

## CONTENTS

<b>Papers of Sir Sam Edwards reprinted, with permission, in this volume</b>	xi
<b>Contributing Authors</b>	xiii
<b>Foreword</b> <i>P.-G. de Gennes</i>	1
<b>Preface</b>	3
<b>1 Reprint: A new method for the evaluation of electric conductivity in metals</b> <i>S. F. Edwards</i>	10
<b>2 Impurity diagrammatics and the physics of disordered metals</b> <i>D. Khmel'nitskii</i>	23
References	28
<b>3 Reprint: The statistical dynamics of homogeneous turbulence</b> <i>S. F. Edwards</i>	30
<b>4 Sam Edwards and the turbulence theory</b> <i>K. R. Sreenivasan and G. L. Eyink</i>	66
4.1 Introduction	66
4.2 Contributions of Edwards	67
4.3 The white-noise passive scalar model	73
4.4 Navier–Stokes turbulence	77
4.5 Conclusion	79
References	80
<b>5 Reprint: The statistical mechanics of polymers with excluded volume</b> <i>S. F. Edwards</i>	86
<b>6 The entry of field theory into polymer science</b> <i>R. C. Ball</i>	99
6.1 Background	99
6.2 The new polymer theory, and excluded volume	100

6.3 Polymer solutions	101
6.4 Mathematical aspects	102
6.5 Future directions	104
References	106
<b>7 Reprint: The theory of polymer solutions at intermediate concentration</b>	
<i>S. F. Edwards</i>	108
<b>8 The coarse grained approach in polymer physics</b>	125
<i>Y. Oono and T. Ohta</i>	
8.1 Introduction	125
8.2 Edwards model and cutoff	125
8.3 Edwards goes beyond dilute solutions	127
8.4 Semidilute solutions	131
8.5 Block copolymer melts	134
8.6 Some reflections on models	139
References	142
<b>9 Reprint: Statistical mechanics with topological constraints: II</b>	
<i>S. F. Edwards</i>	144
<b>10 Notes on ‘Statistical mechanics with topological constraints: I &amp; II’</b>	159
<i>E. Witten</i>	
References	162
<b>11 Reprint: Theory of spin glasses</b>	
<i>S. F. Edwards and P. W. Anderson</i>	164
<b>12 Remarks on the Edwards–Anderson paper</b>	175
<i>P. W. Anderson</i>	
References	177
<b>13 Edwards–Anderson: Opening up the world of complexity</b>	179
<i>D. Sherrington</i>	
13.1 Introduction	179
13.2 Edwards-Anderson spin glass and beyond	181
13.2.1 Edwards-Anderson	181
13.2.2 Exactly soluble model	181
13.2.3 Beyond spin glasses	183
13.2.4 Dynamics	185

13.2.5	Edwards-Anderson again	187
13.2.6	Mathematics	188
13.3	Concluding Remarks	188
	References	189
<b>14</b>	<b>The overlap in glassy systems</b>	<b>192</b>
	<i>G. Parisi</i>	
14.1	Introduction	192
14.2	The original definition of the overlap	193
14.2.1	Only one state	193
14.2.2	Many states	195
14.2.3	A soluble model	197
14.3	The thermodynamic definition of the overlap	198
14.4	The two susceptibilities	199
14.5	Virtual probabilities	202
14.5.1	General considerations	202
14.5.2	A first attempt	202
14.5.3	Generalized susceptibilities	203
14.5.4	Local overlap	205
14.6	Fluctuation-dissipation relations	207
14.6.1	The global fluctuation-dissipation relations	207
14.6.2	The local fluctuation-dissipation relations	208
14.7	Conclusions	209
	References	210
<b>15</b>	<b>Theory of random solid states</b>	<b>212</b>
	<i>M. Mézard</i>	
15.1	A few landmarks	212
15.1.1	Structural glasses	212
15.1.2	From rubber to spin glass and proteins	214
15.1.3	Networks of interacting individuals: global equilibrium	216
15.1.4	Networks of interacting individuals: dynamics	219
15.2	Tools and concepts	221
15.2.1	Statistical description	221
15.2.2	Physics without symmetry: equilibrium	223
15.2.3	Replicas	224
15.2.4	Physics without symmetry: dynamics	227
15.2.5	Simulations	229
15.3	Directions	229
15.3.1	Physical glasses	230
15.3.2	Random systems	231
15.3.3	The unreasonable inefficiency of mathematics	232
15.3.4	Consilience	233
	References	235

<b>16 Reprint: The theory of rubber elasticity</b>	
<i>R. T. Deam and S. F. Edwards</i>	237
<b>17 Sam Edwards and the statistical mechanics of rubber</b>	275
<i>P. M. Goldbart and N. Goldenfeld</i>	
17.1 Introduction	275
17.2 Edwards' formulation of the statistical mechanics of vulcanized macromolecular systems	280
17.2.1 Idealized model	280
17.2.2 Quenched disorder: treating the cross-links statistically	282
17.2.3 Handling the quenched disorder via replicas	282
17.2.4 Modelling the statistics of the cross-links	284
17.2.5 Effective pure theory of coupled replicas	286
17.3 Predictions of the Deam–Edwards theory	287
17.4 Nature of the vulcanization transition	288
17.5 The emergent amorphous solid state	291
17.5.1 Microscopic character	291
17.5.2 Macroscopic character	293
17.5.3 Goldstone fluctuations; low dimensions	294
17.6 Ongoing directions: Dynamics at the liquid to solid transition	295
17.7 Concluding remarks	296
References	297
<b>18 Reprint: Dynamics of concentrated polymer systems</b>	
<b>Part 2.—Molecular motion under flow</b>	
<i>M. Doi and S. F. Edwards</i>	300
<b>19 The Doi–Edwards theory</b>	318
<i>W. W. Graessley and T. C. B. McLeish</i>	
References	326
<b>20 Reprint: The surface statistics of a granular aggregate</b>	
<i>S. F. Edwards and D. R. Wilkinson</i>	328
<b>21 The surface statistics of a growing aggregate</b>	344
<i>M. Kardar</i>	
21.1 The Edwards–Wilkinson equation	344
21.1.1 Derivation	344
21.1.2 Results	345
21.1.3 Numerical simulations	346

