Local Theory of Disordered Systems[*][1]

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The most striking characteristic of crystalline solids is their periodicity. As a result of this feature, theoretical descriptions of physical phenomena in such systems are usually given in wave number or *momentum* space. The reciprocal lattice of a crystal and the Fermi surface of a metal are examples. In a disordered system, on the other hand, there is no such periodicity and momentum space descriptions are much less natural. However, in such systems, physical conditions near a point $\mathbf{r}$, in *coordinate* space, become independent of the conditions at a distant point $\mathbf{r}'$, provided that $|\mathbf{r}'\text{-}\mathbf{r}|$ is large compared to either a characteristic mean free path or some other appropriate length. This suggests that one can analyze a macroscopic disordered system by averaging over the properties of microscopic neighborhoods.

In the present paper we report some details of such a program. Although the point of view is of quite general applicability we have, for the sake of definiteness, studied so far only one type of system: Noninteracting electrons moving in the field of interacting, disordered scattering centers. We have focused especially on the electronic density of states. The macroscopic system is represented by an average over small neighborhoods. If one did not take special precautions, one would encounter one class of errors of the order of d/L where L is a characteristic dimension of the neighborhood, and d is a characteristic atomic dimension; and another class of errors of the order of $1/N$ where N is the number of ions. Both are too large to be tolerable for practical purposes. However, by an appropriate treatment of the statistical mechanics of the scatterers and by periodic repetition of the small neighborhoods, these errors can be avoided. The remaining errors are exponentially small in the ratio $\gamma(L/R)$ where γ is of order unity and R is the smaller of the electronic mean free path or the deBroglie wavelength of the electrons. This exponential convergence of the small neighborhood theory promises to make it a useful practical method for the study of disordered systems, especially very highly disordered ones.

Numerical examples are presented and discussed.

Key words: Binary alloys; density of states; disordered systems; periodically continued neighborhood.

1. Introduction

The physical properties of strongly interacting disordered systems are in general difficult to calculate since simplifying symmetries, present in crystalline materials, are not present. In this paper we present and develop to some small extent a viewpoint which appears to provide a useful line of attack on the theory of disordered systems.

We shall demonstrate and utilize the rather plausible fact that in a disordered system the physical charac-

teristics at a point $\mathbf{r}$ depend significantly only on conditions inside a rather small neighborhood $|\mathbf{r}'\text{-}\mathbf{r}|<R$, where R is of the order of a mean free path l or a characteristic thermal deBroglie wavelength, Λ_t. The effects of the more distant environment fall off exponentially with distance. This suggests that the properties of an infinite disordered system could be accurately calculated by suitable averaging over an ensemble of small neighborhoods. This scheme, furthermore, should be most successful for strongly disordered systems in which the mean free path is short.

In the following sections we sketch an application of these ideas to the much-studied problem of the density

of states of noninteracting electrons moving in the static potential of disordered scattering centers.[3]

2. Demonstration of the Locality Principle

In this section we shall sketch the demonstration that the physical properties near a point $\mathbf{r}$ of a system of noninteracting electrons moving in a disordered external potential are nearly independent of the circumstances outside a characteristic range R. More specifically, the effect of a perturbation at a distant point $\mathbf{r}'$ on physical properties at $\mathbf{r}$ falls off exponentially, on a scale given by a range of influence, R, which is of the order of either the mean free path or, at high temperatures, the thermal wavelength of the electrons, whichever is the smaller.

We consider a very large system of volume Ω described by the Hamiltonian

$$H = H_0 + V + v; \qquad (2.1)$$

here H_0 is a periodic Hamiltonian, which for simplicity we take to be the kinetic energy

$$H_0 = \mathbf{p}^2; \qquad (2.2)$$

V is a potential produced by disordered scattering centers, located at the points $\mathbf{r}_\alpha$,

$$V = \sum_\alpha V_\alpha(\mathbf{r} - \mathbf{r}_\alpha); \qquad (2.3)$$

and v is an additional small perturbation localized at a point $\mathbf{r}'$. We shall study the effect of v on physical conditions at the point $\mathbf{r}$.

