

THE
LATTICE
BOLTZMANN
EQUATION

*For Complex States of
Flowing Matter*

•
SAURO SUCCI

OXFORD

THE LATTICE BOLTZMANN EQUATION

The Lattice Boltzmann Equation

For Complex States of Flowing Matter

Sauro Succi

*Center for Life Nanoscience at La Sapienza,
Istituto Italiano di Tecnologia, 00161, Roma, Italy
Viale Regina Margherita, 295, 00161, Roma, Italy*

*Istituto Applicazioni del Calcolo, National Research Council of Italy,
via dei Taurini 19, 00185, Roma, Italy*

*Institute for Applied Computational Science, J. Paulson
School of Engineering and Applied Sciences, Harvard University,
Oxford Street 29, 02138, Cambridge, USA*

OXFORD
UNIVERSITY PRESS

OXFORD

UNIVERSITY PRESS

Great Clarendon Street, Oxford, OX2 6DP,
United Kingdom

Oxford University Press is a department of the University of Oxford.
It furthers the University's objective of excellence in research, scholarship,
and education by publishing worldwide. Oxford is a registered trade mark of
Oxford University Press in the UK and in certain other countries

© Sauro Succi 2018

The moral rights of the author have been asserted

First Edition published in 2018

Impression: 1

All rights reserved. No part of this publication may be reproduced, stored in
a retrieval system, or transmitted, in any form or by any means, without the
prior permission in writing of Oxford University Press, or as expressly permitted
by law, by licence or under terms agreed with the appropriate reprographics
rights organization. Enquiries concerning reproduction outside the scope of the
above should be sent to the Rights Department, Oxford University Press, at the
address above

You must not circulate this work in any other form
and you must impose this same condition on any acquirer

Published in the United States of America by Oxford University Press
198 Madison Avenue, New York, NY 10016, United States of America

British Library Cataloguing in Publication Data
Data available

Library of Congress Control Number: 2017943732

ISBN 978-0-19-959235-7

Printed and bound by
CPI Group (UK) Ltd, Croydon, CR0 4YY

Links to third party websites are provided by Oxford in good faith and
for information only. Oxford disclaims any responsibility for the materials
contained in any third party website referenced in this work.

*To Claudia and Cate, to the many friends who shine light through my journey.
And to the memory of my parents, up there.*

Preface

Start by doing what is necessary, then do what is possible and suddenly you are doing the impossible.

(Saint Francis of Assisi)

Preface 2018

Since the appearance of my previous book (The lattice Boltzmann equation, Oxford U.P, 2001), Lattice Boltzmann has known an exponential growth of methodologies and applications, especially in connection with the simulation of complex and soft-matter flows. Providing a complete and in-depth account of such burgeoning developments is probably beyond the scope of any self-contained book and by all means beyond the capability, knowledge and time-energy of the present author. As a result, this second book remains more modest in scope: it just provides an account of the major developments, with no aim of completeness. At the same time, it is also more ambitious, because it aims at discussing research items beyond Navier-Stokes hydrodynamics, with special focus on interfaces between fluid dynamics and allied disciplines, such as material science, soft matter and biology. Moreover, it also ventures into the realm of quantum and relativistic fluids.

As with the first book, the only major criticism I have heard of, is lack of self-containedness for readers not trained in physics. A single chapter of kinetic theory, apparently, did not fill the bill. In response to this just criticism, I have considerably expanded the pedagogical part on continuum kinetic theory. To the point that, with some doses of wishful thinking, I hope that this part can be used to stand-alone as an introductory text to the kinetic theory of fluids. In response to significant developments which have occurred in the last decade, I have also expanded the quantum-relativistic part, hoping that this may help capture the attention of the growing community dealing with the fascinating confluence between fluid dynamics, condensed matter and high-energy physics which we are witnessing these days.

This book splits naturally into three main components: the first one deals with basic notions continuum kinetic theory, the fundamentals of early-day lattice kinetic theory, a few applications thereof, and finally a few more advanced topics in lattice kinetic theory. All in all, this first part is basically concerned with *macroscopic* fluid dynamics.

Thes second part deals with lattice kinetic theory for generalized hydrodynamics beyond Navier-Stokes, basically the territory where the physics of *flowing matter* makes contact with its allied disciplines, soft matter in the first place.

Finally, the third part deals with fluids beyond Newtonian mechanics, namely relativistic and quantum fluids. This latter part is less voluminous, but it holds its own place

in view of the amazing developments at the frontier between fluid dynamics, condensed matter and high-energy physics, which have taken place in the last decade, holographic fluids and graphene on the frontline. It is still much less developed than the mainstreams covered in the two parts above, but very rich in promise, I believe.

As usual, I tried to keep math at a minimum, but hopefully never below the threshold where equations cannot be traded for “words and pics.”

As a result, I am reasonably confident that reading this book is not “like chewing glass,” as Sydney Chapman once commented on his wonderful but demanding Chapman-Cowling cornerstone.

I also tried to watch against another danger, wittily described by Sir Winston Churchill: “By its very length, this report defends itself against the risk of being read.” Not sure I managed, but I did my best.

For any mistakes, typos and/or inconsistencies which, I’m afraid, are inevitably left in a near-800 pages, single-handed book, I have no chance but appealing to the reader’s benevolent understanding and cooperation.

Enjoy!

Acknowledgements

This book collects another fifteen years of intense research on the subject of Lattice Boltzmann (LB). Many things have changed since the early days of LB, when nearly every idea was new, fertile and usually well received by a small but growing and self-supportive community. This second fifteens have witnessed an exponential growth of the LB applications, along with many important methodological extensions.

Despite my best intentions for conciseness, this book nearly triples in size its predecessor, and I'm afraid that errors and infelicities grow way more than linearly with size Thus, even though I fully subscribe to Joyce's statement below, I would definitely make my errors zero, if I only could

Therefore, I shall again be grateful to any reader kindly willing to signal mistakes, inconsistencies and any sort of imperfections to me.

The near-three decades long LB adventure has got me in touch with a huge number of colleagues all over the world, from whom I invariably learned more than I can possibly express. Unlike Sinatra's regrets, they are "too many to mention", without incurring a serious risk of self-embarrassing omissions.

Yet, I shall make three exceptions: one for those who took the time and pain of reading selected portions of this manuscript, i.e., Hakan Basagaoglu, M. Bernaschi, L. Biferale, Burkhard Duenweg, Giacomo Falcucci, Iliya Karlin, Tony Ladd, Simone Melchionna, Miller Mendoza, Andrea Montessori, M. Sbragaglia and Stefano Ubertini.

The other for the senior colleagues and friends who inspired and shared substantial stretches of the journey, namely Roberto Benzi, Jean-Pierre Boon, Bruce Boghosian, Hudong Chen, Tim Kaxiras, Iliya Karlin, Hans Herrmann and the late Steven Orszag.

The third is for my early wonderful mentors in kinetic theory, the late V. Boffi, V. Molinari and G. Spiga at Bologna University, K. Appert and J. Vaclavik at the Ecole Polytechnique Federale de Lausanne.

I would also like to acknowledge Sonke Adlung, Ania Wronski and Indumadhi Srinivasan for their continued kind (and patient) help throughout this ordeal.

Finally, I would like to thank my wife Claudia and daughter Caterina, for coping with a rather absent and absent-minded husband and father.

Errors are the portals of discovery (J. Joyce)

S. S.
Rome
March 2018

Contents

Part I Kinetic Theory of Fluids	1
1 Why a Kinetic Theory of Fluids?	3
1.1 The Navier–Stokes Equation	3
1.1.1 Elementary Derivation of the Navier–Stokes Equations	5
1.1.2 Navier–Stokes Equations in Lagrangian Form	8
1.1.3 Navier–Stokes Equations in Coordinate Form	10
1.2 Computational Aspects of the Navier–Stokes Equations	10
1.2.1 Why Is the Reynolds Number so Large?	11
1.3 The Benefits of Kinetic Extra Dimensions	13
1.3.1 Molecular Streaming versus Fluid Advection	14
1.3.2 Molecular Relaxation versus Momentum Diffusivity	15
1.4 Summary	16
References	16
Exercises	16
2 Boltzmann’s Kinetic Theory	17
2.1 Atomistic Dynamics	17
2.2 Statistical Dynamics: Boltzmann and the BBGKY Hierarchy	19
2.3 The Born–Bogoliubov–Green–Kirkwood–Yvon (BBGKY) Hierarchy	20
2.4 Back to Boltzmann	22
2.4.1 Two-Body Scattering	23
2.4.2 Spatial Ordering in Dilute Gases	26
2.4.3 Two-Body Scattering Problem	27
2.4.4 Distinguished Potentials	28
2.4.5 Molecular Chaos (Stosszahlansatz)	32
2.5 Local and Global Equilibria	33
2.5.1 Local Equilibria and Equation of State	35
2.5.2 The Evershifting Battle	38
2.6 Summary	40
References	40
Exercises	41
3 Approach to Equilibrium, the H-Theorem and Irreversibility	42
3.1 Approach to Equilibrium: the Second Principle of Thermodynamics	43
3.2 Approach to Equilibrium, the H -Theorem	44

3.2.1	Sketch of the Proof of the H -Theorem	45
3.2.2	H -theorem and Irreversibility	47
3.3	Collisionless Vlasov Equilibria	49
3.4	The Boltzmann Equation in Modern Mathematics	50
3.5	Summary	54
	References	55
	Exercises	55
4	Transport Phenomena	56
4.1	Length Scales and Transport Phenomena	56
4.2	Mean-Free Path (Again!)	58
4.3	Transport Parameters: Macroscopic Picture	60
4.3.1	Mass Diffusivity	62
4.3.2	Momentum Diffusivity: Kinematic Viscosity	63
4.3.3	Energy Diffusivity: Thermal Conductivity	64
4.4	Transport Parameters: Kinetic Picture	65
4.4.1	The Structure of Dissipation: Micro versus Macro	67
4.5	Dimensionless Numbers	67
4.6	Beyond Fick's Law: Non-Local and Nonlinear Transport	68
4.7	Summary	69
	References	69
	Exercises	69
5	From Kinetic Theory to Navier–Stokes Hydrodynamics	70
5.1	From Kinetic Theory to Hydrodynamics: Heuristic Derivation	70
5.1.1	Moment Balance Equations	72
5.1.2	Closures: the Enslaving Principle	75
5.2	The Hilbert expansion	77
5.3	Beyond Hilbert: the Chapman–Enskog Multiscale Expansion	80
5.3.1	Higher-Order Hydrodynamics	82
5.4	Summary	82
	References	83
	Exercises	83
6	Generalized Hydrodynamics Beyond Navier–Stokes	84
6.1	Grad's Thirteen-Moment Theory	84
6.2	Grad's Approach in (Some) More Detail	87
6.3	R13: Regularized Grad-13 Expansion	89
6.4	Linearized Collision Operator	90
6.4.1	The CSF Spectral Decomposition	92
6.5	Summary: Grad versus Chapman–Enskog	96
	References	97
	Exercises	97

7	Kinetic Theory of Dense Fluids	98
7.1	Cautionary Remark	98
7.2	Finite-Density Extension of the Boltzmann Equation	98
7.3	The BBGKY Hierarchy	100
7.3.1	Statistical Mechanics: The Liouville Equation	101
7.3.2	Liouville Theorem	104
7.3.3	Taking Averages	105
7.3.4	Many-Body Equilibria of the Liouville Equation	108
7.4	Reduced Liouville Equations and the BBGKY Hierarchy	109
7.5	Two-Body Closures	112
7.5.1	Short and Mid-Range Interactions	115
7.6	Theories of Correlation Functions	117
7.7	The Enskog Equation	119
7.8	Entry Computers: Molecular Dynamics	121
7.9	Summary	123
	References	123
	Exercises	124
8	Model Boltzmann Equations	125
8.1	On Models and Theory	125
8.2	Bhatnagar–Gross–Krook Model Equation	125
8.3	Generalized BGK Models	128
8.3.1	Multi-Relaxation BGK	128
8.3.2	Multi-Stage BGK	129
8.4	Discrete Velocity Models	130
8.5	BGK Is Not (Necessarily) a Dilute-Gas Approximation	133
8.6	Summary	135
	References	135
	Exercises	135
9	Stochastic Particle Dynamics	136
9.1	Langevin Dynamics	136
9.2	Brownian Motion	139
9.2.1	Link to the Diffusion Equation	142
9.3	A Note on Coarse-Graining: Boltzmann versus Langevin	143
9.4	More on Langevin Dynamics	144
9.4.1	The Kramers Problem and First Passage Time	144
9.4.2	Driven Systems	147
9.5	Beyond Brownian Motion	148
9.5.1	Correlated Noise and Memory Effects	149
9.5.2	Nonlinear Friction	150
9.5.3	Runaway Electrons in Plasmas	150
9.5.4	Active Matter	151

