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Series Editor: Professor Douglas F Brewer, M.A., D.Phil.
Professor of Experimental Physics, University of Sussex

THE PHYSICS OF
STRUCTURALLY DISORDERED
MATTER:

AN INTRODUCTION

N E CUSACK

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AN INTRODUCTION

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ADAM HILGER, BRISTOL AND PHILADELPHIA

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PREFACE

In this book I have set out to introduce the physics of structurally disordered matter to those who are starting research in some aspect of this vast field, or considering whether to start. I have tried to write the book I wish had been available for my research students—not to speak of myself—when I took up experiments on liquid metals many years ago.

Those who have already begun research in, say, thermal motion in metallic glasses will be rapidly acquiring much more expert knowledge than this introduction offers. I have assumed, however, that this means they will be more, not less, likely to be interested in some other (but possibly related) aspects of some other (but not wholly dissimilar) systems; say, electronic motion in liquid alloys.

I also hope the book might be a useful source for lecturers in universities and polytechnics who like the idea of introducing more about disordered systems into their courses on condensed matter than is usual at present.

It would not be difficult to compile an 'anti-index' of subjects which might have been in the book but are not: liquid crystals, liquid helium, polymers, ionic melts and other things of which I regret the absence. Selection was dictated by the ratio of subject matter to available time—a parameter which showed an alarming tendency to diverge and needed a somewhat arbitrary cut-off.

There should be a word about the references. For the most part they are simply those I found useful myself. However, they are numerous and I should be surprised if they do not help a reader new to the field to become rapidly involved in the literature. This I took to be one of the functions of an Introduction.

I am not particularly attracted to formal dedications but would like to add that while writing the book I often thought of my research students and collaborators, and of the pleasure of working with them.

N E Cusack
March 1986

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Mr Dick Fuller spent much time and photographic expertise preparing diagrams and I am very grateful to him too.

A great many publishers and authors gave permission to reproduce published diagrams and graphs and this help is acknowledged appropriately elsewhere.

N E Cusack
March 1986

ABBREVIATIONS AND ACRONYMS

Abbreviation or acronym	Meaning	First mentioned or defined in section
ACAR	Angular correlation of annihilation radiation	7.6
ARUPS	Angle-resolved ultraviolet photoemission spectroscopy	7.6
BIS	Bremsstrahlung isochromat spectroscopy	11.8
BGY	Born-Green-Yvon	5.3
CA	Cluster aggregation	2.9
CPA	Coherent potential approximation	7.2
CRN	Continuous random network	2.6
CS	Carnahan-Starling	4.3
CSRO	Chemical short-range order	1.7
CVD	Chemical vapour deposition	11.2
DKP	Disordered Kronig-Penney (model)	9.7
DLA	Diffusion-limited aggregation	2.9
DLTS	Deep-level transient spectroscopy	11.7
DOS	Density of states	8.5
DRP	Dense random packing	2.1
EMA	Effective-medium approximation	7.3
EMT	Effective-medium theory	9.4
ESR	Electron spin resonance	11.6
EXAFS	Extended x-ray absorption fine structure	3.13
EXP	Exponential (liquid state model)	5.7
FE	Field effect	11.7
GD	Glow discharge	11.2
GFA	Glass forming ability	12.1
HNC	Hypernetted chain	5.6
HS	Hard sphere	4.3
ICTS	Isothermal capacitance transient spectroscopy	11.7
ID	ideal	6.9
IY	Ishida-Yonezawa	7.3
KKR	Kohn-Korringa-Rostoker	7.2

KP	Kronig-Penney	
LESR	Light-induced electron spin resonance	9.7
LEXP	Linearised exponential	5.7
LJ	Lennard-Jones	4.4
LRO	Long-range order	1.7
MAS-NMR	Magic-angle spinning-nuclear magnetic resonance	10.5
MC	Monte Carlo	4.1
MD	Molecular dynamics	4.2
MHNC	Modified hypernetted chain	5.6
MNM(T)	Metal-non-metal (transition)	9.10
MSA	Mean spherical approximation	5.7
NFE	Nearly free electron	Just before 6.1
OCP	One-component plasma	6.10
OCT	Optimised cluster theory	5.7
ODS	Optical density of states	7.6
ORPA	Optimised random-phase approximation	5.7
OZ	Ornstein-Zernike	5.5
PD	Photodarkening	11.10
PDS	Photothermal deflection spectroscopy	11.7
PECPV	Plasma-enhanced chemical vapour deposition	11.2
PL	Photoluminescence	11.6
PS	Photostructural (change)	11.10
PY	Percus-Yevick	5.6
QCA	Quasicrystalline approximation	7.1
RDF	Radial distribution function	2.3
RKKY	Rudermann-Kittel-Kasuya-Yoshida (interaction)	12.6
RPM	Random-phase model	7.7
SCLC	Space-charge-limited currents	11.7
SO	Spin-orbit	6.14
SRO	Short-range order	1.8
SWE	Staebler-Wronski effect	11.10
TBA	Tight-binding approximation	7.2
TCR	Temperature coefficient of resistivity	12.4
TEM	Transmission electron microscopy	9.4
TLS	Two-level system	10.6
TPA	Transient photoabsorption	11.9
TPC	Transient photocurrent	11.9
TTT	Time temperature transformation (curves)	12.1
UPS	Ultraviolet photoelectron spectroscopy	7.6
VCA	Virtual-crystal approximation	7.2
WCA	Weeks-Chandler-Andersen	5.8
XPS	X-ray photoelectron spectroscopy	11.8