21.2	The Kardar–Parisi–Zhang equation	347
21.2.1	Derivation	347
21.2.2	Scaling behaviour in one dimension	349
21.2.3	Conservative growth	350
21.2.4	Experiments	351
21.3	Directed paths in random media	352
21.3.1	The Cole–Hopf transformation	352
21.3.2	Directed polymers	354
21.3.3	The replica approach	355
21.3.4	Many directed polymers	357
21.4	Perspectives	359
21.4.1	Sequence alignment	359
21.4.2	Textural growth	360
	References	361
<b>22</b>	<b>Reprint: Theory of powders</b>	
	<i>S. F. Edwards and R. B. S. Oakeshott</i>	363
<b>23</b>	<b>Building a thermodynamics on sand</b>	375
	<i>J. Kurchan</i>	
23.1	Introduction	375
23.2	Compact granular matter is an athermal glass. ‘Granularizing’ simple glass models	377
23.3	The assumption	378
23.4	Caveat I. Flat distributions are not generic out of equilibrium	378
23.5	Caveat II. Convection currents, shear bands, inhomogeneities, insufficient relaxation	379
23.6	Encouraging news from the analytic front	380
23.6.1	Closure approximations	380
23.6.2	The athermal situation	383
23.6.3	Intrinsic limitations of the approach	384
23.7	Towards realistic models and experiment	384
23.7.1	Effective temperatures	385
23.7.2	Tests of the flat measure hypothesis	385
23.8	Inherent structures	386
23.9	Counter-examples	387
23.10	Conclusions	388
	References	388
<b>24</b>	<b>Reprint: The transmission of stress in an aggregate</b>	
	<i>S. F. Edwards and R. B. S. Oakeshott</i>	391

<b>25 Granular media: Three seminal ideas of Sir Sam</b>	397
<i>J.-P. Bouchaud and M. E. Cates</i>	
25.1 Introduction	397
25.2 Statistical mechanics of granular matter	399
25.2.1 Force chains and arching granular assemblies	399
25.2.2 Marginal coordination of granular packings	400
25.2.3 Thermodynamics without temperature: the Edwards ensemble	401
25.3 Some related developments	403
25.3.1 The discrete scalar model	404
25.3.2 Continuum closure schemes for granular stresses	406
25.3.3 Slow compaction and dynamics	410
25.4 Concluding remarks	411
References	412
<b>Chapters on the Edwardsian approach to research</b>	417
<b>26 The case for Edwardsian research in solid mechanics: A sermon</b>	419
<i>J. S. Langer</i>	
References	426
<b>27 A scientist for all seasons</b>	428
<i>G. Allen</i>	
<b>Editors' acknowledgements</b>	437
<b>Index</b>	439

1

REPRINT

A NEW METHOD FOR THE EVALUATION  
OF ELECTRIC CONDUCTIVITY IN METALS

by

S. F. Edwards

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[ 1020 ]

## A New Method for the Evaluation of Electric Conductivity in Metals†

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### ABSTRACT

A method is developed which allows the evaluation of the closed formal expressions for electrical conductivity which have recently been developed by several authors. The case of a random set of scatterers is treated in detail and the formal solution made to yield directly the solution to the Boltzmann equation. A brief mention of the application of this method to liquids and alloys is made.

### § 1. INTRODUCTION

RECENTLY it has been realized by several workers (Nakano 1956, Kubo 1956, Kohn and Luttinger 1957, Greenwood 1958), that the electric conductivity in, say, a metal can be written down in a closed formal expression, without going through the intermediate form of deriving a transport equation, and moreover these closed forms are exact. The usual derivation of a transport equation (cf. Peierls 1955) is rather limited in its applicability and cannot in any simple way be extended to the cases of alloys and liquids etc., and moreover, even where it is usually used, it is not at all clear (see e.g. Peierls 1955, p. 123) that there are not temperature dependent corrections which would entirely invalidate the usual solution. Now the formal exact solutions avoid all this, but carry the difficulty that they are still in a rather abstract form, and it is not clear how they are to be evaluated. This paper is concerned with the evaluation of these formulae, and will show that they can readily give the same result as the usual transport equation where the latter has been assumed to be correct, and thus dispose of the possibility of temperature dependent corrections. The use of the exact formulation in new problems will only be very briefly mentioned in this paper, and since the present object is only to illustrate the method, the simplest problem, that of the conductivity of electrons scattered by a random set of scattering centres, will be discussed.