9.6	Back to Phase Space: The Fokker–Planck Equation	152
9.6.1	Fokker–Planck Equation for Nonlinear Processes	154
9.7	Summary	155
	References	156
	Exercises	156
10	Numerical Methods for the Kinetic Theory of Fluids	157
10.1	Introduction	157
10.2	Molecular Dynamics	158
10.3	Direct Simulation Monte Carlo	160
10.4	Mesoscale Particle Methods	162
10.5	Multi-Particle Collisions	162
10.6	Dissipative Particle Dynamics	164
10.7	Grid Methods for the Boltzmann Equation	166
10.8	Lattice Particle Methods	167
10.9	Summary	168
	References	168
	Exercise	168
	Part II Lattice Kinetic Theory	169
11	Lattice Gas-Cellular Automata	171
11.1	Boolean Hydrodynamics	171
11.2	Fluids in Gridland: The Frisch–Hasslacher–Pomeau Automaton	172
11.3	Fluons in Action: LGCA Microdynamic Evolution	173
11.4	From LGCA to Navier–Stokes	181
11.4.1	Discrete Local Equilibria	183
11.5	Practical Implementation	185
11.6	Lattice Gas Diseases and How to Cure Them	187
11.6.1	Statistical Noise	188
11.6.2	Low Reynolds Number	189
11.6.3	Exponential Complexity	190
11.6.4	Spurious Invariants	192
11.7	Summary	192
	References	193
	Exercises	194
12	Lattice Boltzmann Models with Underlying Boolean Microdynamics	195
12.1	Nonlinear LBE	195
12.1.1	Lattice Quantum Fluids	198
12.2	The Quasilinear LBE	199
12.3	The Scattering Matrix A_{ij}	201

12.4	Numerical Experiments	204
12.5	Summary	205
	References	205
	Exercises	206
13	Lattice Boltzmann Models without Underlying Boolean Microdynamics	207
13.1	LBE with Enhanced Collisions	207
13.2	Hydrodynamic and Ghost Fields	211
13.3	Field-Theoretical Analogies	214
13.3.1	Extra-Dimensions	216
13.3.2	Ghost-Busters	217
13.4	The Route to Navier–Stokes: Enslaving Assumption	218
13.5	The Mirage of Zero Viscosity	219
13.6	Early Numerical Simulations	221
13.7	Summary	222
	References	222
	Exercises	222
14	Lattice Relaxation Schemes	223
14.1	Single-Relaxation Time	223
14.2	LBGK Equilibria	224
14.3	LBGK versus Early LBE	228
14.4	Multiple-Relaxation Time (MRT)	229
14.4.1	Constructing the MRT Matrix	231
14.4.2	Enhanced MRT Stability	231
14.5	Further Relaxation Variants	233
14.5.1	Regularized LBGK	233
14.5.2	Cascaded LBE	234
14.6	Summary	235
	References	235
	Exercises	236
15	The Hermite–Gauss Route to LBE	237
15.1	LBE from Continuum-Kinetic Theory: The Hermite–Gauss Approach	237
15.2	Multi-Dimensions, Higher-Order Lattices and Separability	240
15.3	Non-Cartesian Quadrature Schemes	242
15.3.1	Personal Afterthoughts	242
15.4	Relation to Discrete-Velocity Models	243
15.5	Summary: Three Ways to Lattice Boltzmann	244
	References	245
	Exercises	246

16	LBE in the Framework of Computational-Fluid Dynamics	247
16.1	LBE and CFD	247
16.1.1	Causality	248
16.1.2	Accuracy	250
16.2	Stability	252
16.2.1	Consistency	256
16.2.2	Efficiency	259
16.2.3	Parallel Computing	260
16.2.4	Flexibility	262
16.3	Link to Fully Lagrangian Schemes	263
16.4	Summary	266
	References	267
	Exercises	268
Part III	Fluid Dynamics Applications	269
17	Boundary Conditions	271
17.1	Initial Conditions	271
17.2	General Formulation of LBE Boundary Conditions	272
17.3	Survey of Various Boundary Conditions	273
17.3.1	Periodic Boundary Conditions	274
17.3.2	No-Slip Boundary Conditions	277
17.3.3	Free-Slip Boundary Conditions	279
17.3.4	Frictional Slip	279
17.3.5	Sliding Walls	281
17.3.6	Wall Equilibria	281
17.3.7	The Inamuro Method	281
17.3.8	A Word of Caution: Analytical Results	283
17.4	Moving Boundaries	284
17.5	Open Boundaries	284
17.6	Exactly Incompressible LBE Schemes	286
17.6.1	Remark	287
17.6.2	Zou-He Non-Equilibrium Bounce-Back	288
17.7	Curved Boundaries	290
17.7.1	Staircased Boundaries	291
17.7.2	Extrapolation Schemes	291
17.7.3	Multi-Reflection	292
17.7.4	The Surfel Method	293
17.7.5	Bouzidi-Lallemand Bounce-Back Rule	294
17.8	Summary	297
	References	297
	Exercises	298

18	Flows at Moderate Reynolds Numbers	300
18.1	Moderate Reynolds Flows in Simple Geometry	300
18.2	LBE Implementation	302
18.3	Boundary Conditions	305
18.4	Flows Past Obstacles	307
18.5	Hemodynamics	308
18.6	More on the Pressure Field: Poisson Freedom	310
18.7	Summary	312
	References	313
	Exercises	314
19	LBE Flows in Disordered Media	315
19.1	Introduction	315
19.2	Flows Through Porous Media	315
19.3	LBE Flows Through Porous Media	318
19.4	Setting Up the LBE Simulation	319
19.5	Deposition Algorithm	327
19.6	Early-days Numerical Simulations	327
19.7	Synthetic Matter and Multiscale Modeling	328
19.8	Some Recent Developments	329
19.9	Summary	331
	References	331
	Exercises	332
20	Lattice Boltzmann for Turbulent Flows	333
20.1	Fluid Turbulence	333
20.1.1	Two-Dimensional Turbulence	336
20.1.2	Turbulence and Kinetic Scales	337
20.2	Early LBE Simulations of Two-Dimensional Turbulence	338
20.2.1	Sub-Grid Scales and Numerical Stability	342
20.3	Three-Dimensional-Incompressible Turbulence	345
20.3.1	Three-Dimensional Channel Flow	345
20.3.2	Three-Dimensional Turbulence: Parallel Performance	346
20.4	Summary	348
	References	348
	Exercises	349
Part IV Lattice Kinetic Theory: Advanced Topics		351
21	Entropic Lattice Boltzmann	353
21.1	Rescuing the Second Principle	353
21.1.1	Linear Stability and Time Marching	354
21.1.2	Stability and Realizability	354

21.2	Lattice H -Theorem	359
21.2.1	Entropic LB in the Sub-Grid Regime	360
21.3	Entropy Minimization Strategies	361
21.4	Modern ELB Developments	363
21.5	Entropic Misunderstandings	365
21.6	Summary	367
	References	367
	Exercises	368
22	Thermohydrodynamic LBE Schemes	369
22.1	Isothermal and Athermal Lattices	369
22.2	Temperature in a Discrete World	372
22.2.1	Equation of State and Thermodynamic Consistency	373
22.3	Thermodynamic Equilibria and Multi-Energy Lattices	374
22.4	Extended Parametric Equilibria	376
22.4.1	Parametric Equilibria without Nonlinear Deviations	379
22.5	Thermohydrodynamic LB Schemes Get in trouble	383
22.6	Early Attempts to Rescue Thermal LBE	385
22.6.1	Tolerance to Realizability Violations	385
22.6.2	The Kinetic-Closure Approach	385
22.6.3	Non-Space-Filling Lattices	386
22.6.4	Models with Rest Energy	386
22.7	Systematic Third-Order Equilibria	388
22.8	Entropic Schemes with Energy Conservation	388
22.9	Of Fluons and Phonons: The Double-Distribution Method	391
22.9.1	Second-Order Time Marching	392
22.10	Hybrid Methods	393
22.11	Passive-Scalar Schemes	394
22.12	Further Variants for Compressible Flows	394
22.13	Boundary Conditions for Thermal Flows	395
22.14	Summary	395
22.15	Appendix: Parameters of the D1V5 and D2V16 Thermal model	395
	References	398
	Exercises	399
23	Out of Legoland: Geoflexible Lattice Boltzmann Equations	400
23.1	Coarse-Graining LBE	400
23.2	Finite Volume LBE	401
23.2.1	Piecewise-Constant Streaming	403
23.2.2	Piecewise-Linear Streaming	404
23.2.3	Piecewise-Linear Collision Operator	406
23.2.4	Piecewise-Parabolic Interpolation	408

23.3	Unstructured Lattice Boltzmann Equation	408
23.4	Finite Difference LBE	409
23.5	Interpolation-Supplemented LBE	410
23.6	Finite Element LBE	411
23.7	Native LBE Schemes on Irregular Grids	414
23.7.1	Implicit LBE Schemes	415
23.8	Multigrid Lattice Boltzmann Scheme	415
23.9	Summary	420
	References	421
	Exercises	422
24	Lattice Boltzmann for Turbulence Modeling	423
24.1	Sub-Grid Scale Modeling	423
24.2	Lattice Boltzmann Turbulence Models	424
24.3	Hydro-Kinetic: Eddy-Viscosity Smagorinsky Model	426
24.3.1	LBE Formulation of the Smagorinsky SGS Model	427
24.4	Two-Equation Models	429
24.5	Reynolds-Averaged Navier–Stokes (RANS)	430
24.6	Large Eddy Simulation	430
24.6.1	Kinetic Hydro: Lattice Boltzmann Large-Eddy Simulation	431
24.7	The Kinetic Approach to Fluid Turbulence, Again	434
24.7.1	Very Large-Eddy Simulation	437
24.8	Fully Kinetic Approach	439
24.8.1	Relation between Kinetic and Hydrodynamic Closures	440
24.9	Entropic Models: Domesticating the Ghosts	441
24.10	Wall–Turbulence Interactions	441
24.11	Summary	443
	References	443
	Exercises	444
Part V	Beyond Fluid Dynamics: Complex States of Flowing Matter	445
25	LBE for Generalized Hydrodynamics	447
25.1	Introduction	447
25.2	Including Force Fields	448
25.2.1	Including Forces with a Force-Free Formalism: Driven Hydrodynamics	451
25.2.2	Shifted Hydrodynamics	452
25.2.3	Galilean Rescue	453
25.3	Generalized Lattice Hydrodynamics	454
25.3.1	Shifted Lattice Equilibria	455
25.3.2	Multi-Relaxation Time	457

25.4	Lattice Implementation of the Force Term: Details Matter!	457
25.5	Electromagnetic Forces	459
25.5.1	Two-Dimensional Magnetohydrodynamics	460
25.6	Toward Strong Interactions: Hermite Representation	461
25.7	Summary	462
	References	463
	Exercises	463
26	Lattice Boltzmann for reactive flows	464
26.1	Chemical Reactions	464
26.2	Lattice Boltzmann Schemes with Chemical Reactions	466
26.3	Advection-Diffusion-Reaction Equations	469
26.4	Critical Remarks	471
26.4.1	Hybrid Approach	471
26.4.2	Moment-Propagation Method	472
26.4.3	Presence Index Approach	473
26.5	Reactive LBE Applications	474
26.6	Summary	477
	References	478
	Exercises	479
27	Lattice Boltzmann for Non-Ideal Fluids	480
27.1	Introduction	480
27.2	Non-Ideal Equation of State and Surface Tension	481
27.2.1	Non-Ideal Equations of State	481
27.2.2	Surface Tension	482
27.3	Numerical Methods for Flows with Interfaces	485
27.4	LB Schemes for Multiphase Flows: Numerical Challenges	485
27.4.1	Low Density Ratios	486
27.4.2	Thick Interfaces	486
27.5	Chromodynamic Models	488
27.6	The Shan–Chen Pseudo-Potential Approach	489
27.7	The Free-Energy Approach	493
27.8	Free-Energy Finite-Difference Methods	496
27.9	Attempts toward Thermodynamic Consistency	499
27.9.1	Lattice Enskog Equation	500
27.9.2	Two-Body Liouville Equation	500
27.9.3	Merging LB with Dynamic Density Functional Theory	500
27.10	Assorted Multiphase LB Approaches	501
27.10.1	Projection Methods	501
27.10.2	Alternative Equations of State	501
27.10.3	Adaptive Equations of State	503

