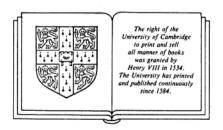
LIQUID METALS Concepts and Theory

N. H. MARCH

Coulson Professor Theoretical Chemistry Department, University of Oxford



CAMBRIDGE UNIVERSITY PRESS Cambridge

New York Port Chester Melbourne Sydney

Contents

Prefac	e	xi
1	Outline	1
2	Pair correlation function and structure factor of ions	3
2.1	Liquid structure factor	3
2.2	Ornstein-Zernike direct correlation function	5
3	Thermodynamics	8
3.1	Simple monatomic fluids	8
3.2	Approximate methods	* 11
3.3	Simple liquid metals	15
3.4	Specifics	18
3.5	One-component plasma as reference liquid	25
4	Electron screening and effective ion-ion interactions	26
4.1	Screening of impurity centre in electron liquid	26
4.2	Lindhard dielectric function	28
4.3	Introduction of exchange and correlation	29
4.4	Effective ion-ion interactions in simple (s-p) metals	31
4.5	Structure factor of alkali metals modelled in terms of	
	one-component plasma	32
5	Interionic forces and structural theories	35
5.1	Force equation	35
5.2	Simple structural theories	37
5.3	Refined structural theories: factorization of triplet correlations	38
5.4	Inversion of structure factor to yield effective interionic	30
5.4	pair potentials	39
6	Statistical mechanics of inhomogeneous systems and	
	freezing theory	43
6.1	Single-particle density related to direct correlation	
	function	43