First, we shall consider the one particle Green's function

$$G(\mathbf{r}, \mathbf{r}'; E) = \left(\mathbf{r} \left| \frac{1}{E - H} \right| \mathbf{r}' \right). \qquad (2.4)$$

In terms of the eigenfunctions ψ_n of H, and the eigenvalues E_n,

$$G(\mathbf{r}, \mathbf{r}'; E) = \sum_n \frac{\psi_n^*(\mathbf{r})\psi_n(\mathbf{r}')}{E - E_n}. \qquad (2.5)$$

Of special interest is the contracted function $G(\mathbf{r}, \mathbf{r}; E)$ which determines the density of states by means of the following relation,

$$n(E) = -\frac{1}{\pi} \operatorname{Im} \int d\mathbf{r} G(\mathbf{r}, \mathbf{r}; E + i0). \qquad (2.6)$$

We see that we may regard the unintegrated quantity

$$n(\mathbf{r}, E) \equiv -\frac{1}{\pi} \operatorname{Im} G(\mathbf{r}, \mathbf{r}; E + i0) \qquad (2.7)$$

as the local density of states density.

We would like to estimate the effect of introducing the weak additional potential v, at the point $\mathbf{r}'$, on $n(\mathbf{r}, E)$ at the point $\mathbf{r}$. The quantity of physical interest is then

$$\left\langle \frac{\delta}{\delta v(\mathbf{r}')} G(\mathbf{r}, \mathbf{r}; E + i0) \right\rangle$$
$$= \langle G(\mathbf{r}, \mathbf{r}'; E + i0) G(\mathbf{r}', \mathbf{r}; E + i0) \rangle_{v=0} \qquad (2.8)$$

where the brackets $\langle \rangle$ denote configuration average. The equation (2.9) follows directly from the equation of motion of G.

Now it is well known that, for weak random potentials V_α,

$$\langle G(\mathbf{r}, \mathbf{r}'; E + i0) \rangle \approx \frac{1}{4\pi|\mathbf{r} - \mathbf{r}'|} e^{i\sqrt{E}|r - r'|} e^{-|\mathbf{r} - \mathbf{r}'|/2l(E)},$$
$$(2.9)$$

where $l(E)$ is the mean free path of an electron of energy E. Similarly, one can show from (2.8) that for large $|\mathbf{r} \text{-} \mathbf{r}'|$

$$\left| \left\langle \frac{\delta}{\delta v(\mathbf{r}')} G(\mathbf{r}, \mathbf{r}; E + i0) \right\rangle \right| \sim e^{-|\mathbf{r} - \mathbf{r}'|/l(E)} \qquad (2.10)$$

Thus we see that when $|\mathbf{r}' \text{-} \mathbf{r}| \gg l(E)$, a change of potential at $\mathbf{r}'$ has a negligible effect on the quantity $n(\mathbf{r}, E)$.

Next we show a similar locality effect, this time not due to a finite mean free path but due to elevated temperature. We consider a system of independent electrons and use Boltzmann statistics for simplicity. We take as Hamiltonian

$$H = H_0 + v, \qquad (2.11)$$

where, in comparison with (2.1), we have eliminated the disordered scattering potentials. We write the partition function as

$$Z = \int d\mathbf{r} \, Z(\mathbf{r}), \qquad (2.12)$$

where

$$Z(\mathbf{r}) \equiv (\mathbf{r}|e^{-\beta H}|\mathbf{r}). \qquad (2.13)$$

Our interest now is in the influence of a small perturbation v at $\mathbf{r}'$ on $Z(\mathbf{r})$. By standard perturbation theory one can show that, for large $|r' - r|$,

$$\frac{\delta Z(\mathbf{r})}{\delta v(r')} \sim -\frac{\pi^{5/2}}{16\beta^{3/2}|\mathbf{r} - \mathbf{r}'|} e^{-|\mathbf{r} - \mathbf{r}'|^2/\Lambda_t^2}, \qquad (2.14)$$