27.10.4 Merging LB with Flux-Limiting Techniques	504
27.10.5 Entropic Method for Multiphase Flows	505
27.11 Miscellaneous Multiphase LBE Applications	505
27.12 Summary	507
References	509
Exercises	511
28 Extensions of the Pseudo-Potential Method	512
28.1 Introduction	512
28.2 Shan–Chen Revisited	512
28.2.1 Equation of State	515
28.2.2 Interface Pressure and Surface Tension	516
28.2.3 Surface Tension	517
28.3 Shan–Chen Limitations and How to Soften Them	517
28.4 Surface Tension Independent of the Equation of State: Multirange Pseudo-Potentials	518
28.5 Vapor Versus Liquid Sound Speed: Alternative Equations of State	521
28.6 Large Density Ratios and Spurious Currents	522
28.6.1 Alternative Discretizations	523
28.6.2 Local Grid Refinement	524
28.6.3 Multi-Range Potentials, Again	524
28.7 Thick Interfaces	525
28.7.1 Weakly Broken Universality	526
28.8 Thermodynamic Consistency: Shan–Chen from Pseudo-Free Energy	530
28.9 Summary	531
References	532
Exercises	533
29 Lattice Boltzmann Models for Microflows	534
29.1 Basics of Microfluidics	534
29.2 Non-Hydrodynamic Behavior Beyond Navier–Stokes	537
29.2.1 Slip-Flow and Knudsen Layers	537
29.3 Multiphase Flows	540
29.3.1 The Moving Contact Line	542
29.4 LB without Chapman–Enskog: An Eluded No-Go?	546
29.5 Early Minimal Models: Density-Dependent Relaxation	547
29.6 High-Order Lattices	549
29.6.1 Counting Degrees of Freedom: Multi-Scalars versus Tensor Fields	550
29.6.2 Structural Organization: Multiscalars versus Tensors	551
29.6.3 Realizable Kinetic Boundary Conditions	552
29.7 Diffuse Boundary Conditions	552
29.7.1 Partial-Accommodation Kinetic Boundary Conditions	554

29.7.2	Volumetric Boundary Conditions	555
29.7.3	Non-Equilibrium Boundary Conditions	556
29.8	Regularization	556
29.9	Exact Solutions	558
29.10	Partial Summary	560
29.11	Multiphase Microflows	560
29.11.1	Fluid-Wall Potentials	561
29.11.2	Fluid-Wall Pseudo-Potentials	562
29.11.3	Heterogeneous Free-Energy Models	562
29.12	Further Miscellaneous Developments	562
29.12.1	Spurious Knudsen Layers	563
29.12.2	High-Order Boundary Conditions	563
29.12.3	Non-Uniform Grids	563
29.12.4	Thermal Microflows	563
29.13	Summary	565
	References	566
	Exercises	567
30	The Fluctuating Lattice Boltzmann	568
30.1	Nanoscale flows	568
30.2	The Fluctuating LBE	570
30.3	Some FLBE Liabilities	573
30.4	Thermal Equipartition at All Scales	573
30.5	Theoretical Foundations of the Fluctuating LB	578
30.6	FLB from Equilibrium Statistical Mechanics	578
30.7	The Boltzmann Number	579
30.7.1	Thermal versus Inertial Mass	580
30.8	FLBE from Fluctuating Kinetic Theory	581
30.9	Numerical Stability and Computational Considerations	582
30.10	Loose Ends and Future Developments	584
30.10.1	Validity of FDT Under Confinement	585
30.10.2	FLBE Under Strong Confinement	586
30.10.3	Handling Strong Fluctuations	586
30.11	Summary	586
	References	587
	Exercises	588
31	LB for Flows with Suspended Objects: Fluid–Solid Interactions	589
31.1	Introduction	589
31.2	Ladd’s Collision-Based Coupling Method	590
31.2.1	Numerical Tests	593

31.3	Improving on Ladd's Model	596
31.3.1	Dealing with Impulsive Forces: the Cover-Uncover Transition	597
31.3.2	Concentrated Suspensions: Near-Contact Problems	599
31.3.3	Higher-Order Boundary Conditions	601
31.4	Force-Based Coupling Methods for Fluid-Structure Interactions	601
31.4.1	Flexible Bodies: Polymers in LB Flows	602
31.4.2	Force-Based Coupling: the "Raspberry" Model	606
31.4.3	A Few Words of Comment	607
31.5	The Immersed Boundary Method	608
31.5.1	Discrete Dirac's Delta: Smoothed Particles	610
31.5.2	Merging LB with IBM: Some Applications	612
31.6	External Boundary Force: A Unified Framework for Force-Based Methods	614
31.6.1	Time Marching	615
31.7	Eulerian-Eulerian Multicomponent Models	615
31.8	Summary	616
	References	617
	Exercises	618

Part VI Beyond Newtonian Mechanics: Quantum and Relativistic Fluids 619

32	Quantum Lattice Boltzmann (QLB)	621
32.1	Fluid Formulation of Quantum Mechanics	621
32.2	The Fluid Formulation of the Schrödinger Equation	623
32.2.1	Relativistic Quantum Mechanics: the Dirac Equation	625
32.2.2	The Majorana Representation	628
32.2.3	Dirac to Schrödinger: the Enslaving Approximation	630
32.2.4	The Interacting Case	632
32.3	The Quantum LBE	632
32.4	Time Marching	633
32.4.1	The QLB Dispersion Relation and Lorentz Invariance	635
32.5	Numerical Tests in One Space Dimension	637
32.5.1	Free Particle Motion	638
32.5.2	Harmonic Oscillator	639
32.5.3	Scattering Over a Rectangular Barrier	640
32.6	Multi-Dimensional QLB	640
32.6.1	Quantum LBE: Move, Turn and Collide	642
32.7	QLB is a Genuine Dirac Solver	643
32.8	The Lattice Wigner Equation	644
32.9	Summary	647

32.10 Appendix: Spinors	647
References	648
Exercises	649
33 QLB for Quantum Many-Body and Quantum Field Theory	650
33.1 The Quantum N -Body Problem	650
33.2 Numerical Quantum Many-Body Methods	651
33.2.1 Quantum Monte Carlo Methods	651
33.2.2 Variational Monte Carlo	652
33.2.3 Matrix Eigenvalue Methods: Exact Diagonalization	653
33.2.4 Dynamic Minimization	653
33.2.5 Quantum LB as the “Perfect” Lattice Monte Carlo?	654
33.3 Electron-Density Functional Theory	655
33.3.1 Kinetic Approach to Electronic Density Functional Theory	656
33.4 Lattice Boltzmann for Quantum Field Theory	656
33.4.1 Second Quantization and Heisenberg Interaction Representation	657
33.4.2 Quantum Fields in Spatially Extended Systems	660
33.4.3 LB for $(1 + 1)$ Quantum Field Theory	662
33.5 Quantum LB for Quantum Computing	663
33.5.1 Bits and Qubits	664
33.5.2 Hamiltonians and Circuits	666
33.6 Quantum Random Walks	667
33.6.1 QLB is a Quantum Random Walk	668
33.7 Quantum Simulators for Classical Kinetic Theory	669
33.7.1 Second-Quantized Kinetic Theory	670
33.7.2 Non-Unitary Hamiltonians	671
33.8 Summary	673
References	673
Exercises	675
34 Relativistic Lattice Boltzmann (RLB)	676
34.1 Relativistic Mechanics	676
34.2 Relativistic Kinetic Theory	679
34.3 Relativistic Boltzmann Equation	681
34.4 Relativistic Equilibria: the Jüttner Distribution	683
34.5 Relativistic Hydrodynamics	687
34.6 Relativistic LBE	688
34.7 Top-Down Approach: RLB by Moment Matching	689
34.7.1 Dissipative Hydrodynamics	690
34.8 Early RLB Applications	691

34.8.1	Shock Wave in Quark-Gluon Plasmas	691
34.8.2	Astrophysics: Supernova Explosions	692
34.8.3	Electron Flows in Graphene	693
34.9	Strongly Interacting Fluids, AdS-CFT Duality and Super-Universality	694
34.9.1	Caveat	696
34.10	Summary	696
	References	697
	Exercises	698
35	Advanced RLB models	699
35.1	Relativistic LBE from Relativistic Kinetic Theory	699
35.1.1	Relativistic Basis Functions	700
35.1.2	Relativistic Lattice Polynomials	701
35.1.3	Third-Order KRLB with Improved Dissipation	704
35.1.4	KRLB Equilibria	705
35.1.5	Kinetic RLB schemes for non-zero mass (finite-temperature) particles	705
35.2	Applications of Kinetic RLB	708
35.3	RLB in Spherical Coordinates	708
35.4	Lattice Boltzmann in Curved Manifolds	710
35.4.1	Hydrodynamics in Curved Manifolds	710
35.4.2	Kinetic Theory in Curved Manifolds	712
35.4.3	Lattice Boltzmann in a Curved Manifold	712
35.5	Future Developments: Fluid-Structure Interactions	714
35.6	General Relativity	715
35.6.1	LB for Numerical Relativity	716
35.6.2	Hybrid Scenarios for Numerical Relativity	717
35.6.3	Kinetic Theory of spacetime	717
35.7	Summary	717
35.8	Appendix: Covariant and Controvariant Coordinates	718
	References	720
	Exercises	721
36	Coda	722
36.1	The Question	722
36.1.1	Biblio-Numbers	722
36.1.2	LB Cannot Be Too Wrong	723
36.1.3	Breakthroughs	723
36.1.4	Weakly Broken Universality and Chimaera Simulation	724
36.2	Boltzmann and Computers	724
	References	726

37	Notation	727
37.1	Vectors and Tensors	727
37.2	Scalar Products and Tensor Contractions	728
37.3	Gradients, Divergence, Curl and All That	728
	Reference	729
Appendices		731
A.1	The Pseudospectral Method	731
A.2	Computer Performance	732
A.2.1	Flops, MLUPS and Bytes per Flop	733
A.3	A Primer on Parallel Computing	734
A.3.1	Fraction of parallel content	734
A.3.2	Communication to computation	735
A.3.3	Load Balancing	737
A.3.4	Again on Thermal Barriers	737
A.4	From Lattice Units to Physical Units	737
A.4.1	Space	738
A.4.2	Time	738
A.4.3	Mass	739
Part VII	Hands-On	741
H.5	Routine List	741
H.5.1	Input	741
H.5.2	InitHydro	741
H.5.3	Equil	742
H.5.4	InitPop	742
H.5.5	Pbc	742
H.5.6	Mbc	742
H.5.7	Move	742
H.5.8	Hydrovar	742
H.5.9	Colli	742
H.5.10	Force	743
H.5.11	Obst	743
H.5.12	Diag0D	743
H.5.13	Movie	743
H.5.14	Profil	743
H.5.15	Config	743
H.6	Warm-up program	743
Index		757

Part I

Kinetic Theory of Fluids

The first Part of this Book is entirely devoted to pedagogical material, namely the kinetic theory of fluids.

Since the Lattice Boltzmann method was historically devised to solve the equations of continuum fluid mechanics, in Chapter I we present a rapid survey of such equations and introduce the motivations for a microscopic approach to fluid dynamics, namely the kinetic theory of fluids.

Chapter II presents the basic notions of kinetic theory, with special focus on its mathematical cornerstone: Boltzmann's kinetic equation. In Chapter III we discuss the approach to equilibrium and the attendant notions of entropy and irreversibility. Chapter IV provides an elementary illustration of transport phenomena and their link to the underlying microphysics. In Chapter V we discuss the hydrodynamic limit of Boltzmann's kinetic theory, taking to the Navier-Stokes equations of continuum fluid mechanics, while in Chapter VI we illustrate Grad's formulation of generalized hydrodynamics, beyond the Navier-Stokes picture. Chapter VII deals with extensions of Boltzmann's kinetic theory to the case of dense fluids. Chapter VIII illustrates simplified versions of the Boltzmann's equation, so called Model Boltzmann equations, which have been devised in order to facilitate its analytical and numerical solution. Finally, Chapter IX provides a cursory view of stochastic processes of direct relevance to the kinetic theory of fluids, such as Brownian motion and the associated Langevin equations.