2

Contents

6.2	Free-energy difference between homogeneous and	
	periodic phases	44
6.3	Relation to the hypernetted-chain method	46
6.4	Verlet's rule related to Lindemann's law of melting	47
6.5	Cluster expansion and density functional theory	50
6.6	Other approximations	51
6.7	Applications	52
6.8	Correlation of melting temperature and vacancy	
	formation energy	54
6.9	Supercooling of liquid Rb	58
7	Electronic and atomic transport	62
7.1	Wiedemann-Franz law and Lorenz number	62
7.2	Exact resistivity formula for finite-range spherical	
	potential	63
7.3	Weak scattering theory of electrical resistivity	67
7.4	Hall coefficient	71
7.5	Atomic transport; generalized Stokes-Einstein relation	73
7.6	Self-diffusion related to shear viscosity at the melting	
	temperature	75
8	Hydrodynamic limits of correlation functions and neutron	
	scattering	77
8.1	scattering Self-motion in liquids and incoherent neutron scattering	77
8.1 8.2,	scattering Self-motion in liquids and incoherent neutron scattering Frequency spectrum (or spectral function) $g(\omega)$	77 78
8.1 8.2. 8.3	scattering Self-motion in liquids and incoherent neutron scattering Frequency spectrum (or spectral function) $g(\omega)$ Van Hove dynamical structure factor $S(k, \omega)$	77 78 80
8.1 8.2 _* 8.3 8.4	scattering Self-motion in liquids and incoherent neutron scattering Frequency spectrum (or spectral function) $g(\omega)$ Van Hove dynamical structure factor $S(k, \omega)$ Friction constant theory of transport	77 78 80 82
8.1 8.2, 8.3 8.4 8.5	scattering Self-motion in liquids and incoherent neutron scattering Frequency spectrum (or spectral function) $g(\omega)$ Van Hove dynamical structure factor $S(k, \omega)$ Friction constant theory of transport Observation of collective modes	77 78 80 82 86
8.1 8.2, 8.3 8.4 8.5 8.6	scattering Self-motion in liquids and incoherent neutron scattering Frequency spectrum (or spectral function) $g(\omega)$ Van Hove dynamical structure factor $S(k, \omega)$ Friction constant theory of transport Observation of collective modes Hubbard-Beeby theory	77 78 80 82 86 88
8.1 8.2 8.3 8.4 8.5 8.6 8.7	scattering Self-motion in liquids and incoherent neutron scattering Frequency spectrum (or spectral function) $g(\omega)$ Van Hove dynamical structure factor $S(k, \omega)$ Friction constant theory of transport Observation of collective modes Hubbard-Beeby theory Generalized shear viscosity in liquid Rb	77 78 80 82 86 88 97
8.1 8.2, 8.3 8.4 8.5 8.6	scattering Self-motion in liquids and incoherent neutron scattering Frequency spectrum (or spectral function) $g(\omega)$ Van Hove dynamical structure factor $S(k, \omega)$ Friction constant theory of transport Observation of collective modes Hubbard-Beeby theory	77 78 80 82 86 88 97
8.1 8.2 8.3 8.4 8.5 8.6 8.7	scattering Self-motion in liquids and incoherent neutron scattering Frequency spectrum (or spectral function) $g(\omega)$ Van Hove dynamical structure factor $S(k, \omega)$ Friction constant theory of transport Observation of collective modes Hubbard-Beeby theory Generalized shear viscosity in liquid Rb	77 78 80 82 86 88
8.1 8.2 8.3 8.4 8.5 8.6 8.7 8.8	scattering Self-motion in liquids and incoherent neutron scattering Frequency spectrum (or spectral function) $g(\omega)$ Van Hove dynamical structure factor $S(k, \omega)$ Friction constant theory of transport Observation of collective modes Hubbard-Beeby theory Generalized shear viscosity in liquid Rb Transport in supercooled liquid Rb Critical behaviour Concept of order parameter	77 78 80 82 86 88 97 101
8.1 8.2. 8.3 8.4 8.5 8.6 8.7 8.8 9	scattering Self-motion in liquids and incoherent neutron scattering Frequency spectrum (or spectral function) $g(\omega)$ Van Hove dynamical structure factor $S(k, \omega)$ Friction constant theory of transport Observation of collective modes Hubbard-Beeby theory Generalized shear viscosity in liquid Rb Transport in supercooled liquid Rb Critical behaviour Concept of order parameter	77 78 80 82 86 88 97 101
8.1 8.2 8.3 8.4 8.5 8.6 8.7 8.8 9 9.1	scattering Self-motion in liquids and incoherent neutron scattering Frequency spectrum (or spectral function) $g(\omega)$ Van Hove dynamical structure factor $S(k, \omega)$ Friction constant theory of transport Observation of collective modes Hubbard-Beeby theory Generalized shear viscosity in liquid Rb Transport in supercooled liquid Rb Critical behaviour Concept of order parameter	77 78 80 82 86 88 97 101
 8.1 8.2, 8.3 8.4 8.5 8.6 8.7 8.8 9 9.1 9.2 9.3 	scattering Self-motion in liquids and incoherent neutron scattering Frequency spectrum (or spectral function) $g(\omega)$ Van Hove dynamical structure factor $S(k, \omega)$ Friction constant theory of transport Observation of collective modes Hubbard-Beeby theory Generalized shear viscosity in liquid Rb Transport in supercooled liquid Rb Critical behaviour Concept of order parameter Liquid-vapour critical point: a second-order phase transition Ornstein-Zernike theory of static structure	77 78 80 82 86 88 97 101 103 103
 8.1 8.2 8.3 8.4 8.5 8.6 8.7 8.8 9 9.1 9.2 9.3 9.4 	scattering Self-motion in liquids and incoherent neutron scattering Frequency spectrum (or spectral function) $g(\omega)$ Van Hove dynamical structure factor $S(k, \omega)$ Friction constant theory of transport Observation of collective modes Hubbard-Beeby theory Generalized shear viscosity in liquid Rb Transport in supercooled liquid Rb Critical behaviour Concept of order parameter Liquid-vapour critical point: a second-order phase transition Ornstein-Zernike theory of static structure Predictions from more general equation of state	77 78 80 82 86 88 97 101 103 103 103
 8.1 8.2 8.3 8.4 8.5 8.6 8.7 8.8 9 9.1 9.2 9.3 9.4 9.5 	scattering Self-motion in liquids and incoherent neutron scattering Frequency spectrum (or spectral function) $g(\omega)$ Van Hove dynamical structure factor $S(k, \omega)$ Friction constant theory of transport Observation of collective modes Hubbard-Beeby theory Generalized shear viscosity in liquid Rb Transport in supercooled liquid Rb Critical behaviour Concept of order parameter Liquid-vapour critical point: a second-order phase transition Ornstein-Zernike theory of static structure Predictions from more general equation of state Critical constants of fluid alkali metals	77 78 80 82 86 88 97 101 103 103 103 104 107 108 111
 8.1 8.2 8.3 8.4 8.5 8.6 8.7 8.8 9 9.1 9.2 9.3 9.4 	scattering Self-motion in liquids and incoherent neutron scattering Frequency spectrum (or spectral function) $g(\omega)$ Van Hove dynamical structure factor $S(k, \omega)$ Friction constant theory of transport Observation of collective modes Hubbard-Beeby theory Generalized shear viscosity in liquid Rb Transport in supercooled liquid Rb Critical behaviour Concept of order parameter Liquid-vapour critical point: a second-order phase transition Ornstein-Zernike theory of static structure Predictions from more general equation of state	77 78 80 82 86 88 97 101 103 103 103 104 107 108