[3] Among fairly recent papers we mention the following: H. Schmidt, *Phys. Rev.* **105**, 425 (1957); S. F. Edwards, *Phil. Mag.* **3**, 1020 (1958); ibid. **6**, 617 (1961); *Proc. Roy. Soc.* **A267**, 518 (1962); J. L. Beeby, *Proc. Roy. Soc.*, **A279**, 82 (1964); *Phys. Rev.* **135A**, 130 (1966); P. Soven, *Phys. Rev.* **151**, 539 (1966); ibid., **156**, 809 (1967).

where Λ_t is the thermal wavelength

$$\Lambda_t \equiv \beta^{1/2}(=\hbar/(2m\,kT)^{1/2}). \qquad (2.15)$$

Of course at high temperature *and* with disorder, the characteristic "range of influence" R will be either a representative mean free path $\bar{l}$, or Λ_t, whichever is the smaller.

3. The Periodically Continued Neighborhood

We shall now develop a concrete method of calculation, based on the locality principle of the previous section. We shall concentrate on the density of states $n(E)$.

The most straightforward way would be as follows. We imagine the large disordered system as given. We choose at random a large number of points $\mathbf{R}_l$ and surround them by spheres of radius ρ considerably larger than the "range of influence" R, but not too large. Each sphere is surrounded by an infinite wall (see fig. 1). The electronic Hamiltonian for each sphere is given by

$$H = H_0 + V \qquad (3.1)$$

where

$$V = \begin{cases} \Sigma V_\alpha(\mathbf{r}-\mathbf{r}_\alpha) & |\mathbf{r}-\mathbf{R}_l| \le \rho \\ +\infty & r > \rho \end{cases} \qquad (3.2)$$

We then calculate for each sphere the density of states density at its center, $n(\mathbf{R}_l,E)$. Because of the relatively small size of the neighborhood this is a much more manageable problem than $n(E)$ for the macroscopic disordered system. In view of the locality principle, $n(\mathbf{R}_l,E)$ is only insignificantly affected by the presence of the infinite wall. Hence, the density of
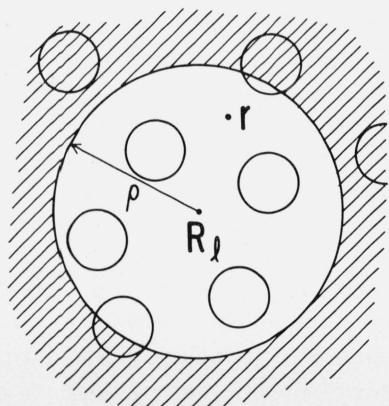
states for the macroscopic system is given by

$$n(E) \approx \Omega n(\mathbf{R}_l,E), \qquad (3.3)$$

where the bar denotes an average over many $\mathbf{R}_l$.[4]

The practical drawbacks, for finite ρ/R_0, are two: (1) The replacement, in the outside region, of the actual potential, ΣV_α, by an infinite repulsive barrier is a quite drastic change and unless ρ/R is very large, will cause sizeable errors. (2) This method does of course not lead to the exact results in the special case of a vanishing or periodic potential.

These drawbacks can be largely overcome by using, instead of a finite and bounded neighborhood, as in figure 1, a periodically continued finite neighborhood as indicated in figure 2. We choose a fundamental cell, say the cube, of volume $\Omega_L \equiv L^3$,