### § 2. FORMULATION OF THE PROBLEM

The starting point will be the formula of Greenwood and Peierls, which states that the conductivity tensor is given by

$$\sigma_{\mu\nu} = -2\pi e^2 \hbar \sum_{n,m} v_{nm}^{\mu} v_{mn}^{\nu} \delta(E_n - E_m) \frac{\partial f}{\partial E_n}, \quad \dots \quad (1)$$

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† Communicated by Professor R. E. Peierls, C.B.E., F.R.S.



*On a New Method for the Evaluation of Electric Conductivity in Metals* 1021

where  $v_{mn}^\mu$  is the matrix element of velocity,  $f$  the electron distribution function, and the  $\delta$  function is to be understood in the sense that the limit  $E_n \rightarrow E_m$  is taken after the system is considered so large that always there are many levels between  $E_n$  and  $E_m$ . This form as it stands is not suitable for computation, so it is rearranged by first writing it out in full :

$$v_{nm}^\mu v_{mn}^\nu = -\frac{\hbar^2}{m^2} \int \psi_n(x) \frac{\partial \psi_n^*(x)}{\partial x_\mu} d^3x \int \psi_m(y) \frac{\partial \psi_m^*(y)}{\partial y_\nu} d^3y. \quad (2)$$

Introduce units so that  $(2m/\hbar^2)^{-1/2} = 1$ , then

$$\begin{aligned} \sum_{m,n} v_{nm}^\mu v_{mn}^\nu = & -\left(\frac{8\pi e^2}{\hbar}\right) \sum_{n,m} \iiint \frac{\partial}{\partial x_\mu} \{\psi_n(x) \psi_n^*(x')\} \frac{\partial}{\partial y_\nu} \{\psi_m(y) \psi_m^*(y')\} \\ & \times \delta(x' - y) \delta(y' - x) d^3x d^3y d^3x' d^3y'. \end{aligned} \quad (3)$$

Now  $\sum_n \psi_n(x) \psi_n^*(x') \delta(E - E_n)$  is a Green function, the solution of the homogeneous Schrödinger equation. If the Schrödinger equation for  $\psi$  is

$$(H - E)\psi = 0 \quad (4)$$

and the Green functions  $G_+$ ,  $G_-$  are given by

$$\left. \begin{aligned} (H - E + i\epsilon)G_+(x, x') &= \delta(x - x') \\ (H - E - i\epsilon)G_-(x, x') &= \delta(x - x') \end{aligned} \right\} \quad (5)$$

where  $\epsilon$  is an infinitesimal quantity used to define the contour defining the  $G_+$ ,  $G_-$ , then

$$G_+(x, x') = \sum_n \psi_n(x) \psi_n^*(x') (E - E_n + i\epsilon)^{-1} \quad (6)$$

$$G_-(x, x') = \sum_n \psi_n(x) \psi_n^*(x') (E - E_n - i\epsilon)^{-1}. \quad (7)$$

From these the sum and the difference can be made

$$\begin{aligned} G_+ - G_- &= 2\pi i \sum_n \psi_n(x) \psi_n^*(x') \delta(E - E_n) \\ &= 2\pi i G \end{aligned} \quad (8)$$

$$\begin{aligned} G_+ + G_- &= 2\pi i P \sum_n \psi_n(x) \psi_n^*(x') (E - E_n)^{-1} \\ &= 2\pi i G_P \end{aligned} \quad (9)$$

$P$  standing for principal part.

In the absence of potentials these functions are just

$$\begin{aligned} (4\pi r)^{-1} e^{i\sqrt{E}r}, \quad (4\pi r)^{-1} e^{-i\sqrt{E}r}, \quad i(4\pi^2 r)^{-1} \sin \sqrt{E}r, \\ i(4\pi^2 r)^{-1} \cos \sqrt{E}r, \quad (r = |\mathbf{X} - \mathbf{X}'|), \end{aligned} \quad (10)$$

assuming that one already is dealing with an infinite system, i.e., a continuum of energy so that the sums over  $n$  become integrals. So if  $G$  is used for the difference of  $G_+$  and  $G_-$ , (8) the sine like function, and also

we now specialize to the case of a diagonal  $\sigma$ , we have

$$\sigma = \frac{1}{3} \left( \frac{8\pi e^2}{\hbar} \right) \sum_{n,m} \iiint (\partial G_n(x, x') / \partial x_\mu) (\partial G_m(y, y') / \partial y_\mu) \times \delta(E_n - E_m) (\partial f / \partial E_n) \delta(x' - y) \delta(y' - x) d^3x d^3y d^3x' d^3y' \quad (11)$$

where  $G_n(x, x')$  is  $G(E_n; x, x')$ . The problem now is to find  $G$  and  $f$  in the presence of the scattering potential, and finally to average  $\sigma$  over all configurations of this potential†. It is convenient to express this in the following way: the Schrödinger equation is now

$$(\nabla^2 - E \pm i\epsilon + V(\mathbf{x}))G_\pm(x, x') = \delta(x - x'), \quad (12)$$

where

$$V(\mathbf{x}) = \sum_{\alpha} u(\mathbf{x} - \mathbf{X}_\alpha) \quad (13)$$

$\mathbf{X}_\alpha$  being the positions of the scattering centres, and  $u$  the potential they exert on the electron. It is convenient to use the Fourier transform of this potential, defining

$$\rho_{\mathbf{k}} = \sum_{\alpha} e^{i\mathbf{k}\mathbf{X}_\alpha}, \quad (14)$$

$$V(x) = \int u(k) e^{i\mathbf{k}\mathbf{x}} \rho_{\mathbf{k}}^* d^3k. \quad (15)$$

