_0(\vec{R}_i) = \psi_i + \sum_j \int d\vec{r}' \, \theta(\vec{R}_i, \vec{r}' | \tilde{E}_0) v_j(\vec{r}') \tilde{\psi}_0(\vec{r}')$$
$$= \psi_i + \int d\vec{r}' \, \theta(\vec{R}_i, \vec{r}' | \tilde{E}_0) v_i(r') \tilde{\psi}_0(r') + \sum_{j \neq 1} \int d\vec{r}' \, \theta(R_i, \vec{r}' | \tilde{E}_0) v_j(r') \tilde{\psi}_0(r') . \quad \text{(A24)}$$

Ultimately, we will put $v_j = 2\pi a \delta(\vec{r} - \vec{R}_j)$. This gives no trouble in the last term of (A24) if we do it now, or in the $\tilde{\psi}_0(r')$ of the second term, but it is not permissible in $\theta(\vec{R}_i, \vec{r}' | \tilde{E}_0)$ since this diverges when $\vec{r}' = \vec{R}_i$. Therefore, we may write (A24) as

$$\tilde{\psi}_i = \psi_i + 2\pi a \gamma_i(\tilde{E}_0) \tilde{\psi}_i + 2\pi a \sum_{j \neq i} \tilde{\theta}_{ij} \tilde{\psi}_j , \quad \text{(A25)}$$

where

$$\gamma_i(\tilde{E}_0) = \frac{1}{2\pi a} \int d\vec{r}' \, \theta(\vec{R}_i, \vec{r}') v_i(\vec{r}') . \quad \text{(A26)}$$

Similarly, (A4) becomes

$$\tilde{E}_0 - E_0 = 2\pi a \sum_j \psi_j \tilde{\psi}_j . \quad \text{(A27)}$$

Now (A25) and (A27) only differ from (A13) and (A15) in that $\tilde{\psi}_j$ [which is eliminated in the second line of (A15)] replaced B_j and $\gamma_i(\tilde{E}_0)$ replaces $\tilde{\theta}_{ii}$. But in the leading contribution to $\Delta^{12\cdots n}$, we saw that the diagonal element $\tilde{\theta}_{ii}$ does not contribute. Therefore, this difference does not contribute to the leading term, and we have proven our assertion.

APPENDIX B: ESTIMATES OF THE $\Delta^{12\cdots n}$ AND RELATED QUANTITIES

The estimates which we need all refer to the $\Delta^{12\cdots n}$ when the $\vec{R}_1, \ldots, \vec{R}_n$ are all in the skin depth, i.e., within about λ_0 of b_0. We estimate these as follows: Take for the potential ϕ, instead of the actual one we obtain, a potential well which is zero until b_0, then infinite. If we then write $|\vec{R}_i| = b_0 - \xi_i$ ($\xi_i > 0$), and put $\xi_i \sim \lambda_0$, we should have reliable estimates, since all that the real potential ϕ does is smooth the transition (but still it is spread over a distance of the order of λ_0). Clearly, from (3.7) we have in the skin depth

$$\psi(\vec{R}_1) \sim \frac{\sin(\pi/b_0)R_1}{r\sqrt{2\pi b_0}} \sim \frac{\pi \xi_1}{\sqrt{2\pi} b_0^{5/2}} \sim \frac{\lambda_0}{b_0^{5/2}} . \quad \text{(B1)}$$

Therefore, from (A17) and (3.11),

$$\Delta^1 = 2\pi a \psi_1^2 \sim \frac{\lambda_0^2 a}{b_0^5} \sim \frac{\rho a \lambda_0^2}{t} \sim \frac{1}{t} \quad \text{(B2)}$$

($\Delta^1 t \sim 1$ in the skin depth as we had before). Next we estimate Δ^{12} in the skin depth. From (A21) this

is

$$\Delta^{12} = 2(2\pi a)^2\,\theta(\vec{R}_1, \vec{R}_2 | E_0)\psi_1\psi_2 \,. \tag{B3}$$