$$|x|, |y|, |z| \le \frac{L}{2}$$

$$L \gg 2R \qquad (3.4)$$

and construct the space-lattice generated by it. Let us call $\boldsymbol{\tau}^{(\nu)}$ the lattice translation vectors. Then we place any number of scatterers in some definite configuration c in the fundamental cell and populate the other cells in the identical way (see fig. 2). The electrons now move in a periodic cubic lattice. Their energy eigenvalues
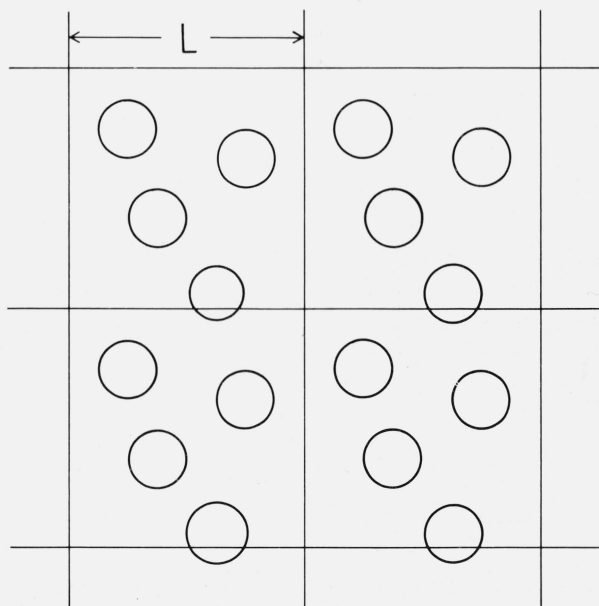

FIGURE 2. *Periodically continued neighborhood.*

[4] If we would use the total densities of states of the spherical neighborhoods, rather than the quantities $n(\mathbf{R}_l,E)$ computed at their centers, we would incur large errors behaving as L^{-1}, due to the presence of the infinite wall boundaries.

FIGURE 1. *Spherical neighborhood centered at $\mathbf{R}_l$.*

are, because of the relatively small size of the unit cell, much more amenable to calculation than the eigenvalues of the macroscopic disordered system. Let us call the density of states, corresponding to the configuration c and total volume Ω, $n_c(E)$. Then our approximation for the density of states of the actual macroscopic system will be

$$n(E) \approx \sum_c w_c n_c(E). \qquad (3.5)$$

where w_c are weights, which we shall presently discuss, and the approximate equality, $\approx$, will signify accuracy to within terms exponentially small in $L/2R$.[5]

We shall now describe a suitable choice of w_c and later demonstrate that it leads to the claimed accuracy. Let us suppose that in the actual, macroscopic system under consideration there are given two-body forces between the scatterers,

$$\varphi_{\alpha\beta} = \varphi_{\alpha\beta}(\mathbf{r}_\alpha - \mathbf{r}_\beta), \qquad (3.6)$$

which vanish beyond a range a which is much smaller than L. Let us suppose further than the scatterers obey classical statistics. Thus, in the macroscopic system the probability of a given configuration $c = (\mathbf{r}_1, \mathbf{r}_2, \ldots)$ is given by the grand canonical weight function,

$$w_c^{(\infty)} = A^{(\infty)} \exp\left\{ -\beta \left[\frac{1}{2} \sum_{\alpha \neq \beta} \varphi_{\alpha\beta} - \sum_j \mu_j N_j \right. \right. \qquad (3.7)$$

where $A^{(\infty)}$ is the normalization constant, μ_j is the chemical potential of scatterer of type j, and N_j is the total number of scatterers of this type.[6]

A suitable choice of w_c, for the periodically continued neighborhood, is obtained as follows. We take the unit cell and associate with each original position vector $\mathbf{r}$, the infinite set of vectors

$$\mathbf{r}^{(\nu)} \equiv \mathbf{r} + \boldsymbol{\tau}^{(\nu)} \qquad (3.8)$$

This corresponds to the topology of a three dimensional torus and is illustrated in figure 3 in one dimension.