The above material was prompted in response to the only substantial criticism received by the previous book, namely lack of self-containedness for readers with no specific training in statistical physics, and particularly in kinetic theory. This material is meant precisely to those readers, hopefully providing a satisfactory fix to the gap they have kindly highlighted. Those with no urge of filling such gap, can safely skip to Part 2.

Why a Kinetic Theory of Fluids?

In this chapter we present the Navier–Stokes equations of fluid mechanics and discuss the main motivations behind the kinetic approach to computational fluid dynamics.

For, sometimes, the longest tour is the shortest way home.

(C.S. Lewis)

1.1 The Navier–Stokes Equation

Fluid flows are a pervasive presence across most branches of human activity and daily life in the first place. Although the basic equations governing the motion of fluid flows have been known for nearly two centuries, since the work of Claude-Louis Navier (1785–1836) and Gabriel Stokes (1819–1903), these equations still set a formidable challenge to our quantitative, and sometimes even qualitative, understanding of the way fluid matter flows in space and time. Climate and meteorological phenomena are among the most popular examples in point, as expressed by Bob Dylan’s vivid metaphor “The answer, my friend, is blowing in the wind.”

At a first glance, the Navier Stokes equations (NSEs) look relatively harmless. In conservative Eulerian form (1):

$$\begin{cases} \partial_t \rho + \nabla \cdot (\rho \vec{u}) = 0 \\ \partial_t (\rho \vec{u}) + \nabla \cdot (\rho \vec{u} \vec{u} + p) = \nabla \cdot \vec{\sigma} + \vec{f}^{ext} \end{cases} \quad (1.1)$$

In (1.1), n and $\rho = nm$ are the fluid number and mass density (m is the mass of the molecules), respectively, p is the fluid pressure, $\vec{u}$ is the fluid velocity and $\vec{f}^{ext}$ is the external force per unit volume. Whenever such force can be derived from a potential, say Φ , the latter adds to the total fluid pressure, $p_{tot} = p + n\Phi$. The shear-stress tensor $\vec{\sigma}$ represents dissipative effects, as induced by the deformation of the fluid elements.

The first of these two equations is simply a statement of mass conservation, as applied to a small but finite volumlet of fluid. The change in time of the mass in the volumlet is due to the unbalance between the incoming and outgoing mass fluxes. The second equation is basically Newton's equation in reverse, $m\vec{a} = \vec{F}$, as applied to the same volumlet. In this, "small" means much smaller than the typical scale of change of the macroscopic fields, and yet, large enough to allow the neglect molecular fluctuations.

The first term on the left-hand side of the second equation is the change per unit time of the momentum in the fluid volumlet at a fixed position in space (Eulerian representation). The second term on the right-hand side is the flux of momentum across the surface of the volumlet due to the fluid motion itself, namely the inertial forces per unit volume. The third term on the left-hand side is the force per unit volume exerted by the adjacent fluid along the normal surface (pressure gradient). The first term on the right-hand side represents the contact forces tangential to the surface, the main source of strain, hence dissipation, on the fluid.

The NSE represents four equations for eleven unknowns, density, pressure, three components of the velocity field and six components of the (symmetric) stress tensor. Hence, to close the system, they must be supplemented with seven extra-relations.

The first is the *equation of state*, relating pressure to density and temperature

$$p = p(\rho, T) \quad (1.2)$$

For an ideal gas, pressure depends linearly on the density

$$p = n\mathcal{R}T \quad (1.3)$$

where $\mathcal{R}$ is the universal gas constant. For non-ideal gases, the relation is no longer linear due to the contribution of potential energy.

The other six constraints come from the so-called *constitutive relations*, namely an expression of the stress tensor in terms of the gradient of the velocity field.

In the simplest instance, the so-called Newtonian fluids, this relation takes the following linear form:

$$\vec{\sigma} = \lambda(\nabla \cdot \vec{u})I + \mu(\nabla\vec{u} + \vec{u}\nabla) \quad (1.4)$$

where μ is the shear viscosity and λ is related to the bulk viscosity, μ_b , via

$$\mu_b = \lambda + \frac{2}{3}\mu. \quad (1.5)$$

On stability grounds, both viscosities must be non-negative, although the bulk viscosity is often taken to be zero (Stoke's hypothesis).

Note that these *constitutive relations* are heuristic in nature; they state that the strain of the fluid resulting from a given applied stress is linearly proportional to the stress itself.

Although fairly reasonable (for small enough strains), this does *not* follow from any fundamental law of Newtonian mechanics. Indeed, constitutive relations are not universal, i.e., they take different forms depending on the specific class of fluid considered.

The simplest case, λ and μ constant, designates so-called Newtonian fluids.¹ For more complex fluids, typically endowed with internal structure, the constitutive relations may become nonlinear, nonlocal in space and time, and non-isotropic as well.

Regardless of the specific form of the constitutive relations, the physical content of the NSE remains quite transparent, basically mass and momentum conservation as applied to a small, yet *finite*, volume of fluid (volumlet).

1.1.1 Elementary Derivation of the Navier–Stokes Equations

Having noted that the continuity equation is simply a statement of mass conservation, while the second NSE is basically Newton’s law plus a statement of strain-stress linearity, we now proceed to an elementary derivation of the statements based on simple arguments of continuum mechanics. With reference to the square volumlet of size $\Delta V = \Delta x \Delta y$ depicted in Figures 1.1 and 1.2 (in two dimensions for simplicity), the change of mass in the volumlet over a time interval δt is given by

$$\begin{aligned} \frac{\delta(\rho \Delta x \Delta y)}{\delta t} = & \left[(\rho u_x) \left(x - \frac{\Delta x}{2}, y \right) - (\rho u_x) \left(x + \frac{\Delta x}{2}, y \right) \right] \Delta y \\ & + \left[(\rho u_y) \left(x, y - \frac{\Delta y}{2} \right) - (\rho u_y) \left(x, y + \frac{\Delta y}{2} \right) \right] \Delta x \end{aligned} \quad (1.6)$$

where the right-hand side is the sum of the incoming and outgoing mass fluxes.

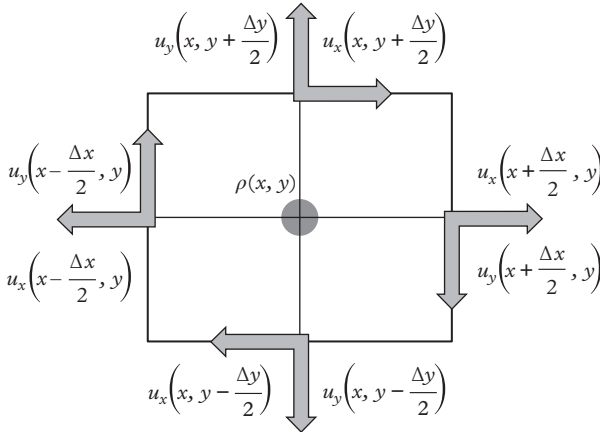


Figure 1.1 The mass balance illustrating the elementary derivation of the continuity equation. For simplicity, the two-dimensional case is considered.

¹ This is a bit ironic, given that constitutive equations represent precisely the only component of the NSEs which goes beyond a plain transcription of Newtonian physics from the microscopic to the macroscopic level!

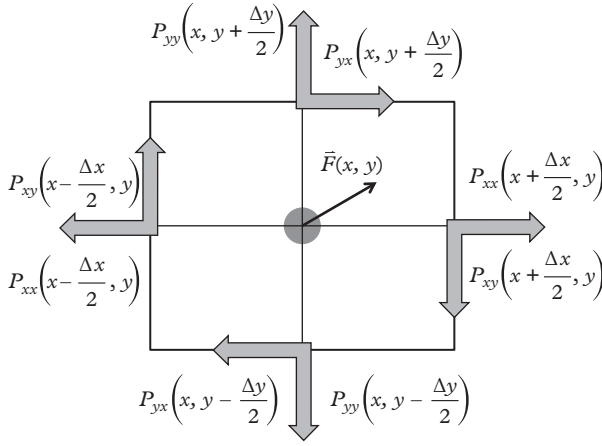


Figure 1.2 *The momentum balance illustrating the elementary derivation of the NSEs.*

Dividing by $\Delta x \Delta y$, and taking the continuum limit $\delta t \rightarrow 0$ and $\Delta x \rightarrow 0$, we obtain

$$\partial_t \rho = -\partial_x(\rho u_x) - \partial_y(\rho u_y) \quad (1.7)$$

which is precisely the continuity equation.

By the same token, the change of momentum along the x direction in the volumlet over a time interval δt is given by

$$\begin{aligned} \frac{\delta(\rho u_x \Delta x \Delta y)}{\delta t} = & \left[(\rho u_x u_x) \left(x - \frac{\Delta x}{2}, y \right) - (\rho u_x u_x) \left(x + \frac{\Delta x}{2}, y \right) \right] \Delta y \\ & + \left[(\rho u_x u_y) \left(x, y - \frac{\Delta y}{2} \right) - (\rho u_x u_y) \left(x, y + \frac{\Delta y}{2} \right) \right] \Delta x \end{aligned} \quad (1.8)$$

The first two terms on the right-hand side represent the flux of momentum along x , entering across the left facelet at $x - \Delta x/2$, minus the same flux exiting across the right facelet at $x + \Delta x/2$. The other two terms represent the mass flux along x , entering along y across the top and bottom boundaries, respectively (see Fig. 1.1). Dividing by $\Delta x \Delta y$, and taking the continuum limit $\delta t \rightarrow 0$ and $\Delta x \rightarrow 0$, delivers

$$\partial_t(\rho u_x) = -\partial_x(\rho u_x^2) - \partial_y(\rho u_x u_y) \quad (1.9)$$

This accounts for the convective term on the left-hand side of the momentum equation.

Pressure and dissipative effects are represented by the contact forces acting on the four surfaces of the two-dimensional volumlet. By summing the forces, i.e., change of momentum per unit time, acting upon the four faces of the volumlet along x , we obtain

$$f_x \Delta x \Delta y = \left[P_{xx} \left(x - \frac{\Delta x}{2}, y \right) - P_{xx} \left(x + \frac{\Delta x}{2}, y \right) \right] \Delta y \\ + \left[P_{xy} \left(x, y - \frac{\Delta y}{2}, y \right) - P_{xy} \left(x, y + \frac{\Delta y}{2}, y \right) \right] \Delta x$$

Using the standard definition of the pressure, namely

$$p = P_{xx} = P_{yy} = P_{zz}$$

and dividing again by the area of the volumlet, we obtain

$$f_x = \partial_x p - \partial_y P_{xy} \quad (1.10)$$

Summing this to (1.9) delivers precisely the x component of the NSEs.

This shows that the NSEs are essentially Newton's equations

$$\frac{d}{dt}(m\Delta N \vec{u}) = \Delta V \vec{f} \quad (1.11)$$

as applied to the finite volumlet of volume ΔV and mass $m\Delta N = \rho \Delta V$.

The forces on the right-hand side of the NSE are most conveniently split into *conservative* and *dissipative* components, respectively.

The former is given by

$$\vec{f}^{con} = -\nabla(p + n\Phi) \quad (1.12)$$

where we have assumed that the external force derives from a potential Φ , i.e., $\vec{F} = -\nabla\Phi$. The overall pressure

$$p_{tot} = p + n\Phi \quad (1.13)$$

plays the role of a generalized potential. The most familiar case is perhaps the one of a fluid in a gravitational field, in which case $\Phi = -mgz$, g being the gravitational acceleration and z the elevation of the fluid element (minus sign indicates that lower-lying fluid layers experience higher hydrostatic pressure).

For *perfect* fluids, i.e., (idealized) fluids with strictly zero dissipation, NSE go by the name of Euler equations. Even though Euler fluids represent a very useful idealization, any real fluid is bound to display some form of dissipation, especially in the vicinity of solid walls (we dispense here with quantum effects leading to superfluidity).

According to the NSE, the dissipative force is given by

$$\vec{f}^{dis} = \nabla \cdot \vec{\sigma} \quad (1.14)$$

As anticipated, this is *not* implied by Newtonian physics.

Indeed, at the level of continuum mechanics, it cannot be derived from first principles, but must be postulated based on general heuristics guidelines. As we shall see, such

first-principle microscopic derivation comes quite naturally at the level of the kinetic theory of fluids.