We can estimate θ by replacing it by its angular average $\langle\theta\rangle$ over the directions of $\vec{R}_1$ and $\vec{R}_2$. Then only the S waves survive in (A5), and the calculation becomes a completely elementary one for the infinite well of radius b_0. We find

$$\langle\theta(\vec{R}_1, \vec{R}_2 | E_0)\rangle$$

$$= \frac{1}{2\pi^2 k R_1 R_2}\left(k(R_2 \sin kR_1 \cos kR_2 + R_1 \sin kR_2 \cos kR_1)\right.$$

$$\left. - \pi \times \begin{cases} \sin kR_1 \cos kR_2 \,, & R_1 < R_2 \\ \sin kR_2 \cos kR_1 \,, & R_1 > R_2 \end{cases}\right) \,, \tag{B4}$$

where $k \equiv \pi/b_0$. Putting $R_1 = b_0 - \xi_1$, $R_2 = b_0 - \xi_2$ we find, for $\xi_1, \xi_2 \ll b_0$,

$$\langle\theta(\vec{R}_1, \vec{R}_2 | E_0)\rangle = -\frac{1}{2\pi b_0^2} \times \begin{cases} \xi_1, & \xi_1 < \xi_2 \\ \xi_2, & \xi_2 < \xi_1 \end{cases} \,. \tag{B5}$$

Therefore, we have the estimates in the skin depth,

$$|\theta(\vec{R}_1, \vec{R}_2 | E_0)| \sim \frac{\lambda_0}{b_0^2} \,, \tag{B6}$$

and

$$|\Delta^{12}| \sim a^2\left(\frac{\lambda_0}{b_0^{5/2}}\right)^2 \frac{\lambda_0}{b_0^2} = \frac{a\lambda_0}{t b_0^2} \,, \tag{B7}$$

$$t|\Delta^{12}| \sim \frac{a\lambda_0}{b_0^2} \ll 1 \,. \tag{B8}$$

Similarly, we may estimate the higher order Δ's. A typical term of $\Delta^{12\cdots n}$ [one which comes from ignoring the "energy shift" $E_0 - E$ in the θ's in (A15)] is

$$(\Delta^{12\cdots n})_{\text{typical}} = (2\pi a)^n \psi_1 \theta_{12}\theta_{23}\cdots\theta_{n-1,n}\psi_n$$

$$= a^n\left(\frac{\lambda_0}{b_0^{5/2}}\right)^2\left(\frac{\lambda_0}{b_0^2}\right)^{n-1} \sim \frac{1}{t}\left(\frac{\lambda_0 a}{b_0^2}\right)^{n-1} \,. \tag{B9}$$

By means of these estimates, we can estimate the $\rho^n S_n$ ($n \geq 2$), using (4.23), (4.24), (4.25), etc. Since the integrands of these quantities only differ appreciably from zero when we are in the skin depth, we can replace each $\vec{R}_i$ integration by a factor $\lambda_0 b_0^2$ and $t\Delta^{12\cdots n}$ by $(\lambda_0 a/b_0^2)^{n-1}$. Thus

$$\begin{aligned} \rho^2 S_2 &\sim \rho^2\left(\frac{\lambda_0 a}{b_0^2}\right)(\lambda_0 b_0^2)^2 \sim \rho\lambda_0 b_0^2 \,, \\ \rho^3 S_3 &\sim \rho^3\left(\frac{\lambda_0 a}{b_0^2}\right)(\lambda_0 b_0^2)^3 \sim \rho\lambda_0 b_0^2 \,, \\ \rho^n S_n &\sim \rho^n\left(\frac{\lambda_0 a}{b_0^2}\right)^{n-1}(\lambda_0 b_0^2)^n \sim \rho\lambda_0 b_0^2 \,. \end{aligned} \tag{B10}$$

These same estimates apply to all the terms of F_n as they must, since cancellation takes place among them eventually.

Finally, we mention that the terms we have dropped in writing (4.24), (4.25), etc., are easily seen from these same estimates to be of lower order in b_0 since they involve extra factors of $t\Delta^{1\cdots n}$ ($n \geq 2$) or the replacement of lower order Δ's by higher-order ones without extra integrations.