Now if the  $\mathbf{X}_\alpha$  are random, it can be shown by standard probability theory that the distribution function for the  $\rho$ 's is

$$\left. \begin{aligned} P(\rho_{\mathbf{k}}) &= \xi \exp \left[ - \iint R(\mathbf{k}, \mathbf{j}) \rho_{\mathbf{k}} \rho_{\mathbf{j}} d^3k d^3j \right. \\ &\quad \left. - \iiint Q(\mathbf{k}, \mathbf{j}, \mathbf{l}, \mathbf{m}) \rho_{\mathbf{k}} \rho_{\mathbf{j}} \rho_{\mathbf{l}} \rho_{\mathbf{m}} d^3k d^3j d^3l d^3m - \dots \right] \\ R(\mathbf{k}, \mathbf{j}) &= N^{-1} \delta(\mathbf{k} + \mathbf{j}) + O(N^{-2}) \\ Q(\mathbf{k}, \mathbf{j}, \mathbf{l}, \mathbf{m}) &= N^{-2} \left( \frac{1}{24} \right) \left[ \delta(\mathbf{k} + \mathbf{j} + \mathbf{l} + \mathbf{m}) - 3 \sum_{\text{perm}} \delta(\mathbf{k} + \mathbf{j}) \delta(\mathbf{l} + \mathbf{m}) \right] + O(N^{-3}) \end{aligned} \right\}, \quad (16)$$

where  $N$  is the total number of scatterers, and  $\xi$  the normalization to give total probability unity. When  $N$  is large, this can be used with  $k$  running over the whole continuum of  $k$  space. So we reach the final formula

$$\sigma = \frac{1}{3} \left( \frac{8\pi e^2}{\hbar} \right) \int \dots \int \xi P(\rho_{\mathbf{k}}) (\partial G_n(x, x') / \partial x_\mu) (\partial G_m(y, y') / \partial y_\mu) \times \delta(E_n - E_m) (\partial f / \partial E_n) \delta(x - y') \delta(y - x') d^3x d^3y d^3x' d^3y' \Pi d\rho_{\mathbf{k}} d\rho_{\mathbf{k}}^*. \quad (17)$$

This form has the great advantage that it is essentially the same form as that of electrons interacting with the quantized electromagnetic field, and so techniques for evaluating it are already in existence. Moreover, there are none of the divergence problems of electrodynamics here and the various approximate techniques of electrodynamics can be applied with confidence.

† The meaning of the averaging is discussed in detail by Kohn and Luttinger (1957).

### § 3. EVALUATION

The essential difference between (1) and (17) is that the averaging over the scatterers can be carried out before the integrations over coordinates and allows manipulations which are meaningless when applied to (1). Although one can, on the basis of (17), derive integral equations for the average of  $G(x, x')$ ,  $G(y, y')$ , it is simplest to consider the perturbation expansion of the  $G$ 's, from which the structure of the integral will become clear. However, one should emphasize that there is no need to approach the evaluation by a perturbation approach and the results to be obtained below can be got directly.

Consider firstly a simpler problem, that of obtaining the average of just one  $G$  alone. This is the difference of the averages of  $G_+$  and  $G_-$ , which are more convenient to consider. Now in perturbation theory one can write, using  $G^{(0)}$  for the  $\rho$ -independent functions (10),

$$G_+(x, x') = G_+^{(0)}(x, x') - \iint G_+^{(0)}(x, y) u(\mathbf{k}) e^{i\mathbf{k}\mathbf{y}} \rho_{\mathbf{k}}^* G_+^{(0)}(y, x') d^3y d^3k \\ + \iiint \iiint G_+^{(0)}(x, y) u(\mathbf{k}) e^{i\mathbf{k}\mathbf{y}} \rho_{\mathbf{k}}^* G_+^{(0)}(y, z) u(\mathbf{j}) e^{i\mathbf{j}\mathbf{z}} \rho_{\mathbf{j}}^* G_+^{(0)}(z, x') \\ \times d^3y d^3z d^3k d^3j + \dots \quad (18)$$

Upon averaging, using brackets for average value

[illegible]

$$\langle \rho_k \rho_i \rangle = N \delta(\mathbf{k} + \mathbf{j}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

$$\langle \rho_{\mathbf{k}} \rho_{\mathbf{j}} \rho_{\mathbf{l}} \rho_{\mathbf{m}} \rangle = N^2 \sum_{\text{perm}} \delta(\mathbf{k} + \mathbf{j}) \delta(\mathbf{l} + \mathbf{m}) + N \delta(\mathbf{k} + \mathbf{j} + \mathbf{l} + \mathbf{m}) \quad . \quad (21)$$

and so on, neglecting terms relatively of order  $N^{-1}$ . This can be obtained directly of course, without using the expansion (16). This gives

$$\begin{aligned} \langle G_+(x, x') \rangle = & G_+^{(0)}(x, x') + \iiint NG_+^{(0)}(x, y) e^{ik(y-z)} u^2(\mathbf{k}) \\ & \times G_+^{(0)}(y, z) G_+^{(0)}(z, x') d^3y d^3z d^3k + \dots \quad (22) \end{aligned}$$