Notwithstanding the heuristic nature of the dissipative force, the NSEs prove amazingly robust, whence their spectacular success in describing the physics of fluids under an impressively broad range of conditions.

The reason is that they encode very basic principles of Newtonian mechanics, plus a (very reasonable) assumption of linearity between the applied stress and the resulting strain. This immunizes them against the vagaries of the underlying microscopic interactions, a strong manifestation of what statistical physicists use to call by the beautiful name of *Universality*.

1.1.2 Navier–Stokes Equations in Lagrangian Form

The NSEs, as given in eqns (1.1), come in *mathematically* conservative form, in that the time change of density and momentum is driven by the divergence of a corresponding vector or tensor.

For many fluid-dynamic problems it proves expedient to recast them in a form which emphasizes the transport along the material-fluid lines, i.e., the lines whose tangent identifies with the fluid velocity itself.

Using the identities: $\nabla \cdot (\rho \vec{u}) = \vec{u} \cdot \nabla \rho + \rho \nabla \cdot \vec{u}$ and $\nabla \cdot (\rho \vec{u} \vec{u}) = \vec{u} \cdot \nabla (\rho \vec{u}) + \rho \vec{u} \cdot \nabla \vec{u}$, the NSE can be cast in so-called Lagrangian form, namely (2):

$$D_t \rho \equiv \partial_t \rho + \vec{u} \cdot \nabla \rho = -\rho \nabla \cdot \vec{u} \quad (1.15)$$

$$D_t \vec{u} \equiv \partial_t \vec{u} + \vec{u} \cdot \nabla \vec{u} = -\frac{\nabla p}{\rho} + \frac{1}{\rho} \nabla \cdot \vec{\sigma} \quad (1.16)$$

The Lagrangian representation emphasizes the role of the material derivative D_t ; both density and velocity are advected by the velocity itself, with no change along the fluid trajectory. Changes, on the other hand, are described by the terms on the right-hand side.

The qualitative difference between the Eulerian and Lagrangian viewpoints is sketched in Fig. 1.3.

For instance, the continuity equation describes a process whereby the density is carried with no change “on the back” of a fluid element, from position $\vec{x}$ to $\vec{x} + \vec{u} dt$ in a time lapse dt . Changes then occur due to the compressibility term on the right-hand side.

For the case of *incompressible* fluids, characterized by a divergence-free (solenoidal) flow velocity:

$$\nabla \cdot \vec{u} = 0 \quad (1.17)$$

the density loses the status of a space-time dependent field and can be set to a constant, conventionally $\rho = 1$. In this case, the solenoidal condition (1.17) takes the role of a *kinematic constraint* on the velocity field.

Since the material derivative is nothing but the acceleration in a frame moving with the fluid, the Lagrangian form of the Euler equation (zero-dissipative force) best reveals its genuine relation to Newtonian mechanics. The left-hand side is the acceleration, and

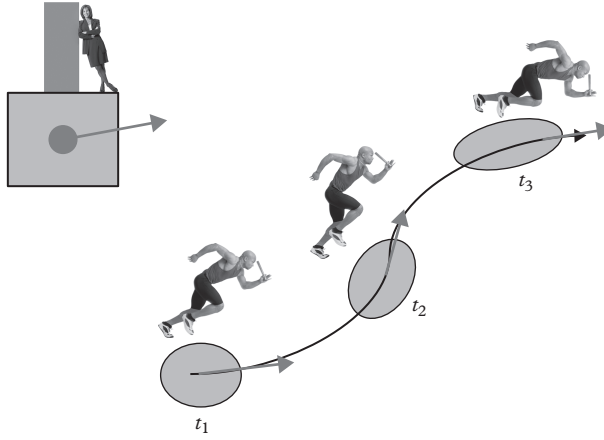


Figure 1.3 *The Eulerian (top-left) and the Lagrangian (bottom-right) approaches to the physics of fluids. In the Eulerian approach, the observer stands still at a given space location and watches the fluid moving in and out of the observing box. In the Lagrangian approach the observer “goes with the flow.”*

the right-hand side is the force per unit mass stemming from the generalized potential $p_{tot} = p + n\Phi$.

In fact, leaving only $\partial_i \vec{u}$ on the left-hand side identifies three type of conservative forces per unit mass, namely:

- Inertial: $\frac{\vec{f}^{ine}}{m} = -\vec{u} \cdot \nabla \vec{u}$
- Pressure: $\frac{\vec{f}^{pre}}{m} = -(\nabla p)/\rho$
- External: $\frac{\vec{f}^{ext}}{m} = -n \nabla \Phi$

The inertial forces account for the kinetic energy of the fluid. In the absence of dissipation, the total energy per unit volume

$$h = \rho \frac{u^2}{2} + p + n\Phi \quad (1.18)$$

is conserved along a fluid trajectory. This important statement of conservation is known as Bernoulli theorem, a cornerstone of hydrostatics.

Finally, we note that for an observer living in a local frame moving with the fluid, i.e., $\vec{u} \equiv 0$, the inertial forces disappear altogether. This substantial simplification lies at the heart of an important family of Lagrangian techniques for the numerical solution of the NSEs.

1.1.3 Navier–Stokes Equations in Coordinate Form

For the purpose of deriving hydrodynamics from kinetic theory, a task that shall be undertaken in chapter 5, it proves expedient to cast the NSE in coordinate form, that is

$$\partial_t \rho + \partial_a (\rho u_a) = 0 \quad (1.19)$$

$$\partial_t (\rho u_a) + \partial_b (\rho u_a u_b + p \delta_{ab} - \sigma_{ab}) = n F_a^{\text{ext}} \quad (1.20)$$

where Latin indices denote the spatial coordinates x, y, z and δ_{ab} is the Kronecker delta. As usual, repeated indices are summed upon.

This form emphasizes the conservative nature of the NSEs, while the coordinate notation lends transparency to the algebraic manipulations required to derive it from the underlying Boltzmann kinetic equation.

In particular, the momentum-flux tensor

$$P_{ab} \equiv \rho u_a u_b + p \delta_{ab} - \sigma_{ab} \quad (1.21)$$

will be shown to play a key role in the kinetic theory of fluids.

It is left as an exercise for the reader to verify that expressions (1.1) and (1.19–20) are basically the same wine in two different bottles.

1.2 Computational Aspects of the Navier–Stokes Equations

The NSEs rest on the representation of the fluid as continuum media, a pervasive field filling up space, with “no holes” in between. For more than a century, and with special thanks to Ludwig Boltzmann (1844–1906), we know that, at the atomic scale, matter is granular, made up of tiny atoms or molecules of sub-nanometric size. Being so tiny, these atoms are also very many, of the order of the Avogadro number $N_{av} \sim 6 \times 10^{23}$ in a little more than a centimeter cube of water (in fact, about $20 N_{av}$). As a result, it would be foolish, and needless as well, to attempt a quantitative description of a macroscopic fluid as collection of Avogadro numbers of atoms! The continuum representation achieves a spectacular compression of information: from Avogadro’s number of molecules, to just a fistful of continuum fields, density, velocity and pressure.

Beware, though, that such simplification is subtler than it seems. Indeed, by definition, a continuum field contains an *infinite* amount of information, and consequently this compression is, strictly speaking, an infinite inflation instead!

Of course, whenever analytical techniques are available to deal with such infinities, theory comes into its zenith.

However, as for most nonlinear theories, such glorious achievements are mostly confined to idealized situations.

As a result, the actual import of the previous compression of information is basically dictated by the discrete scale at which numerical solutions can be worked out.

Be that as it may, the continuum picture is the dominant one, to the point that the quantitative study of fluid dynamics is still often taken as a by-name for solving the NSEs.

This has spawned a very successful and still fast-growing discipline known as Computational Fluid Dynamics (CFD), a leading forefront of Computational science. CFD has made tremendous progress over the last half century, with a distinguished tradition tracing back to the famous John von Neumann’s (1903–57) 1949 “breaking-the-deadlock” report, where he advocated the use of digital simulation to gain knowledge on a variety of fluid phenomena (3).

Von Neumann’s bold vision is well captured by his famous statement: “[W]hat we cannot control, we shall predict, what we cannot predict, we shall control.”

In actual facts, such bold vision was depleted by the discovery of chaos and, more specifically, by the phenomenon of turbulence, which is a prominent reason (but surely not the only one) why fluid dynamics cannot be declassified under the rubric of “old science.”

Indeed, along with major progress, CFD has also taught us a very down-to-earth lesson: despite their harmless look, the NSEs prove *exceedingly* hard to solve on digital computers (let alone analytics).

As anticipated, one of the main reasons is *turbulence*, the name of nonlinearity when it comes to the physics of fluids.

Let us consider for simplicity the case of *incompressible* flows, for which the continuity equation reduces to the solenoidal condition on the velocity field given by (1.17). For such flows, the density is constant in space and time and, consequently, it can be scaled out from the equations by setting it to the conventional value $\rho = 1$.

The momentum equation then simplifies as follows:

$$\partial_t \vec{u} + \vec{u} \cdot \vec{\nabla} \vec{u} = \nu \Delta \vec{u} - \nabla p \quad (1.22)$$

where $\nu = \mu/\rho$ is the kinematic viscosity.

Turbulence results from the competition between large-scale advection, the term $\vec{u} \cdot \nabla \vec{u}$, and small-scale dissipation, the term $\nu \Delta \vec{u}$.

This ratio is measured by the Reynolds number

$$Re = \frac{UL}{\nu} \quad (1.23)$$

This number easily exceeds a million in many daily-life fluid phenomena, such as a car at a standard speed of 100 Km/h.

1.2.1 Why Is the Reynolds Number so Large?

The next natural question is: why is the nonlinearity so overwhelming over dissipation?

The reason is best highlighted by recasting the Reynolds numbers as follows:

$$Re = \frac{U}{c_s} \frac{L}{l_\mu} = \frac{Ma}{Kn} \quad (1.24)$$

an expression also known as the Von Karman relation (after Theodor von Karman, 1981–63).

In (1.24), c_s is the speed of sound and $l_\mu = v/c_s$ is the mean-free path, i.e., the average distance traveled by a molecule before colliding with another molecule. Furthermore,

$$Ma = \frac{U}{c_s} \quad (1.25)$$

is the Mach number (Ernst Mach, 1838–1916), the ratio of fluid to sound speed, and

$$Kn = \frac{l_\mu}{L} \quad (1.26)$$

is the Knudsen number, after the Danish scientist Martin Knudsen (1871–1949).

In air, molecules travel about one-tenth of a micron before colliding, which means that for an ordinary macroscopic object, say a car, featuring $L \sim 1$ m, the ratio L/l_μ is about 10 million: here we are with huge Reynolds numbers!

Indeed, the Mach number U/c_s is typically in the order of unity or less; a car traveling at 100 Km/h features $Ma \sim 0.1$, since the speed of sound in air in standard conditions is about $c_s \sim 300$ m/s.

In summary, the Reynolds number is large because it measures the length of the car in units of the mean-free path! The point is that advection acts at macroscopic scales, while dissipation takes over at much shorter scales, known as the dissipative or Kolmogorov scale, after the famous scaling theory formulated by the Russian mathematician A.N. Kolmogorov (1903–87) back in 1941.

According to this theory, the smallest dynamically active scale in a turbulent flow at a given Reynolds number Re is given by

$$l_d = \frac{L}{Re^{3/4}} \quad (1.27)$$

Thus, the number of degrees of freedom in a turbulent flow of size L is approximately:

$$N_{def} = \left(\frac{L}{l_d} \right)^3 \sim Re^{9/4} \quad (1.28)$$

For an ordinary flow at $Re = 10^6$, this makes about $N_{def} \sim 10^{14}$ degrees of freedom, still way less than the some 50 Avogadro's number of molecules contained in a cubic meter of air, and yet far in excess of those affordable even on the most powerful supercomputers (current leading-edge simulations of fluid turbulence are handling of the order of ten billion degrees of freedom).

This, combined with the fact that fluids of practical interest typically move in highly complex geometries (cars, airplanes and the like), makes the ordeal of solving the NSE an extremely difficult one. This is essentially the reason behind the relentless pursuit of innovative computational methods for fluid flows.

The overwhelming majority of CFD methods focus on various discretizations of the NSE, as a set of nonlinear partial differential equations. That is, one starts from the NSE in their continuum form, and devises different methods to represent such equations on a discrete grid, be it fixed in space (Eulerian approach) or moving along with the fluid (Lagrangian approach).