APPENDIX C

From (4.8) and (4.13), we can write F_n for $n \geq 2$ in the form

$$F_n = \int d\vec{R}_1 \cdots d\vec{R}_n f_{12\cdots n} \,, \tag{C1}$$

where

$$f_{1\cdots n} = (-\rho)^n D_{1\cdots n}\prod_1^n e^{-t\Delta^i} + (-\rho)^{n-1}\sum^p \phi_1 \frac{\delta}{\delta\phi_1}\left(D_{2\cdots n}\prod_2^n e^{-t\Delta^i}\right)$$

$$+ \cdots + (-\rho)^{n-l}\sum^p \phi_1\cdots\phi_l \frac{\delta^l}{\delta\phi_1\cdots\delta\phi_2}\left(D_{l+1\cdots n}\prod_{l+1}^n e^{-t\Delta^i}\right) + \cdots + \phi_1\cdots\phi_n \frac{\delta^n}{\delta\phi_1\cdots\delta\phi_n}(-tE_0) \,. \tag{C2}$$

Here $\delta/\delta\phi_i$ means $\delta/\delta\phi(\vec{R}_i)$, and Σ^p means that we sum over all permutations by which the subset $\{1\cdots l\}$ is transformed into other subsets of $\{1\cdots n\}$. This summation replaces the factor $\binom{n}{l}$ in (4.8). The parameter μ need no longer appear, since all derivatives are shown explicitly. Our purpose is to show that the integrand $f_{1\cdots n}$ vanishes when we (i) keep only terms that will contribute to F_n in $O(\rho\lambda_0 b_0^2)$; (ii) use the pseudopotential approximation for the Δ's; and (iii) require that ϕ satisfy (2.52) so that F_1 is minimized.

We begin with a diagrammatic representation of each term in $(-\rho)^m D_{1\cdots m}\Pi_1^n e^{-t\Delta^i}$. Let us represent each factor $-\rho e^{-t\Delta^i}$ by a square and each factor $-t\Delta^{i_1 i_2\cdots i_s}$ by a circle connected to each of the squares numbered $i_1, i_2, \ldots, i_s$. Thus we obtain a graph in which circles are connected only to squares and squares only to circles.

Moreover, only *connected* graphs contribute to $D_{i_1\cdots i_m}$; terms corresponding to disconnected graphs drop out in the expansion of (4.14), (4.15), etc. The proof of this is the same as that of the statement that only connected graphs contribute to the logarithm of the grand-partition function in the Ursell-Mayer expansion for gases.

Again, by the arguments of Appendix B, we may

neglect any graphs that are overconnected (i.e., not simply connected). For (B9) shows that each circle brings in a factor $\lambda_0 a/b_0^2$ for all but one of the lines connected to it. Thus the number of factors $\lambda_0 a/b_0^2$ in the whole graph is the number of lines minus the number of circles. In a simply connected graph, the number of lines is just one less than the total number of squares and circles, so that the graph carries a factor $(\lambda_0 a/b_0^2)^{m-1}$, if there are m squares. Thus the simply connected graphs for S_m are all comparable to one another, but the overconnected graphs have additional lines, hence extra factors $\lambda_0 a/b_0^2$, and they are therefore neglected.

The simply connected graphs with which we now have to deal are of the kind elsewhere called "dual trees."[13] They are equivalent to Husimi or "star trees"—the circles correspond to stars and the squares to points—but we find that the dual form facilitates manipulation.

The diagrammatic representation of $-\rho^3 e^{-t(\Delta^1+\Delta^2+\Delta^3)} D_{123}$ is shown in Fig. 1 [cf. (4.23)].

We now wish to extend the dual-tree representation to the quantities

$$\phi_{J_1}\cdots\phi_{J_l}\frac{\delta^l}{\delta\phi_{J_1}\cdots\delta\phi_{J_l}}\left[\rho^m\exp\left(-t\sum_s^m\Delta_{i_s}\right)D_{i_1\cdots i_m}\right]$$

appearing in (C2). When we differentiate a term in $e^{-t\sum\Delta_i}D_{i_1\cdots i_m}$, we obtain a sum of terms, each arising from the differentiation of one of the factors. Consider a term in $D_{i_1\cdots i_m}$ containing a factor $\Delta_{\{i\}}$, where $\{i\}$ is some subset of $\{i_1\cdots i_m\}$. This factor is represented by a circle in the corresponding dual tree. When we replace the factor $\Delta_{\{i\}}$ by $\phi_j\,\delta\Delta_{\{i\}}/\delta\phi_j$, we obtain an expression which we may represent by a new dual tree, obtained from the old by inserting a new line in the circle for $\Delta_{\{i\}}$ and connecting it with a new square bearing the index j. We may then associate the factor ϕ_j with the new square and $-t\,\delta\Delta_{\{i\}}/\delta\phi_j$ with the circle bearing the extra insertion. However, we must also *mark* the new square in some special way so as to distinguish the new dual tree from an ordinary one in which the square would represent $\rho e^{-t\Delta_j}$ and the circle $-t\Delta_{\{i,j\}}$.