This is conveniently expressed in diagrams, which are slightly different from those of electrodynamics. Consider  $G(x, x')$  before averaging, draw a full line for every  $G_+^{(0)}$  and a dotted line for every  $u\rho$ . Then the expansion of  $G(x, x')$  is written

$$G_+ = \text{---} + \text{---} \overset{\cdot}{\underset{\cdot}{\mid}} + \text{---} \overset{\cdot}{\underset{\cdot}{\mid}} \overset{\cdot}{\underset{\cdot}{\mid}} + \text{---} \overset{\cdot}{\underset{\cdot}{\mid}} \overset{\cdot}{\underset{\cdot}{\mid}} \overset{\cdot}{\underset{\cdot}{\mid}} + \text{---} \overset{\cdot}{\underset{\cdot}{\mid}} \overset{\cdot}{\underset{\cdot}{\mid}} \overset{\cdot}{\underset{\cdot}{\mid}} \overset{\cdot}{\underset{\cdot}{\mid}} + \dots \quad (23)$$

$$\langle G_+ \rangle = \text{---}(\alpha) + \text{---}(\beta)$$

$$+ \left\{ \begin{array}{l} \text{(e)} \\ \text{(g)} \\ \text{(d)} \end{array} \right. + \text{(h)} + \dots \quad (24)$$

$$\text{---} + \text{---} \text{ (loop) } + \text{---} \text{ (two loops) } + \quad (26)$$
$$\left(G_+^{(0)-1}(p) - N \int G_+^{(0)}(q) u^2(\mathbf{p}-\mathbf{q}) d^3q\right)^{-1}. \quad (27)$$

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Since  $G_+^{(0)}(q) = (2\pi)^{-3}(q^2 - E + i\epsilon)^{-1}$  the integral can be written

$$\frac{1}{2}P \int G_+(q)u^2(p-q) d^3q + \frac{i\pi}{(2\pi)^3} \int \delta(q^2 - E)u^2(p-q) d^3q. \quad (28)$$

If now  $u$  is taken as isotropic so that  $u^2$  is  $u^2(p^2 + q^2 - 2pq \cos \theta)$  this can be written as  $A + iB$ , where  $A, B$  are real

$$A = \frac{1}{2}NP \int (q^2 - E)^{-1}u^2(p^2 + q^2 - 2pq \cos \theta) d^3q \quad . \quad . \quad . \quad (29)$$

$$B = (2\pi)^{-3}\pi N \int \delta(q^2 - E)u^2(p^2 + q^2 - 2pq \cos \theta) d^3q. \quad . \quad . \quad (30)$$

These can be expanded as series in  $p^2 - E$  so that this approximation to  $\langle G \rangle^{-1}$  is in the form

$$(p^2 - E + i\epsilon + a_1 + ib_1 + (p^2 - E)(a_2 + ib_2) + \dots) \quad . \quad . \quad . \quad (31)$$

where

$$a_1 = \frac{1}{2}(2\pi)^{-3}NP \int (q^2 - E)^{-1}u^2(E + q^2 - 2q\sqrt{E} \cos \theta) \delta(p^2 - E) d^3q d^3p \quad (32)$$

$$b_1 = N\sqrt{E}(8\pi)^{-1} \int \sin \theta d\theta u^2(2E(1 - \cos \theta)). \quad . \quad . \quad . \quad (33)$$

$u^2$  is in fact the differential scattering probability in Born approximation,  $w_0(\theta) = (4\pi^2)^2 2\pi \hbar^{-1} u^2(2E(1 - \cos \theta))$

$$b_1 = (2\pi)^{-6} \sqrt{E} \hbar N \int \sin \theta w_0(\theta) d\theta. \quad . \quad . \quad . \quad (34)$$

A rather more refined treatment is to expand not in terms of  $p^2 - E$  but  $p^2 - E + a_1 + ib_1$  an important step in electrodynamics where only  $a_1 - E$  is defined, but here it makes little odds as we are anyway taking all the  $a$ 's to be small, and the effect of the terms  $a_2, b_2$  etc. will come out very small. So it has been found that this series summed gives effectively a complex displacement of the energy  $E$

$$\langle G_+(E) \rangle \cong G_+(E + \delta E) \quad . \quad . \quad . \quad . \quad (35)$$

where

$$\begin{aligned} (E + \delta E)^{1/2} &= (E + a_1 + ib_1)^{1/2} \\ &\cong \sqrt{E} + (a_1 + ib_1)/2\sqrt{E} \\ &= \sqrt{E'} + i\Gamma. \end{aligned} \quad . \quad . \quad . \quad . \quad (36)$$

So in configuration space

$$\langle G_+ \rangle = (4\pi r)^{-1} e^{-i\sqrt{(E')}r - \Gamma r} \quad . \quad . \quad . \quad . \quad (37)$$

(cf. Bardeen 1956). If this calculation had been performed for  $G_-$  the result would have been

$$\langle G_- \rangle = (4\pi r)^{-1} e^{i\sqrt{(E')}r - \Gamma r}. \quad . \quad . \quad . \quad . \quad (38)$$

Now consider to what extent one can take the forms (26), (37) as adequate approximations to the whole series. Consider first those terms containing one dot only, in particular the series


(39)