In order for the simulation to be spatially resolved, the grid spacing must be smaller than the Kolmogorov dissipative scale, namely

$$\Delta x < l_d \quad (1.29)$$

This shows that the actual number of grid points, $N_{grid} = (L/\Delta x)^3$, must necessarily exceed the number of physical degrees of freedom. These bounds are dictated by the basics physics of turbulence; hence they do not depend on the specific discretization procedure. However, they speak clearly for computational requirements of CFD.

As we shall see, the Lattice Boltzmann equation falls in the line of a major paradigmatic shift, first opened up by its forerunner, the Lattice Gas Cellular Automata (LGCA) method.

That is computational fluid dynamics without directly discretizing the NSEs.

Instead of discretizing partial differential equations, the idea is to track the dynamics of a fictitious set of *representative particles*, supporting macroscopic fluid behavior described by the NSEs, as an *emergent* phenomenon.

In other words, one does not solve the emergent equation itself (Navier–Stokes), but the underlying stylized microscopic dynamics instead.

The obvious question is: what's the point of such an indirect approach?

The answer, which we shall spell out in the sequel, is indeed not completely obvious.

1.3 The Benefits of Kinetic Extra Dimensions

The advantage is that, as we shall expound in the course of this book, particle dynamics can be made much simpler than the dynamics of hydrodynamic fields.

For instance, force-free particles move along straight trajectories, while material lines follow the fluid velocity itself, which is typically highly complex field even in a force-free fluid.

Let's expand on the point.

As we shall see, the basic object of Boltzmann's kinetic theory (see Fig. 1.4) is the one-particle distribution function (4): $f(\vec{x}, \vec{v}; t)$, which represents the probability density of finding a molecule at position $\vec{x}$ in space at time t , with a given velocity $\vec{v}$.

In actual practice,

$$\Delta N = f \Delta \vec{x} \Delta \vec{v} \quad (1.30)$$

is the mean number of particles in the *phase-space* element of volume $\Delta \vec{x} \Delta \vec{v}$. From a mere fluid dynamic perspective, $f(\vec{x}, \vec{v}; t)$ is a highly redundant object, as the information on the molecular velocity has no explicit bearing on the fluid equations, which only depend on space and time. As a result, at first sight, the Boltzmann equation looks like a total overkill when it comes to fluid dynamics, six dimensions: three in ordinary space and three in velocity space, against just three!

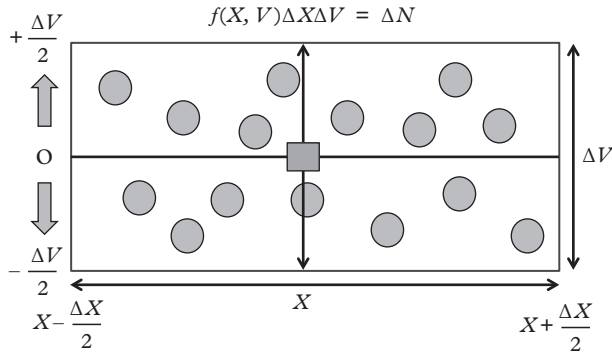


Figure 1.4 *The meaning of the Boltzmann distribution function. Fifteen particles lying in the segment Δx each with its own velocity in the range $-\frac{\Delta v}{2} < v < \frac{\Delta v}{2}$ are represented by fifteen points in the phase-space element $\Delta x \Delta v$. The distribution function is the density of particles in this six-dimensional phase space (two dimensional in the figure).*

1.3.1 Molecular Streaming versus Fluid Advection

However, precisely because velocity and space coordinates are independent variables, *in phase space the information travels in a much simpler way than in ordinary configuration space.*

In fact, the Boltzmann distribution $f(\vec{x}, \vec{v}; t)$ moves along straight lines defined by the molecular speed, namely

$$d\vec{x}_v = \vec{v} dt, \quad (1.31)$$

where $\vec{v}$ carries no dependence on space or time.

This is what we refer to as *molecular free-streaming*, as opposed fluid advection, which proceeds along the *material* lines in ordinary space (see Fig. 1.5).

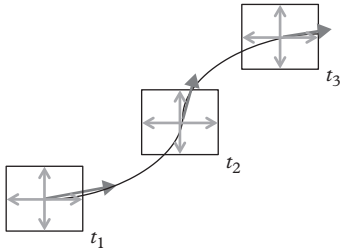


Figure 1.5 *Fluid trajectory (curved line) versus molecular streamlines, here represented by just four directions for simplicity. The four directions are independent of the spatial location of the fluid element.*

The latter are defined by

$$d\vec{x}_u = \vec{u}(\vec{x}; t) dt, \quad (1.32)$$

The inertial term $\vec{u} \cdot \nabla \vec{u}$ in the NSE is just the acceleration along a material line.

In general, the flow field $\vec{u}$ may be a fairly complicated function of space and time, in contrast to the simple straight molecular trajectories. In the kinetic picture, all this complexity is absorbed by the Boltzmann distribution $f(\vec{x}, \vec{v}; t)$, while the streaming of molecules keeps going along straight lines, no matter how complex the macroscopic field.

In slightly more technical language, hydrodynamic transport in ordinary space, i.e., *advection*, is nonlinear because the material lines are defined by the flow velocity itself, while molecular transport in phase space, i.e., *streaming*, is linear because the molecular trajectories do not depend on the transported quantity, namely $f(\vec{x}, \vec{v}; t)$.

1.3.2 Molecular Relaxation versus Momentum Diffusivity

The kinetic representation also has profound implications on the description of dissipative effects. In the Navier–Stokes picture, these are described by the divergence of a gradient, i.e., the Laplace operator. This is because, at a macroscopic level, dissipation is due to momentum diffusivity across the fluid and the equivalence between space and time has to be broken to describe irreversible behavior. Consider a fluid driven by a moving wall; the layers near the wall are set in motion by direct contact with the wall, and transmit these motions thanks to the diffusion of momentum in the direction perpendicular to the wall. If the momentum would not diffuse, the wall would move on its own with no effect on the fluid. Conversely, the fluid would move along a fixed wall with no friction (superfluid).

Kinetic theory, on the other hand, does not know about diffusion (an emergent phenomenon); it only knows about molecular collisions. These collisions act in such a way as to relax the Boltzmann distribution to a local equilibrium, on a time scale which is basically the average time traveled by a molecule before colliding with another molecule. The local equilibrium is a Gaussian (Maxwell–Boltzmann) distribution in velocity space, which depends parametrically on the local fluid density, velocity and temperature. Here, local means the same spatial position $\vec{x}$ and time t at which the Boltzmann distribution is evaluated.

By definition, fluid quantities show appreciable variations on space and time scales well above those associated with molecular relaxation. Such scale separation is quintessential to obtain hydrodynamics as the asymptotic limit of kinetic theory as the Knudsen number is sent to zero.

It can be shown that momentum diffusivity is precisely the macroscopic manifestation of molecular relaxation. However, since momentum diffusivity *emerges* from collisions, and since Boltzmann's collisions are completely local in space and time, they do not involve any space-time communication, such communication being in full charge of the streaming operator only. Nor do they demand any symmetry breaking between space and time, since relaxation to local equilibrium takes place through molecular collisions.

As a result, the kinetic formalism does not need any Laplacian operator to represent diffusion processes, which is again a significant simplification, both from the conceptual and computational points of view.

1.4 Summary

Summarizing, the NSEs of continuum fluid mechanics prove exceedingly difficult to solve, as they assemble two nightmares of computational physics: strong nonlinearity and complex geometry, within a fully three-dimensional, time-dependent formulation.

The kinetic picture trades three extra-velocity dimensions for linearity and locality: *linear streaming versus nonlinear advection* and *local relaxation versus non-local momentum diffusion*. More precisely, it disentangles non-locality and nonlinearity: nonlocality (streaming) is linear and nonlinearity (collisions) is local. It turns out that lattice versions of the Boltzmann-kinetic equation make a very attractive computational bargain of such disentanglement. This is the bottom line of the lattice Boltzmann story to be told in this book.

REFERENCES

1. L. Landau and E. Lifshitz, *Fluid Mechanics*, Pergamon Press, Oxford, 1987.
2. R. Peyret, *Computational Methods for Fluid Flow*, Springer Verlag, 1983.
3. U. Frisch, *Turbulence*, Cambridge Univ. Press, Cambridge, 1999.
4. L. Boltzmann, *Vorlesungen über Gastheorie*, in Lectures on Gas Theory, J.A. Barth Editor, unab. Dover, Leipzig, 1995.

EXERCISES

1. Prove the equivalence between eqns (1.1) and (1.19).
2. The ratio l_d/l_μ measures the separation between the smallest hydrodynamic and the microscopic scale. Does this ratio increase or decrease in the limit of infinite Reynolds number?
3. Derive the equations for incompressible flows from the general eqns (1.1). Hint: use the identities $\nabla \cdot (\rho \vec{u}) = \vec{u} \cdot \nabla \rho + \rho \nabla \cdot \vec{u}$ and $\nabla \cdot (\rho \vec{u} \vec{u}) = \vec{u} \cdot \nabla (\rho \vec{u}) + \rho \vec{u} \cdot \nabla \vec{u}$.

Boltzmann's Kinetic Theory

Kinetic theory is the branch of statistical physics dealing with the dynamics of non-equilibrium processes and their relaxation to thermodynamic equilibrium. Established by Ludwig Boltzmann (1844–1906) in 1872, his eponymous equation stands as its mathematical cornerstone. Originally developed in the framework of dilute gas systems, the Boltzmann equation has spread its wings across many areas of modern statistical physics, including electron transport in semiconductors, neutron transport, quantum liquids, to cite but a few. In this chapter, we shall provide a basic introduction to the Boltzmann equation in the context of classical statistical mechanics.

I am conscious of being only an individual struggling weakly against the stream of time. But it still remains in my power to contribute in such a way that, when the theory of gases is again revived, not too much will have to be rediscovered.

(L. Boltzmann)

2.1 Atomistic Dynamics

Let us consider a collection of N molecules moving in a box of volume V at temperature T and mutually interacting via a two-body intermolecular potential $V(\vec{r})$, $\vec{r}$ being the intermolecular separation between two generic molecules.²

If the linear size s of the molecules, basically the effective range of the short-range interaction potential, is much smaller than their *mean-interparticle separation* $d = (V/N)^{1/3}$,

² The symbol $V(\vec{r})$ denotes the interparticle potential, not to be confused with plain V , the volume of the system, and $\vec{V}$ the barycentric velocity of the two-body problem.

the molecules can, to a good approximation, be treated like *point-like structureless* particles.

To the extent where the De Broglie length $\lambda = \hbar/mv$ of these particles is much smaller than any other relevant length scale, their dynamics is governed by the classical Newton's equations:

$$\begin{cases} \frac{d\vec{x}_i}{dt} = \vec{v}_i, \\ \frac{d\vec{v}_i}{dt} = \frac{\vec{F}_i}{m}, \quad i = 1, N \end{cases} \quad (2.1)$$

where $\vec{x}_i$ is the position coordinate of the i -th particle, $\vec{v}_i$ its velocity and $\vec{F}_i$ is the force experienced by the i -th particle as a result of intermolecular interactions and possibly external fields (gravity, electric field, etc.).

Upon specifying initial and boundary conditions, equations (27.50) can in principle be solved in time, to yield a fully exhaustive knowledge of the state of the system, namely a set of $6N$ functions of time $\{\vec{x}_i(t), \vec{v}_i(t)\}$, $i = 1, N$.

This programme is totally unviable and, fortunately, needless as well. Unviability stems from two main reasons: first, N is generally of the order of the Avogadro number $N_{Av} \sim 10^{23}$, far too big for any foreseeable computer. Second, even if one could store it, tracking so much information for sufficiently long times would be utopia, since any tiny uncertainty on the initial conditions would blow up in the long run because of dynamical instability of phase space. By dynamical instability, we refer to the fact that any uncertainty δ_0 on the initial positions and/or momenta grows exponentially in time as $\delta(t) = \delta_0 e^{\lambda t}$. The coefficient λ , known as *Lyapunov exponent*, is a measure of the temporal horizon of deterministic behavior of the N -body system, in that at times greater than λ^{-1} , the growth of uncertainty is such to prevent any deterministic prediction of the state of the system. It is estimated that a centimeter cube of Argon in standard conditions (300 K, 1 *Atm*) produces as much as 10^{29} digits of information per second. This means that in order to keep an exact record of the state of the system over a 1 s lifespan, we need a number with nothing less than 10^{29} digits. Fortunately, we manage to survive with less than that, reason being that *we are much larger than the molecules our body is made of* !