vi

R

10	Electron states, including critical region	121
10.1	Electron states in simple s-p metals	121
10.2	Electronic structure of nonsimple liquid metals	124
10.3	Partition function of a liquid metal	129
10.4	Electron states in expanded liquid Hg	131
10.5	Band model for electronic structure of expanded liquid	
	caesium	134
10.6	Optical properties	138
11	Magnetism of normal and especially of expanded liquid	
	metals	147
11.1	Spin susceptibility of normal liquid metals	147
11.2	Relation between spin and orbital magnetism of simple	
	liquid metals	148
11.3	Effects of electron-ion interaction	151
11.4	Nuclear magnetic resonance: normal conditions	151
11.5	NMR study of expanded liquid caesium	152
11.6	Experimental results: Knight shift for Cs	155
11.7	Theory for NMR shifts and relaxation in fluid metals	159
11.8	Interactions between electrons	161
11.9	Characteristics of high-density liquid Cs	164
11.10	Dynamic nonuniform susceptibility in expanded Cs	169
11.11	Evolution of electronic structure of expanded liquid Cs	172
11.12	Phenomenology and heavy Fermion theory of magnetic	
	susceptibility of expanded fluid alkali metals	174
12	Liquid-vapour surface	180
12.1	Thermodynamics of liquid surfaces	180
12.2	Model using theory of inhomogeneous electron gas	182
12.3	Formally exact pair potential theory	184
12.4	Triezenberg-Zwanzig formula for surface tension: direct	
	correlation function	186
12.5	Microscopic foundation of Cahn-Hilliard	
	phenomenology	188
12.6	Nonequilibrium problems: condensation and	
	evaporation	192
13	Binary liquid-metal alloys	202
13.1	Simple binary fluid mixtures	203
13.2	Thermodynamics in terms of number-concentration	
	correlation functions	206

1

Conten	te
Comen	us

13.3	Number-concentration structure factors as response	
	functions	208
13.4		210
13.5		212
13.6	Cet /	213
13.7		215
13.8	Regular and conformal solutions	216
13.9		
	fluctuations	219
13.10	Complex formation as model for $S_{cc}(0)$	225
13.11	Phase diagrams	227
13.12	Vacancies and melting curve in binary alloys	233
13.13	Theory of freezing	237
13.14	Surface segregation	239
13.15	Metal-insulator transitions	247
13.16	Magnetic properties of alloys	249
14	Two-component theory of pure liquid metals	260
14.1	Electron-ion Hamiltonian and density fluctuation	
	operators	260
14.2	Wigner distribution functions	263
14.3	Electronic effects in dynamical structure	268
14.4	Longitudinal response of a two-component pure liquid	
	metal	269
14.5	Random phase approximation (RPA) for response	
	functions	275
14.6	Thermodynamics	277
14.7	Hydrodynamics in two-component theory	283
14.8	Electrical resistivity	291
14.9	Elastic scattering of neutrons by liquid metals	295
14.10	Single-particle motion from two-component theory	297
14.11	Diffraction evidence on pair correlation functions in	
	two-component theory	302
15	Shock-wave studies	303
15.1	Shock compression	303
15.2	Dynamics of shock waves	304
15.3	Some results on hot expanded metals	306
16	Liquid hydrogen plasmas and constitution of Jupiter	309
16.1	Biil-Jastrow variational theory of liquid metal hydrogen	310