COMMON SYMBOLS

Symbol	Meaning	Introduced in section
a	Thermal diffusivity	8.4
a_i	Activity	6.9
b	Scattering length	3.7
B	Tight-binding band width	9.6
B_n	n th virial coefficient	4.3
c_i	Concentration of i	
$c_{ij}(r), c(r)$	Direct correlation function	5.5
C, C_v, C_p	Heat capacity	
d, d_c	Density, critical density	
d_f	Fractal dimension	2.9
$D, D_{\mu\nu}$	Diffusion coefficient	7.7
D^0, D^-, D^+	Dangling bond energies	11.4
E	Energy	
E_c, E_v	Mobility edges	9.10
E_F	Fermi level	
f, F	Force	
$f, f^{(0)}, f(E, T)$	Fermi function	6.11
$f(\theta), f(Q), f_A$	Scattering amplitude	3.1
F	Helmholtz free energy	
$F(Q)$	Total structure factor	3.5
g	g -factor (density of states)	7.7
g	g - or splitting factor	11.6
$g, g^{(2)}, g^{(3)} \dots$	Pair, triplet, ..., distribution function	2.3
g_T	Total pair distribution function	3.10
g_{ij}	Partial pair distribution function	2.4
g_{ij}	Conductance i to j	9.13
$g(\varepsilon)$	Density of states in energy	6.15, 7.1
$g(L)$	Non-dimensional conductance	9.9
$G, G^{(0)}$	Gibbs free energy	
G	Shear modulus	8.4
G	Conductance	9.4
$G, G(E),$	Green operator,	
$G(r, r', E)$	Green function	7.1

$G(\mathbf{r}, t)$	Space-time correlation function	8.1
$h(\mathbf{r})$	Pair correlation function	5.2
H	Hamiltonian	
H	Enthalpy	6.9
$I(\theta), I(Q)$	Scattered intensity	3.1
j	Current density	
k	Wavevector	3.1
$k(\omega)$	Optical extinction coefficient	6.15
l_e, l_i	Elastic, inelastic scattering length	9.11
L_i	Diffusion length	9.11
L	Lorenz number	6.14
$L_{\mu\nu}^{\alpha\beta}$	Onsager coefficient	7.7
m^*	Effective mass	
M	Magnetisation	
$n, n(\mathbf{r})$	Particle number density	
n_0	Average number density	
$n^{(1)}, n^{(2)}, \dots$	Particle distribution function	2.3
n_1, n_{ij}	Coordination number	2.4
$n_e(\mathbf{r})$	Electron number density	3.2
$n(\omega)$	Refractive index	6.15
$n(\epsilon), N(E)$	Particle energy distribution	7.6
N	Number of particles in system	
p	Pressure	
\mathbf{p}	Momentum	
p_c	Percolation threshold	9.2
p_c	Critical pressure	
P	Probability	
Q	Configurational partition function	4.1
Q	Wavevector	3.1
\mathbf{r}	Position vector	
r_s	Radius of spherical volume per electron	6.6
\mathbf{R}, \mathbf{R}_i	Position vector	
R	Resistance	
R_H	Hall coefficient	6.11
S	Order parameter	1.3
S	Entropy	
S_F	Fermi surface area	6.11
$S(Q)$	Structure factor	3.2
$S(Q, \omega)$	Dynamic structure factor; scattering law	3.7 8.1