We must also provide for differentiating the factors $e^{-t\Delta_i}$. Since

$$\phi_j\frac{\delta}{\delta\phi_j}e^{-t\Delta_i}=\phi_i\left(-t\frac{\delta}{\delta\phi_j}\Delta_i\right)e^{-t\Delta_i}, \qquad \text{(C3)}$$

the effect of the operator $\phi_j\,\delta/\delta\phi_j$ applied to a square is to leave the factor $-\rho e^{-t\Delta_i}$ belonging to that square unchanged, and add two new factors ϕ_j and $-t\,\delta\Delta_i/\delta\phi_j$. We represent this by connecting the square to a *new* circle and connecting the new circle to a new marked square.

In Fig. 2 we show how this construction represents the quantity

$$\phi_1\frac{\delta}{\delta\phi_1}\left(-t\Delta_{23}e^{-t(\Delta_2+\Delta_3)}\right),$$

which contributes to f_3 through the second term in (C2).

Now suppose we wish to differentiate a second time. Clearly the same rule applies: To any circle we may attach a new marked square, or to any *unmarked* square we may attach a new circle and marked square in tandem. But we make *no new attachments to marked squares* since they represent the factors ϕ_j which are explicitly outside the derivatives in (4.18). In Fig. 3 we show the construction for

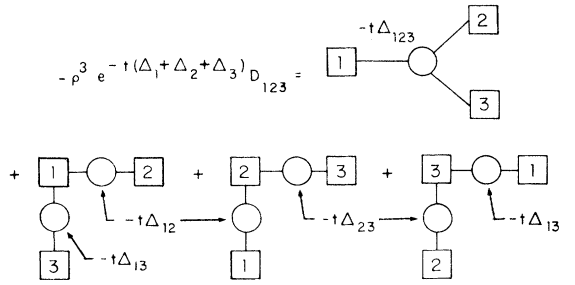

FIG. 1. Diagrammatic representation of ρ^3 term in Eq. (C2) for $n=3$. Values of circles are shown; value of ith square is $-\rho e^{-t\Delta_i}$.

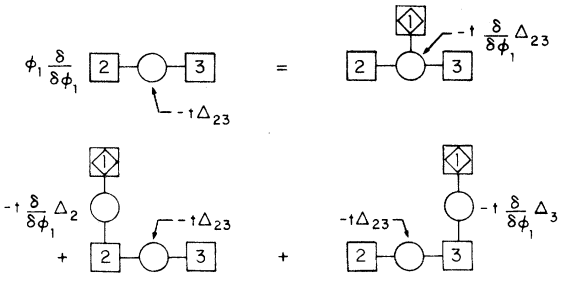

FIG. 2. Diagrammatic representation of one ρ^2 term in Eq. (C2) for $n=3$. Value of marked square is ϕ_i. Other values as in Fig. 1.

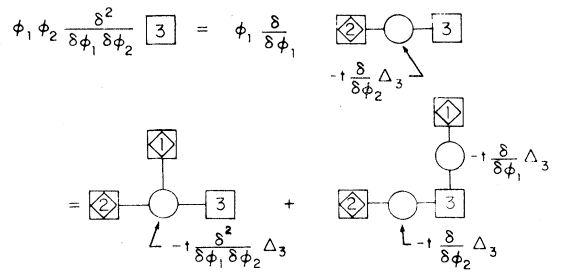

FIG. 3. Diagrammatic representation of one ρ term in Eq. (C2) for $n=3$. Values as in Figs. 1 and 2.

$$\phi_1\phi_2 \frac{\delta^2}{\delta\phi_1\delta\phi_2}(\rho e^{-t\Delta_3})$$

$$= \phi_1\phi_2 e^{-t\Delta_3}\left(-t\frac{\delta^2\Delta_3}{\delta\phi_1\delta\phi_2}+t^2\frac{\delta\Delta_3}{\delta\phi_1}\frac{\delta\Delta_3}{\delta\phi_2}\right). \qquad \text{(C4)}$$

To summarize our rules: (i) Each unmarked square (index i) carries a factor $-\rho e^{-t\Delta_i}$. (ii) Each marked square (index i) carries a factor ϕ_i. (iii) Each circle, connected to unmarked squares $i_1\cdots i_p$ and marked squares $J_1\cdots J_q$, carries a factor $-t(\delta^q/\delta\phi_{J_1}\cdots\delta\phi_{J_q})\Delta_{i_1\cdots i_p}$. (iv) All marked squares must be end squares; that is, a marked square must be connected to just one circle. (v) Every circle is connected to at least two squares. (vi) For $n\geq 2$, $f_{1\cdots n}$ is given by the sum of all dual trees with n squares satisfying Rules iv and v each tree being evaluated according to Rules i–iii.