The physical observables we are interested in, say the fluid pressure, temperature, visible flow originate from a statistical average over a large number of individual molecular histories.

A rigorous definition of what is meant by statistical average is not trivial, but here we shall be content with the intuitive notion of spatial average over a thermodynamic volume, namely a region of space sufficiently small with respect to the global dimensions of the macroscopic domain, and yet large enough to contain a statistically meaningful sample of molecules.

Typical numbers help getting the picture. The density of air in standard conditions is about $n_L = 2.687 \cdot 10^{25}$ molecules/ m^3 (known as *Loschmidt number*). Hence, a centimeter cube of air contains about $2.7 \cdot 10^{19}$ molecules, corresponding to a statistical error of less than one part per billion.

2.2 Statistical Dynamics: Boltzmann and the BBGKY Hierarchy

Given the very huge numbers involved, it appears therefore wise to approach the collective behavior of the ensemble of molecules from a *statistical* point of view.

This can be done at various levels of complexity, but, for a start, we shall begin with the simplest one: the *single-particle kinetic* level.

The chief question of single-particle kinetic theory is:

What is the probability of finding a molecule around position $\vec{x}$ at time t with velocity $\vec{v}$?

Let $f(\vec{x}, \vec{v}, t)$ the probability density, more often simply denoted as distribution function.

The quantity $\Delta N = f \Delta \vec{x} \Delta \vec{v}$ represents the mean number of molecules in a finite volume $\Delta \vec{x} \Delta \vec{v}$, centered about $(\vec{x}, \vec{v})$ in the so-called single-particle *phase space*:

$$\Gamma_1 = \{\vec{z} \equiv (\vec{x}, \vec{v}); \vec{x}, \vec{v} \in R^3\}$$

Integration upon the velocity degrees of freedom delivers the number of particles per unit volume, i.e., the number density of the system at any given time t :

$$\int f(\vec{x}, \vec{v}; t) d\vec{v} = \frac{\Delta N}{\Delta V}$$

which recovers the continuum density $n(\vec{x}, t)$ in the limit $\Delta V \rightarrow 0$.

As a result, integration upon the entire phase space delivers the total number of molecules in the system at any given time t ,

$$\int f(\vec{x}, \vec{v}; t) d\vec{x} d\vec{v} = N(t)$$

The distribution function $f(\vec{x}, \vec{v}; t)$ is the pivotal object of Boltzmann's kinetic theory.

In 1872, Ludwig Boltzmann (1844–1906) was able to derive an equation describing the evolution of $f(\vec{x}, \vec{v}; t)$ in terms of the underlying microdynamic interactions. This is the celebrated Boltzmann equation (BE), one of the greatest achievements of theoretical physics of the nineteenth century (1).

The BE represents the first quantitative effort to attack the grand-issue of why time goes “one-way only” on a macroscopic scale while the underlying microdynamics is apparently perfectly reversible.³ In this book, we shall not be much concerned with fundamental issues, but rather keep the focus on the BE as a mathematical tool to investigate, analytically or numerically, the properties of fluid flows far from equilibrium.

³ We shall stick to the common tenet that microscopic equations, either classical or quantum, are invariant under time reversal.

The kinetic equation for the one-body distribution function in the presence of an external force $\vec{F}(\vec{x})$ reads as follows (2):

$$\partial_t f + \vec{v} \cdot \partial_{\vec{x}} f + \vec{a} \cdot \partial_{\vec{v}} f = C_{12} \quad (2.2)$$

where $\vec{a} = \vec{F}/m$ is the particle acceleration due to external and internal forces.

The left-hand side represents the streaming of the molecules along the trajectories associated with the force field $\vec{F}$ (straight lines if $\vec{F} = 0$) and C_{12} represents the effects of intermolecular (two-body) collisions taking molecules in/out the streaming trajectory.

Let us comment on the two sides separately.

Once it is accepted that the cloud of N molecules moves like a lump of fluid in phase space Γ_1 , the streaming term reduces to a mere mirror of Newtonian mechanics.

To convince oneself, simply rewrite the streaming term as a Lagrangian derivative along the trajectory $\vec{x}(t)$,

$$\frac{df}{dt} \equiv \partial_t f + \frac{d\vec{x}}{dt} \cdot \partial_{\vec{x}} f + \frac{d\vec{v}}{dt} \cdot \partial_{\vec{v}} f$$

Using Newton's equations, $\frac{d\vec{x}}{dt} = \vec{v}$, $\frac{d\vec{v}}{dt} = \vec{F}/m$, this returns precisely the left-hand side of the Boltzmann equation. The streaming term carries the information contained in the distribution function untouched from place to place in phase-space.

Indeed, the solution of the collisionless Boltzmann equation $\frac{df}{dt} = 0$, with initial conditions $f(\vec{x}, \vec{v}, t = 0) = f_0(\vec{x}, \vec{v})$, is simply

$$f(\vec{x}, \vec{v}, t) = f_0[\vec{x}(t), \vec{v}(t)], \quad (2.3)$$

where $\vec{x}(t)$ and $\vec{v}(t)$ is the solution of the Newton's equations with initial conditions $\vec{x}(t = 0) = \vec{x}$ and $\vec{v}(t = 0) = \vec{v}$. The key physical point is the following: the streaming term moves the distribution function in phase space with no loss of information, hence no loss of memory of the initial conditions: *reversible* motion.

2.3 The Born–Bogoliubov–Green–Kirkwood–Yvon (BBGKY) Hierarchy

The right-hand side of the BE, on the other hand, takes care of exchanging information across different trajectories, through intermolecular interactions.

The collision operator encodes two-body collisions, between, say molecule one, sitting at point $\vec{x}_1$ with speed $\vec{v}_1$ and molecule two, sitting at $\vec{x}_2$ with speed $\vec{v}_2$, both at time t .

Formally, this information is stored in the *two-body* distribution function

$$f_{12}(\vec{x}_1, \vec{v}_1, \vec{x}_2, \vec{v}_2; t),$$

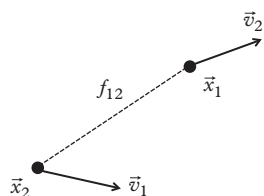


Figure 2.1 Sketch of the two-body distribution function f_{12} . The two molecules are correlated to each other, so that if one moves the other must move too. In the one-body representation, each molecule moves independently, although it feels the effects of the other molecules through short-range collisions described by the collision operator C_{12} .

expressing the *joint* probability of finding molecule one around $\vec{x}_1$ with speed $\vec{v}_1$ and molecule two at $\vec{x}_2$ with speed $\vec{v}_2$, both at time t (see Fig. 2.1).

More precisely, the quantity

$$\Delta N_{12} = f_{12} \Delta \vec{x}_1 \Delta \vec{v}_1 \Delta \vec{x}_2 \Delta \vec{v}_2$$

gives the average number of *pairs* of molecules sitting at points $\vec{z}_1 \equiv (\vec{x}_1, \vec{v}_1)$ and $\vec{z}_2 \equiv (\vec{x}_2, \vec{v}_2)$ of phase space at time t .

Living as it does in a $(6 + 6 = 12)$ -dimensional phase space (13 with time), it goes without saying that f_{12} is a very heavy-duty object to work with.

The one-body distribution is recovered by integrating over the second particle phase-space coordinates:

$$f_1(\vec{x}_1, \vec{v}_1; t) = \frac{2}{N-1} \int f_{12}(\vec{x}_1, \vec{v}_1, \vec{x}_2, \vec{v}_2; t) d\vec{x}_2 d\vec{v}_2 \quad (2.4)$$

where the factor 2 accounts for the fact that there are $N(N-1)/2$ symmetric pairs out of a pool of N particles.

Clearly, this projection from 13 to 7 dimensions erases a huge amount of information, the two-body correlations. The loss of this information prevents an exact reconstruction of f_{12} from $f_1 \equiv f(\vec{z}_1; t)$ and $f_2 \equiv f(\vec{z}_2; t)$, separately.

However, as we shall see shortly, educated guesses on the physical nature of the system under consideration, can (partially) make up for this fundamental limitation. In principle, it is not difficult to write down the dynamic equation for f_{12} , the only trouble being that this equation calls into play the three-body distribution function f_{123} , which in turn depends on f_{1234} and so on, down an endless line known as the BBGKY hierarchy, after Bogoliubov, Born, Green, Kirkwood and Yvon (4).

The physical origin of such open structure is that a N -body system can in principle host molecular collisions at all orders, from binary onward up to order N . If one could solve the BBGKY hierarchy, one would obtain a complete *statistical* knowledge of the full N -body problem described by the Newtonian equations for the N molecules. This is again utopia, only in statistical rather than dynamic vests!

Consequently, one must settle for less ambitious goals, i.e., approximate descriptions. The loss of information inevitably associated with such approximations is responsible for *irreversibility*, to be literally intended as our inability to reconstruct the initial conditions exactly (loss of memory).

Fortunately, powerful heuristics are available to guide the search for sensible approximations to the BBGKY hierarchy.

Indeed, in actual practice, the probability of a simultaneous interaction between, say, k molecules, decays very fast with k , approximately like $(s/d)^{3k}$, where

$$d = 1/n^{1/3}$$

is the mean-intermolecular separation and n is the number density, the two being related via $nd^3 = 1$, i.e., one particle on average in a cublet of volume d^3 .

The ratio

$$\tilde{n} = \left(\frac{s}{d}\right)^3 \equiv ns^3 \quad (2.5)$$

sometimes called “granularity,” provides a direct measure of the degree of diluteness of the system. Indeed, in a system at density n , each molecule inhabits a volume d^3 , and $\tilde{n}$ is the fraction of that volume occupied by the molecule itself (here a cublet of side s).

From its very definition, it is clear that $\tilde{n}$ controls the strength of many-body interactions, which fade away as $\tilde{n} \rightarrow 0$. For instance, air at standard conditions features $\tilde{n} \sim 10^{-3}$, so that many-body interactions are largely negligible. Water in standard conditions, on the other hand, provides $\tilde{n} \sim 1$, which surely calls for careful consideration of many-body effects. Nevertheless, as we shall see in Chapter 3, the structure of the Navier–Stokes equations of continuum fluid dynamics is to a large extent independent of many-body effects. This is a great gift of mother nature, known as *Universality*.

2.4 Back to Boltzmann

The simple, yet basic, considerations previously suggested, set the stage for Boltzmann's clever way out of the BBGKY hierarchy.

To close equation (2.2), Boltzmann made a few stringent assumptions on the nature of the physical system: a *dilute* gas of *point-like*, *structureless* molecules interacting via a *short-range* two-body potential.

Under such conditions, intermolecular interactions can be described solely in terms of localized binary collisions, with molecules spending most of their lifespan on free trajectories (in the absence of external fields), merrily unaware of each other.

Within this picture, the collision term splits into Loss and Gain components:

$$C_{12} \equiv \mathcal{G} - \mathcal{L} = \int (f_{1'2'} - f_{12}) v_r \sigma(v_r, \vec{\Omega}) d\vec{\Omega} d\vec{v}_2 \quad (2.6)$$

corresponding to direct(inverse) collisions taking molecules out(in) the volume element $d\vec{v}_1 d\vec{v}_2$ respectively (see Fig. 2.2).

The right-hand side requires a number of detailed comments.

First, the shorthand f_{12} stands for $f_{12}(\vec{z}_1, \vec{z}_2; t)$.

In the above, v_r is the magnitude of the relative speed between particle 1 and particle 2 and $\vec{\Omega}$ denotes the solid angle associated with the scattering event (see Fig. 2.3). The

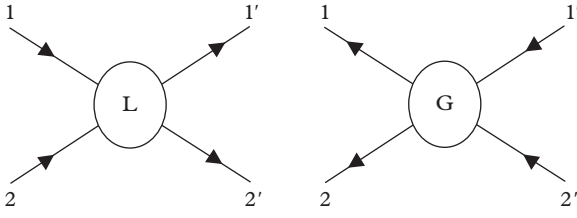


Figure 2.2 Symbolic diagram of direct and inverse collisions-. Inverse collisions (Gain) place particles in state one, while direct collisions (Loss) take them away from it.

symbol σ denotes the differential cross section, i.e. the effective area presented by a particle in the plane across its center and perpendicular to the relative velocity.