This series is in fact building up the exact scattering of one electron by one scattering centre, instead of its first Born approximation, and if instead of taking the unit



in the series (26) one took all one dot diagrams one would just replace the Born approximation scattering by the true differential scattering cross section in (34),  $w(\theta)$ . This can be important in strong interaction, and this way of looking at it will be valuable if one can think of the electron in strong interaction with the scattering centres one at a time, as is usually considered to be the case. In a dense system, however, the electron interacts with many centres at once, and one cannot disentangle the scattering with one centre from that of all the others, i.e. the other terms to be discussed below. Henceforward these diagrams will be ignored except inasmuch as the differential scattering cross section can be understood as the true one rather than Born approximation. Now turn to the other terms in (24), in particular, say,  $(\delta)$  and  $(\epsilon)$ . The electrical conductivity based on the approximate sum (31) and further calculations to be given below comes out to be of order  $\Gamma^{-1}$ , i.e. inversely with the square of the interaction. Terms like  $(\delta)$ ,  $(\epsilon)$  and the higher terms, if included, give a series in the interaction, but do not alter the first term which will still dominate the calculation. To see this it is perhaps simplest to look at  $G_+$  in configuration space. The series which has been considered so far (26) amounts to

$$(4\pi r)^{-1} e^{i\sqrt{E'}r - \Gamma r} = (4\pi r)^{-1} e^{i\sqrt{E}r} (1 + Lr + \frac{1}{2}L^2r^2 + \dots) \quad (40)$$

where

$$L = i(\sqrt{E'} - \sqrt{E}) - \Gamma. \quad (41)$$

The inclusion of terms like  $(\delta)$ ,  $(\epsilon)$  etc. adds in terms so that in first order  $Lr$  is corrected by a constant, in second order  $\frac{1}{2}L^2r^2$  is corrected by a term in  $r$ , and so on, always a power of  $r$  less in any order, so that summing on the basis of (31) one has

$$\langle G_+ \rangle = (4\pi r)^{-1} e^{i\sqrt{E'}r - \Gamma r} (1 + k_0r + k_1r^2 + \dots) \quad (42)$$

and, as will appear below, this affects the conductivity by second and higher terms in  $u^2$

$$\sigma \sim O(\Gamma^{-1}) + O(1) + O(\Gamma) + O(\Gamma^2) + \dots \quad (43)$$

Thus (37) is a good basis for the evaluation of  $\langle G_+ \rangle$  and hence, of course,  $\langle G \rangle$ .

To summarize in a rather formal way the above discussion, consider the identity

$$\begin{aligned} G_+(x, x') &= G_+^{(0)}(x, x') - \iint G_+^{(0)}(x, y) e^{ik_y u(\mathbf{k})} \rho_{\mathbf{k}} G_+^{(0)}(y, x') d^3y d^3k \\ &+ \iiint G_+^{(0)}(x, y) e^{ik_y u(\mathbf{k})} \rho_{\mathbf{k}} G_+^{(0)}(y, z) u(\mathbf{j}) e^{ijz} G_+(z, x') \\ &\times d^3y d^3z d^3k d^3j. \quad (44) \end{aligned}$$

Then

$$\begin{aligned} \langle G_+(x, x') \rangle &= G_+^{(0)}(x, x') - \iint G_+^{(0)}(x, y) e^{ik_y y} u(\mathbf{k}) \langle \rho_{\mathbf{k}} \rangle G_+^{(0)}(y, x') d^3 y d^3 k \\ &\quad + \iiint G_+^{(0)}(x, y) e^{ik_y y} u(\mathbf{k}) \langle \rho_{\mathbf{k}} G_+^{(0)}(y, z) u(\mathbf{j}) e^{ij_z z} \rho_{\mathbf{j}} G_+(z, x') \rangle \\ &\quad \times d^3 y d^3 z d^3 k d^3 j \quad . . . . . (45) \end{aligned}$$

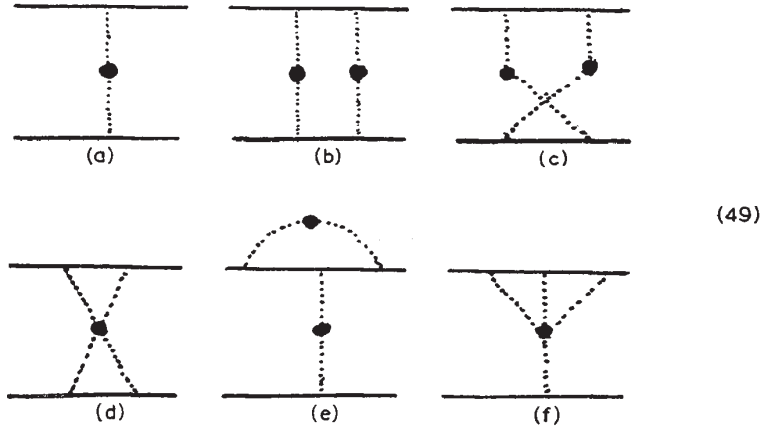
$$\begin{aligned} &= G_+^{(0)}(x, x') + \iiint G_+^{(0)}(x, y) v(\mathbf{k}) v(\mathbf{j}) e^{ik_y y + ij_z z} G_+^{(0)}(y, z) \\ &\quad \times \langle \rho_{\mathbf{k}} \rho_{\mathbf{j}} G_+(z, x') \rangle d^3 y d^3 z d^3 k d^3 j \quad . . . . . (46) \end{aligned}$$

$$= G_+^{(0)}(x, x') - \iint G_+^{(0)}(x, y) \Sigma(y, z) \langle G_+(z, x') \rangle d^3 y d^3 z, \quad . . . . . (47)$$

which defines  $\Sigma(y, z)$ . Then symbolically

$$[(G_+^{(0)})^{-1} + \Sigma] \langle G_+ \rangle = \delta. \quad . . . . . (48)$$