viii

Contents

	·	
16.2	Inverse problem: proton-proton interaction in hydrogen	320
16.3	plasmas Hudrogen belium mintures and constitution of cient	520
10.5	Hydrogen-helium mixtures and constitution of giant planets	325
	Appendices	332
2.1	Fluctuation theory derivation of $S(0)$ in terms of compressibility	332
3.1	Percus-Yevick hard sphere solution for direct correlation	552
2.1	function	335
3.2	Weeks-Chandler-Andersen (WCA) approximation to	000
0.2	structure factor	338
5.1	Pressure dependence of pair function related to	
	three-particle correlations	340
5.2	Conditions to be satisfied by thermodynamically	
	consistent structural theories	342
5.3	Gaussian core model and Kirkwood decoupling of	
	triplet correlations	345
5.4	Specific heats of liquids in terms of higher-order	
	correlation functions	348
5.5	Inversion of measured structure, constrained by	
	pseudopotential theory, to extract ion-ion interaction	350
6.1	Vacancy formation energy evaluated in a hot (model)	
	crystal	353
6.2	Vacancy formation energy related to Debye temperature	355
7.1	Inverse transport theory for noninteracting electrons	361
8.1	Method of fluctuating hydrodynamics	365
8.2	Asymptotic behaviour of other Green-Kubo time	
	correlation functions	368
8.3	Dynamics of $S(k, \omega)$ included through self-function	
	$S_{s}(k,\omega)$	370
8.4	Fourth moment theorem for dynamical structure factor	373
8.5	One-dimensional barrier crossing: Kramers' theory	375
8.6	Mode-coupling and velocity field methods	382
9.1	Ornstein-Zernike treatment of critical correlations	385
9.2	Homogeneity, scaling, and an introduction to	
	renormalization group method	387
9.3	Compressibility ratios and thermal pressure coefficients	
	of simple monatomic liquids from model equations of	
	state	392
9.4	Mode coupling applied to critical behaviour	393

ix

2

Contents

9.5	Proof of Wiedemann-Franz law up to metal-insulator	
10.1	transition for Fermi liquid model	398
10.1	Plasmon properties as function of phenomenological	401
	relaxation time	401
11.1	Heavy Fermion theory	405
13.1		100
	structure	408
13.2	Results for concentration fluctuations from	
	quasi-chemical approximation	410
13.3	Density profiles, direct correlation functions, and surface	
	tension of liquid mixtures	413
13.4	Relation of surface segregation phenomenology to	
	first-principles statistical mechanics	417
13.5	Long-time behaviour of correlation functions in binary	
	alloys	420
13.6	Hydrodynamic correlation functions in a binary alloy	422
13.7	Metallic binary liquid-glass transition	426
13.8	Haeffner effect, electromigration, and thermal transport	434
13.9	Theory of disorder localization of noninteracting	
	electrons	444
14.1	Phonon-plasmon model	447
14.2	Response functions for mass densities	449
14.3	Quantum hydrodynamic limit of two-component theory	451
14.4	Evaluation of transport coefficients	454
14.5	Electron-ion structure factor in a nonequilibrium	
	situation	456
14.6	Relations between long-wavelength limit structure	
	factors in binary metallic alloys	457
16.1	Integral equations for correlations in liquid metals,	
	especially hydrogen	460
16.2	Quantum Monte Carlo calculations of ground state of	
	solid hydrogen	467
	References	471
	Notes added in proof	485
	Index	487

х

-S