$S_{NN}, S_{Nc}, S_{cc},$ $S_{ij}, S_{ij}^{(AL)}$	Partial structure factors	3.5, 3.12
$S^p(Q)$	Resistivity structure factor	6.16, 12.4
t_i, T	Scattering amplitude matrix	7.2
T	Absolute temperature	
T_c	A critical temperature	
T_{CR}	Crystallisation temperature	12.1
T_G	Glass transition temperature	10.1
T_L	Liquidus temperature	
T_M	Melting point	
T_{RG}	Reduced glass transition temperature	12.1
U	Total energy	
$U_{ps}, u(r), u(Q)$	Pseudopotential	6.3
v_i	Partial molar volume	3.12
v	Velocity	
V	Volume	
V	Tight-binding transfer integral	9.8
$V, v_i, V(r)$	Potential energy operator, function	7.1
V_G	Gate voltage	11.7
W	Debye-Waller factor	12.4
z	A complex energy	7.1
z	Valency	6.6, 6.8
Z	Canonical partition function	
\mathcal{Z}	Grand canonical partition function	
$\alpha, \alpha(T)$	Thermoelectric power	6.11
$\alpha, \alpha(\omega)$	Optical, ultrasonic absorption coefficient	6.15, 10.7
α^{-1}	Localisation length	9.5
α_p	Thermal expansivity	
β	$(k_B T)^{-1}$	
γ_{el}	Electronic specific heat coefficient	12.3
Γ	One-component plasma parameter	6.10
Γ	Acoustic attenuation coefficient	8.4
$\varepsilon; \varepsilon_{ij}$	Energy; strain component	
$\varepsilon(Q)$	Dielectric screening function	6.4
$\varepsilon(\omega)$	Permittivity	6.15
ζ	Electrochemical potential	6.11
η	Viscosity	

η_{ij}, η_{ij}^0	Short-range order parameter	2.7
θ_D	Debye temperature	
κ_T	Isothermal compressibility	
λ	Thermal conductivity	6.11
Λ	Mean free path	6.11
μ	Absorption coefficient	3.12
$\mu, \mu(E)$	Carrier mobility	11.9
μ_d	Drift mobility	11.9
μ_i	Chemical potential	6.9
μ_H	Hall mobility	9.4
ν	Frequency	
$\nu^{(1)}, \nu^{(2)}, \dots$	Density function	2.3
ξ	Thermoelectric coefficient	12.4
$\rho, \rho(T)$	Electrical resistivity	6.11
$\rho(r), \rho_{ij}(r)$	Radial distribution function	2.3, 2.4
$\rho(r)$	Electric charge density	12.3
$\rho(E), \rho(k, E)$	Spectral operator, function	7.1
σ	Molecular diameter	4.3
$\sigma, \sigma(\omega)$	Electrical conductivity	6.11
σ_{ij}	Stress component	12.6
$\sigma_{\mu\nu}$	Conductivity component	7.7
$\Sigma, \Sigma(k, E)$	Self-energy operator, function	7.3
τ	Relaxation or collision time	6.11, 9.11
φ, Φ	Potential energy function	4.1, 4.3
$\chi, \chi(Q)$	Susceptibility, admittance	6.4, 7.7
$\psi(t)$	Velocity autocorrelation function	8.3
ω	Angular frequency	
Ω	Volume	7.1
$d\Omega$	Element of solid angle	

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ORDER AND DISORDER: AN INTRODUCTORY DISCUSSION

It would be businesslike to open with clear definitions of order and disorder and then to proceed at once to introduce the physics of disordered matter. This is not so easy. The word 'order' in English, and even within science, has many meanings. Like other verbal borrowings by science, it carries a number of associations from everyday life. It has been argued that it is something of a waste of time to seek a definition of order: everyone knows more or less what is meant, precise definitions can always be given when it comes to detailed scientific problems and that is what really matters. This is somewhat reminiscent of the words of Robert Herrick in a theological context:

God is above the sphere of our esteem
And is the best known not defining Him.

There is a great deal to be said for this opinion and certainly it appears to be widely held in so far as there are many cogent writings on matters of order and disorder in physics which manage perfectly well without any discussion of the general concept. Nevertheless, while accepting that order might be defined in various ways using language from more than one discipline, it seems worth spending a little space trying to formulate at least one definition.

What is required is a definition of order that covers all that is needed in physics but does not exclude things in other spheres, such as nature or art, which common intuition would also regard as ordered. Disorder then follows as absence of, or a detraction from, order. This immediately raises the question: must order be either present or absent, or is it a matter of degree? It is necessary to have the concept of perfect, complete or ideal order and perfection is indeed either present or not; it is equally necessary to recognise that greater or smaller departures from perfection are conceivable and that numerical measures of the amount of order, called order parameters, will be indispensable.

1.1 Ordering rules

The first proposition is, that a set of things is ordered or not in respect of a particular property that all the things possess. Since an object can have n