The weight w_c is then determined by the equation

$$w_c = A \exp\left\{ -\beta \left[\frac{1}{2} \sum_{\alpha\beta} \varphi_{\alpha\beta}(\bar{\mathbf{r}}_{\alpha\beta}) - \sum \mu_j N_j \right] \right\} \qquad (3.9)$$
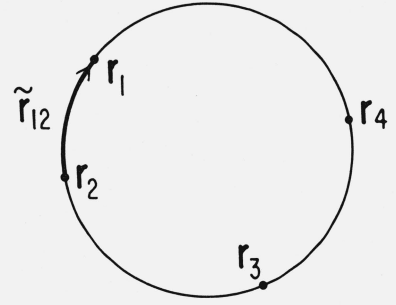

FIGURE 3. *Schematic representation of the toroidal topology. The circumference is* L.

where $\mathbf{r}_{\alpha\beta}$ is the shortest vector contained in the set $\mathbf{r}_\alpha^{(\mu)} - \mathbf{r}_\beta^{(\mu)}$. For example, $\mathbf{r}_{12}$ is shown schematically in figure 3. The normalization constant A is chosen so that

$$\sum_c w_c = 1, \qquad (3.10)$$

where the sum goes over all configurations, including all possible numbers of the scatterers.

It can be shown that, with the choice (3.10), the correlation functions, $n_s(\mathbf{r}_1 \ldots \mathbf{r}_s | L)$, in the finite toroidal system, differ negligibly from those of the infinite system, $n_s(\mathbf{r}_1, \ldots \mathbf{r}_s | \infty)$, for values of $|\mathbf{r}_\alpha - \mathbf{r}_\beta| \leqslant L/2$ and s up to $s \leqslant L/a$. The error of a given correlation function behaves as $\exp[-\alpha_s L/a]$, where α_s is of order unity. This fact assures that, if $L \gg a$, the statistical distributions of the ions in any neighborhood of size $< L/2$ are practically identical in the ensemble of periodically continued neighborhoods and in the macroscopic system. Hence, in view of the locality principle demonstrated in section 2, the density of states $n(E)$ of the infinite system may be determined, via eq (3.5), from the density of states in the periodically continued neighborhoods. The error will be exponentially small in the quantity L/R or L/a, whichever is the smaller. Typically both a and R are of the order of 1 Å, so that one must work with neighborhoods of dimensions of several in order to obtain quantitatively useful results.

It is evident that this method will give exact results for perfectly periodic systems. Since it is also very accurate for highly disordered systems (small R), it should give good answers for most intermediate situations.

The ensemble of systems defined by eq (3.9) is a grand canonical ensemble in which the volume $\Omega_L (=L^3)$ is fixed while the numbers of particles N_j assumes all possible values. For a single species of atoms it has been found practically preferable to work with a periodically continued isothermal-isobaric ensemble, in which N is fixed but the volume Ω_L is variable. Here

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[5] Provided the forces between the scatterers are sufficiently short range.

[6] For the macroscopic system, one could of course equally well use a canonical distribution. However, in our local neighborhood theory, this would lead to unacceptable errors of order $1/N$, where N is a mean number of scatterers in Ω_L.

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a unit cell of volume Ω_L, with the N atoms in a configuration c must be given the weight

$$w_{\Omega_L, c} = \frac{A}{\Omega_L} \exp\left\{-\beta\left[\frac{1}{2}\sum_{\alpha, \beta}\varphi_{\alpha\beta}(\bar{\mathbf{r}}_{\alpha\beta}) - R\Omega_L\right]\right\} \quad (3.11)$$

where P is the pressure. The density of states of the actual macroscopic system is approximated by

$$n(E) \approx \int d\Omega_L \sum_c w_{\Omega_L, c} n(E; \Omega_L; c) \quad (3.12)$$

where $n(E; \Omega_L; c)$ is the density of states, per unit cell Ω_L, in the periodically continued neighborhoods. The normalization A of $w_{\Omega_L, c}$

$$\int d\Omega_L \sum_c w_{\Omega_L, c} = N_{\text{tot}}/N \quad (3.13)$$

where N_{tot} is the total number of scatterers in the macroscopic system. Again the convergence of (3.13) to the exact result is exponential, as for the case of the grand canonical ensemble.