The discussion above has shown that when the interaction is weak, an evaluation of  $\Sigma$  by perturbation theory is adequate. So far all the discussion has concerned  $\langle G_+ \rangle$ , but (17) involves the evaluation of  $\langle G_n' G_m' \partial f / \partial E \rangle$ , and the two  $G$ 's and the  $f$  will interfere. The dependence of  $f$  upon the  $p$ 's in the averaging does not affect the answer in its leading term, so it is ignored for the present. Since the problem is already being considered for an infinitely large conductor the distinction between  $n$  and  $m$  can be dropped at this stage. Consider at first the quantity  $\langle G(x, x') G(y, y') \rangle$ . In terms of the diagrams, this consists of two full lines, with dotted lines leaving and entering both, in particular, in addition to the types of series (24) one also has types



Types (d), (f) clearly belong to the same category as those of (24,  $\lambda$ ) and will be considered no further. Also disregard type (e) which is an interference between type ( $\alpha$ ) and ( $\beta$ ), and corresponds to the Lamb shift in electrodynamics: it can readily be found to be small when the interaction is weak. Of the remainder, types (a), (b) are again the first two of a simple

series analogous to  $(\beta)$ ,  $(\gamma)$  of (24). Assuming then that terms like  $(a)$ ,  $(b)$  do not interfere with terms like  $(\beta)$ ,  $(\gamma)$  one has the equation for  $\langle GG \rangle$ :

$$\begin{aligned} \langle G(x, x')G(y, y') \rangle &= \langle G(x, x') \rangle \langle G(y, y') \rangle \\ &+ N \iiint \langle G(x, z) \rangle \langle G(y, w) \rangle u^2(\mathbf{k}) \\ &\quad \times e^{i\mathbf{k}(\mathbf{x}-\mathbf{w})} \langle G(z, x')G(w, y') \rangle d^3k d^3z d^3w, \quad (50) \end{aligned}$$

or in the spirit of (48) the exact equation can be written symbolically in terms of a generalized 'interaction'  $I$

$$\langle GG \rangle = \langle G \rangle \langle G \rangle + \langle G \rangle \langle G \rangle I \langle GG \rangle \quad (51)$$

and as in (48), by explicit calculation of the errors, one finds that  $I$  can be evaluated by perturbation theory if the interaction is weak. The first approximation, the sum of  $(a)$ ,  $(b)$  . . . , is then (51) with

$$I(\alpha, \beta) = N \int d^3k u^2(\mathbf{k}) e^{i\mathbf{k}(\alpha-\beta)}. \quad (52)$$

The quantity required has  $x' = y$ ,  $y' = x$ , so let  $\Delta$  be  $\langle GG \rangle$  in this case. Then if  $\Delta$  is written in momentum space, the quantity required in (17) is, where  $\Omega$  is the total volume,

$$\Omega \int \mathbf{p} \cdot \mathbf{q} \Delta(\mathbf{p}, \mathbf{q}) d^3p d^3q \quad (53)$$

where (52) becomes, putting

$$\langle G(\mathbf{p}) \rangle \langle G(-\mathbf{p}) \rangle = g(\mathbf{p}) \quad (54)$$

$$\Delta(\mathbf{p}, \mathbf{q}) = g(\mathbf{p})\delta(\mathbf{p} - \mathbf{q}) + N \int g(\mathbf{p})u^2(\mathbf{p} - \mathbf{s})\Delta(\mathbf{s}, \mathbf{q}) d^3s. \quad (55)$$

Let

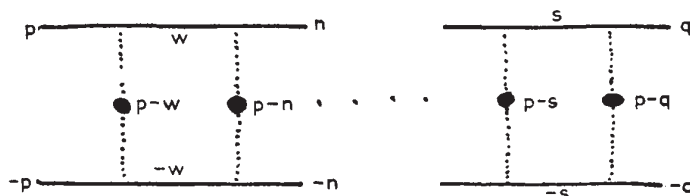
$$\int \mathbf{p} \cdot \mathbf{q} \Delta(\mathbf{p}, \mathbf{q}) d^3q = K(\mathbf{p}) \quad (56)$$

then

$$K(\mathbf{p}) = p^2 g(\mathbf{p}) + N \int g(\mathbf{p})u^2(\mathbf{p} - \mathbf{s})\mathbf{p} \cdot \mathbf{q} \Delta(\mathbf{s}, \mathbf{q}) d^3s d^3q \quad (57)$$

$$\begin{aligned} &= p^2 g(\mathbf{p}) + 2\pi N \int g(\mathbf{p})u^2(p^2 + \delta^2 - 2ps \cos \theta) \cos \theta \sin \theta \\ &\quad \times K(\mathbf{s}) s^2 ds d\theta. \quad (58) \end{aligned}$$

The fact that  $\mathbf{p} \cdot \mathbf{q} = pq \cos \theta_{pq}$  effectively contributes  $pq \cos \theta_{ps}$  is seen by writing all the quantities concerned in spherical harmonics, or perhaps simpler by considering the series of which (52) is the sum, consisting of terms like





The integration over  $\mathbf{q}$  with  $\cos \theta_{pq}$  leaves a  $\cos \theta_{ps}$  for the  $s$  integration, and so right through the diagram, which is in effect (58).