We note that Rule iii does not cover the case $p=0$, in which a circle is connected only to marked squares. By Rule iv, this can happen only in a diagram containing only one circle. To handle this diagram, we supplement Rule iii as follows: (iii a) Each circle connected only to marked squares $J_1\cdots J_q$ carries a factor $-t(\delta^q/\delta\phi_{J_1}\cdots\delta\phi_{J_q})E_0$.

The one-circle diagram with n marked squares then accounts for the last term of (C2).

We are now ready to make the pseudopotential approximation. First we apply (4.24) and (4.25), etc., so as to express all Δ's as functional derivatives of E_0. Rules iii and iii a then simplify to the following: (iii′) Each circle connected to squares $i_1\cdots i_s$ (marked or unmarked) carries a factor $(2\pi a)^p\delta^s E_0/\delta\phi_{i_1}\cdots\delta\phi_{i_s}$, where p is the number of unmarked squares.

To eliminate all asymmetry, let us replace $(2\pi a)^p$ by $(2\pi a)^s$ and compensate by attaching a new factor $1/2\pi a$ to each marked square. Then the rule for circles loses all reference to marked or unmarked: (iii″) Each circle connected to squares $i_1\cdots i_s$ carries a factor $(2\pi a)^s\delta^s E_0/\delta\phi_{i_1}\cdots\delta\phi_{i_s}$.

Now the only effect of marking a square is on the factor directly associated with it, $-\rho e^{-t\Delta_i}$ if unmarked, $\phi_i/2\pi a$ if marked. So we can dispense with marking and simply attach the sum of these factors to each end square: (i″) Each interior square (connected to ≥ 2 circles) carries a factor $-\rho e^{-t\Delta_i}$. (ii″) Each end square (connected to 1 circle) carries a factor $-\rho e^{-t\Delta_i}+\phi_i/2\pi a$.

But according to (2.52), the factor described in Rule ii″ vanishes. Since there are no end circles by Rule v, every dual tree has at least one end square. Therefore, $f_{1\cdots n}$ vanishes under the stated approximations.

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[1]A concise review may be found in M. H. Cohen, J. Non-Cryst. Solids 4, 391 (1970).

[2]I. M. Lifshitz, Vsp. Fiz. Nauk 83, 617 (1964) [Sov. Phys.–Vsp. 7, 549 (1965)]. Many related questions are also discussed in this excellent review.

[3]We choose three dimensions to be specific, but the same arguments go through for an arbitrary dimension. In one dimension, however, only the leading (Lifshitz) term is given correctly. A more refined variational method is possible in this case which corrects this deficiency, but we shall not discuss it here.

[4]This is what we mean by saying that the impurities are put in "at random."

[5]Assuming periodic boundary conditions, this introduces a slight inconsistency in what follows, where we are essentially choosing instead a potential which is infinite outside of V; but this procedure is easily made rigorous.

[6]M. Kac, *Probability and Related Topics in Physical Science* (Interscience, New York, 1959), Vol. I, p. 161 ff.

[7]S. F. Edwards and V. B. Gulyaev, Proc. of Phys. Soc. Lond. 83, 495 (1965). Their result was for "time" rather than "temperature" Green's functions, i.e., $t\to it$.

[8]Easily established by saddle-point arguments. We omit the proof here.

[9]A good reference for this is R. Kubo, J. Phys. Soc. Jpn. 17, 1100 (1962).

[10]An exposition of this technique may be found in J. Blatt and V. Weisskopf, *Nuclear Physics* (Wiley, New York, 1956).

[11]Actually, we may add an arbitrary constant to λ and ϕ. [ϕ is determined only up to an additive constant as may be seen at once from (2.26), and the choice of this constant does not affect the inequality (2.25)]. The choice given by (2.51) is convenient and corresponds most closely to the Lifshitz picture.

[12]In computing K_2 and D_2 we may use the leading term of the wave function, since these terms already represent small corrections.

[13]R. Friedberg, J. Math. Phys. 16, 20 (1975).