4. Numerical Illustration

To illustrate the theory of the previous sections we have numerically studied the following model of a one-dimensional alloy:

$$H = -\frac{d^2}{dx^2} + \sum_\alpha \lambda_\alpha \delta(x - \alpha d) \quad (4.1)$$

where the distance between potentials, d, was taken as 1, and λ_α was taken, with equal probability, as -2 and -4. (This corresponds to a high temperature limit for the two different kinds of scatterers, an idealized model for ·crystalline Cu Au well above the ordering temperature.) Here the grand canonical method was appropriate. Two calculations were performed, with $L = 6$ and $L = 10$. Let us take the case $L = 6$. A typical, periodically continued neighborhood is shown schematically in figure 4. Each configuration of potentials in the fundamental interval $0 < x \leqslant 6$ has the same weight, 2^{-6}.

In this simple example all correlation functions are evidently exact, as long as the crystal sites considered are all contained in a single unit cell.
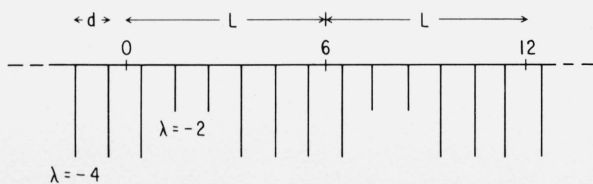
FIGURE 4. *A typical periodically continued neighborhood of the illustrative model.*

The density of states curves was calculated for each of the 2^6 configurations and then averaged. For $L = 10$ a sampling procedure was used. The results are shown in figure 5, together with the exact result obtained for the infinite system using the Schmidt method.[3] Our approximation reproduces quite accurately all the details of the density of states structure, even for $L = 6$. To obtain similar accuracy from a single randomly populated chain would require a length of the order of $L \approx 10^3$.
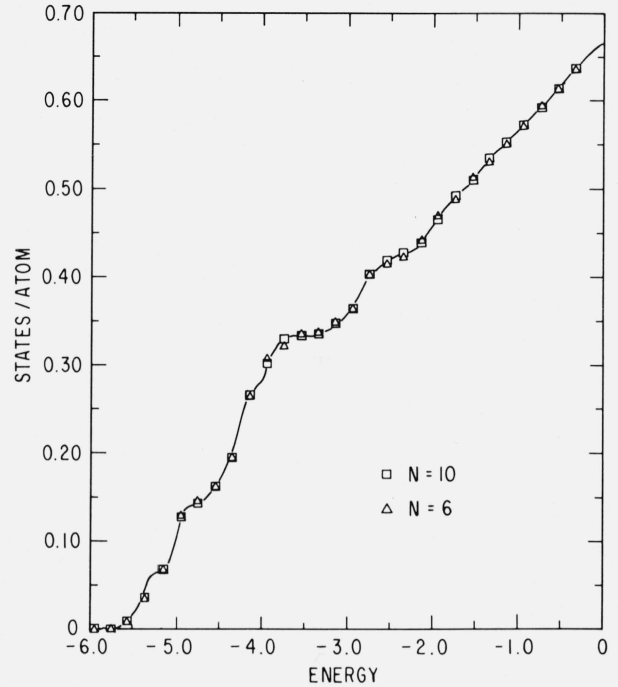
FIGURE 5. *Integrated density of states for binary alloy. The solid line is the exact result.*

5. Concluding Remarks

It is commonplace to emphasize the theoretical difficulties caused by disorder. In the present paper we draw attention to a favorable feature: For a highly disordered system the physical properties near a given point depend only on circumstances in a small neighborhood, whose dimension is of the order a mean free path. Consequently, a macro-system may be treated, so to speak, neighborhood by neighborhood and the macro-problem can be reduced to an ensemble of micro-problems. We have shown that the errors of such a procedure can be made to vanish exponentially with the size of the neighborhood. A numerical model calculation bears out these considerations.

A more complete account of this program will be published elsewhere.