Now  $g(p)$ , apart from the displacement  $\Gamma$  is just a function with  $p = \sqrt{E}$  or more accurately  $p = \sqrt{E'}$ .  $K(p)$  has essentially this same feature, so to the accuracy that has been used so far, the solution of (58) can be written down at once

$$K(p) = p^2 g(p) \left[ 1 - 2\pi N \int u^2(2E(1 - \cos \theta)) \cos \theta \sin \theta \int q(s) \delta^2 ds \right]^{-1}. \quad (59)$$

The integral of  $K$  can be obtained by contour integration or by the discussion below in equations (64)–(66).

$$\int K(p) d^3p = \frac{E'/2\Gamma'}{1 - \Gamma'/\Gamma} \quad . \quad . \quad . \quad . \quad . \quad (60)$$

$$= \frac{E'}{2} (\Gamma - \Gamma')^{-1} \quad . \quad . \quad . \quad . \quad . \quad (61)$$

where

$$\Gamma' = (8\pi)^{-1} N \hbar \int u^2(2E'(1 - \cos \theta)) \sin \theta \cos \theta d\theta \quad . \quad . \quad (62)$$

or in the notation of (34)

$$\Gamma' = \frac{1}{2} (2\pi)^{-6} N \hbar \int \cos \theta \sin \theta w_0(\theta) d\theta. \quad . \quad . \quad . \quad . \quad (63)$$

It is perhaps useful to look at (60) in configuration space. Without scattering the conductivity is

$$\sigma = \frac{1}{3} \left( \frac{8\pi e^2}{\hbar} \right) \frac{\Omega}{(2\pi)^4} \sum_E \int \nabla \frac{\sin \sqrt{E}r}{r} \nabla \frac{\sin \sqrt{E}2}{r} (\partial f / \partial E) d^3r. \quad (64)$$

This diverges at large distances where the integral over  $r$  looks like

$$\sim \int^\infty dr.$$

When the scattering is introduced, the term  $\sin \sqrt{E}r$  is replaced by  $\sin \sqrt{E'}r e^{-\Gamma' r}$  and also the averaging process introduces the cross term  $e^{\Gamma' r}$  giving altogether, at large distances,

$$\int e^{-2(\Gamma - \Gamma')r} dr \quad . \quad . \quad . \quad . \quad . \quad (65)$$

$$\sigma = \Omega e^2 / (12\pi^2 \hbar (\Gamma - \Gamma')). \quad . \quad . \quad . \quad . \quad (66)$$

This, of course, is the usual answer (cf. Peierls 1955, eqns. (6.16), (6.20)); Peierls  $w$  is our  $Nw/\Omega$ , in particular for free electrons where  $\partial f / \partial E$  is approximately a  $\delta$  function at the Fermi surface, so integration over the Fermi surface gives the final result

$$\sigma = e^2 n_e \left( 4\pi m n_s \int w(\theta) (1 - \cos \theta) \sin \theta d\theta \right)^{-1} \quad . \quad . \quad . \quad (67)$$

where  $n_e$  is the density of electrons, and  $n_s$  the density of the scatterers.

The dependence of  $f$  upon the configuration of scatterers can be expressed by expanding it in a power series in the density of scatterers and adding in the terms so produced. These corrections are of the same order as those in (43), and since they are well defined at  $T=0$ , do not involve the temperature in any critical form.

It is worth remarking that in averaging over all configurations, one includes those configurations for which the conductivity is infinite, for example an ordered lattice system. The method of calculating presented here automatically gives these configurations negligible weight, but a rigorous treatment would require a more careful treatment.

#### § 4. DISCUSSION

It has been shown that the exact formal solution of the equation of motion can be evaluated to give the usual solution of the Boltzmann transport equation, and within the framework of weak interaction it is quite easy to write down higher order corrections, though of course these rapidly become very numerous. Of more interest is the possibility of evaluating formula (11) in cases where perturbation theory is not applicable. An example, which is still far from being the most general state of affairs but is of physical interest, is the case when the distribution of scatterers (which may be lattice vibrations, etc.) is known through a partition function, and the electrons still interact weakly with the scattering centres. This is a model of a liquid or an alloy. For a liquid, eqns. (20), (21) and so on, are not satisfied, and the averages can only be found from the partition function. If it could be assumed to a reasonable degree of approximation that

$$\langle \rho_{\mathbf{k}} \rho_{\mathbf{j}}^* \rho_{\mathbf{l}} \rho_{\mathbf{m}}^* \rangle = \sum_{\text{perm}} F(\mathbf{k} - \mathbf{j}) F(\mathbf{l} - \mathbf{m}) \quad . . . . (68)$$

where

$$F(\mathbf{k} - \mathbf{j}) = \langle \rho_{\mathbf{k}} \rho_{\mathbf{j}}^* \rangle \quad . . . . . (69)$$

then one could immediately write down the conductivity by replacing

$$\int w(\theta)(1 - \cos \theta) \sin \theta d\theta \quad . . . . . (70)$$

by

$$\int F(2E(1 - \cos \theta)) w(\theta)(1 - \cos \theta) \sin \theta d\theta \quad . . . (71)$$

in (67). Since one is dealing with smooth averages this approximation may be adequate for this problem, even if it is not so for the theory of liquids as a whole. In general, however, the conductivity will involve not only the two body correlation function  $F$ , which is available experimentally, but the whole partition function, which at present is not available. There are models available for alloys, however, in particular for super lattice forming alloys and this problem is being considered further. Methods are in existence for evaluation of formulae like (17) in cases where perturbation methods are inapplicable, but a discussion of these will be left until they have been successfully applied.

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