Likewise, $f_{1'2'}$ stands for $f_{12}(\vec{z}'_1, \vec{z}'_2; t)$, where prime indicates the molecular positions and velocities *after* a direct collision.

These two factors are purely statistical in nature. Note that *all* four spatial coordinates, both pre- and post-collisional, lie within a sphere of radius $s \ll d$, on account of the diluteness assumption. Therefore, in the Boltzmann limit $s/d \rightarrow 0$, they can be reconduced to the same spatial location $\vec{x} = \vec{x}_1 = \vec{x}'_1 = \vec{x}_2 = \vec{x}'_2$.

This is a major simplification of the Boltzmann equation, with far-reaching consequences on theoretical as well as computational aspects.

The pre- and post-collisional velocities $\vec{v}_1, \vec{v}_2$ and $\vec{v}'_1, \vec{v}'_2$ are related through the three basic Mass–Momentum–Energy conservation laws, that is

$$\begin{cases} m_1 + m_2 = m'_1 + m'_2 \\ m_1 \vec{v}_1 + m_2 \vec{v}_2 = m'_1 \vec{v}'_1 + m'_2 \vec{v}'_2 \\ m_1 v_1^2 + m_2 v_2^2 = m'_1 v'^2_1 + m'_2 v'^2_2 \end{cases} \quad (2.7)$$

Since mass can be assumed invariant across a collision, $m'_1 = m_1$ and $m'_2 = m_2$, the first equation is basically a statement of number conservation, 2 = 2, two molecules before collisions, two molecules after.

The other two conservation laws, however, deliver a great deal of information, as we shall see in the sequel.

2.4.1 Two-Body Scattering

The two-body collision problem is best treated as the scattering of a single particle of reduced mass m_r impinging on a target particle of mass $M = m_1 + m_2$, sitting at the median position $\vec{X}$, with median velocity $\vec{V}$, defined as follows:

$$\begin{cases} \vec{X} = (m_1 \vec{x}_1 + m_2 \vec{x}_2)/M \\ \vec{V} = (m_1 \vec{v}_1 + m_2 \vec{v}_2)/M \end{cases} \quad (2.8)$$

The reduced mass is given by

$$m_r = \frac{m_1 m_2}{m_1 + m_2} \quad (2.9)$$

and it is seen to coincide with the lightest mass, say m_1 , in the limit $m_2 \gg m_1$. For equal mass molecules, the case assumed hereafter, $m_r = m/2$ and $M = 2m$.

The two-body scattering problem is best treated in a frame with the origin located at $\vec{X}$.

Using a polar representation (r, θ) for the interparticle separation

$$\vec{r} = \vec{x}_1 - \vec{x}_2 \quad (2.10)$$

the total energy writes as

$$E = \frac{m_r v_r^2}{2} + \frac{\mathcal{J}^2}{2m_r r^2} + V(r) \quad (2.11)$$

where

$$\mathcal{J} \equiv m_r r^2 \dot{\theta} = m_r v_r b \quad (2.12)$$

is the angular momentum and $V(r)$ the interparticle potential.

In (2.12), b is the so-called impact parameter, i.e., the distance of the colliding molecule from the origin perpendicular to its relative velocity (see Fig. 2.2).

After noting that mass-momentum conservation yields

$$\vec{V}' = \vec{V}$$

it is readily appreciated that energy conservation implies that the relative velocity vector

$$\vec{v}_r = \vec{v}_2 - \vec{v}_1 \quad (2.13)$$

is conserved in magnitude.

As a result, the only effect of the collision is to rotate the relative velocity by an angle χ in the scattering plane defined by $\vec{r}$ and $\vec{v}_r$.

The kinematic identity $\vec{v}_i = \vec{V} - (m_j/M)\vec{v}_r$, $i = 1, 2$, $j = 2, 1$, delivers the following mapping between post- and pre-collisional velocities:

$$\begin{cases} \vec{v}'_1 = \vec{v}_1 - \frac{m_2}{M} \vec{v}_r \\ \vec{v}'_2 = \vec{v}_2 + \frac{m_1}{M} \vec{v}_r \end{cases} \quad (2.14)$$

It can be checked that this one-to-one mapping preserves the volume element in velocity space, i.e.,

$$|d\vec{v}'_1 d\vec{v}'_2| = |d\vec{v}_1 d\vec{v}_2| \quad (2.15)$$

a property which shall prove very useful in the sequel.

With the two-body kinematics in place, one can compute the number of molecules, dN , scattered around the solid angle $d\vec{\Omega} = \sin\chi d\chi d\alpha$, where α fixes the orientation of the scattering plane in three-dimensional space.

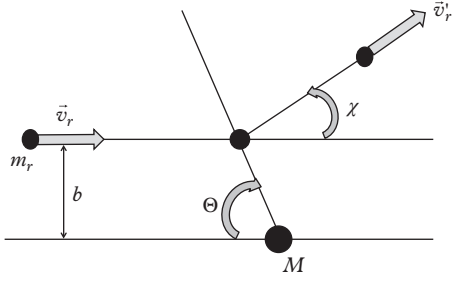


Figure 2.3 Scattering angle associated with a binary collision. The collision takes place in the plane defined by the interparticle separation $\vec{x}_1 - \vec{x}_2$ and the relative speed $\vec{v}_r = \vec{v}_1 - \vec{v}_2$. The solid angle $\vec{\Omega}$ is defined by the scattering angle χ in the collisional plane and by the azimuthal angle ϕ around the collisional plane (not shown).

The relation

$$dN = \sigma(v_r, \vec{\Omega}) d\vec{\Omega}$$

defines the so-called *differential cross section* σ .

The next task is to compute the scattering angle $\chi = \chi(b, v_r)$ as a function of the impact parameter and the relative velocity (see Fig. 2.3).

To this purpose, let us consider all impinging particles sitting in the annulus of radius b and thickness db . The conservation of the number of these particles implies, namely:

$$2\pi b db = 2\pi \sigma(\chi, v_r) \sin\chi d\chi \quad (2.16)$$

$$\sigma(\chi, v_r) = \frac{b}{\sin\chi} \frac{db}{d\chi} \quad (2.17)$$

This reveals that the differential cross section is fixed by the functional relation $b = b(\chi, v_r)$, which in turn depends on the details of the scattering potential $V(r)$.

A quantity of major interest is the *cross section*:

$$\sigma(v_r) = \int \sigma(\chi, v_r) \sin\chi d\chi \quad (2.18)$$

and its integral version:

$$\Sigma(T) = 4\pi \int \sigma(v_r) f(v_r) v_r^2 dv_r = n\sigma_T \quad (2.19)$$

also known as total cross section. Note that σ_T , as defined above, is generally a function of the temperature T , so that one can write

$$\sigma_T = \kappa(T) s^2 \quad (2.20)$$

s being the size of the molecule, identified with the range of the potential. For short-range potentials one can further assume $\kappa(T) \sim O(1)$, i.e., the effective cross section does not differ drastically from the geometrical one.

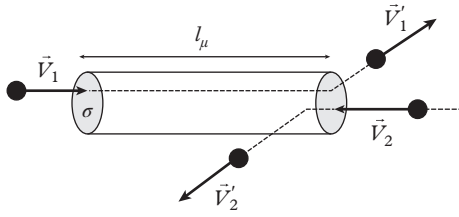


Figure 2.4 Geometrical representation of the mean-free path. The molecule two travels a distance l_μ before colliding with molecule two. The associated cross section defines the collisional cylinder, whose volume is $V_{col} = \sigma l_\mu$. In the dilute gas limit $\tilde{n} \rightarrow 0$, the collisional cylinder collapses to a needle-like shape with $\sigma/l_\mu \rightarrow 0$.

The total cross section defines the molecular mean-free path (see Fig. 2.4):

$$l_\mu = \frac{1}{\Sigma} \quad (2.21)$$

and the associated collisional timescale

$$\tau_\mu = \frac{l_\mu}{v_T} = \frac{1}{n\sigma_T v_T}. \quad (2.22)$$

where

$$v_T = \sqrt{\frac{k_B T}{m}}$$

is the thermal speed.

The mean-free path is the mean distance traveled by a molecule before colliding with another molecule and represents the pivotal lengthscale of kinetic theory and transport phenomena.

2.4.2 Spatial Ordering in Dilute Gases

Based on the definitions (2.19) and (2.21), one obtains

$$n\sigma_T l_\mu = 1$$

indicating that by construction, the so-called collisional cylinder of volume $\sigma_T l_\mu$ contains just a single colliding molecule.

Recalling the definition of the mean-interparticle distance, $nd^3 = 1$, the previous section yields

$$\frac{l_\mu}{d} = \frac{d^2}{\sigma_T}.$$

Based on the relation (2.20) with $\kappa \sim 1$, one further obtains

$$s \ll d \ll l_\mu$$

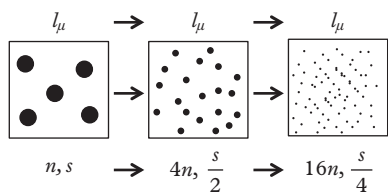


Figure 2.5 Geometrical representation of the dilute gas limit in Boltzmann kinetic theory. By halving the size s , density quadruples and the total area ns^2 , inversely proportional to the mean-free path, stays the same (at least this is the intention of the picture.).

which is the typical scale ordering of dilute gases.

It is of interest to note that the proper meaning of “dilute gas” in the Boltzmann framework does *not* correspond at all to a gas in the ordinary sense, i.e., a fluid of vanishingly small density. Quite on the contrary, the proper limit is the one where density is formally sent to infinity! The point is that, at the same time, the size s is sent to zero, in such a way as to keep the product ns^2 constant. In other words, size goes to zero, density goes to infinity and the mean-free path is left constant. Putting all together, the mean-intermolecular distance scales like $d \sim n^{-1/3}$ while the molecular size scales like $s \sim n^{-1/2}$, so that the diluteness parameter $\tilde{n} = (s/d)^3$ scales like $n^{-1/2}$ and goes to zero in the limit $n \rightarrow \infty$, (see Fig. 2.5).

Summarizing, the dilute gas limit corresponds to the following limiting scenario:

$$s \rightarrow 0, n \rightarrow \infty, l_\mu = \text{Const.}, \tilde{n} \rightarrow 0 \quad (2.23)$$

This further witnesses the crucial role of the mean-free path as the fundamental length scale of Boltzmann kinetic theory and shows that $\tilde{n}$ is the appropriate smallness parameter describing many-body effects in dense gases and liquids. We shall return to these matters in Chapter 7 devoted to the kinetic theory of dense fluids.

2.4.3 Two-Body Scattering Problem

To sort out the explicit dependence $\chi = \chi(b, v_r)$, one needs to solve the two-body scattering problem. To this aim, it proves expedient to move to polar coordinates in the scattering plane.

The equations of motion resulting from conservation of energy E and angular momentum $\mathcal{J}$ read as follows:

$$E = \frac{1}{2}m_r \dot{r}^2 + \frac{m_r^2 v_r^2 b^2}{r^2} + V(r) = \frac{m_r}{2} v_r^2 \quad (2.24)$$

$$\mathcal{J} = m_r r^2 \dot{\theta} = m_r v_r b \quad (2.25)$$

where the right-hand side corresponds to the limit $r \rightarrow \infty$.

Dividing the two, one obtains

$$\frac{dr}{d\theta} = \frac{r^2}{b} \left[1 - \frac{b^2}{r^2} \phi(r) \right]^{1/2} \quad (2.26)$$

where

$$\phi(r) = \frac{2V(r)}{m_r v_r^2} \quad (2.27)$$

is the ratio of potential to kinetic energy in the rest frame.

For purely repulsive potentials, there exists a minimum-approach distance, r_{min} defined by the condition $\frac{dr}{d\theta} = 0$.

Some algebra delivers the implicit relation:

$$\frac{r_{min}}{b} = \sqrt{\frac{m_r v_r^2 / 2}{E - V(r_{min})}} \quad (2.28)$$

Note that for repulsive potentials, $V(r) > 0$, $r_{min} > b$, while the opposite is true for attractive ones.

Integrating upon r from r_{min} to infinity, one obtains

$$\Theta \equiv \theta_{min} - \theta_{\infty} = b v_r \int_{r_{min}}^{\infty} \frac{dr}{r^2 \sqrt{1 - \phi(r)}} \quad (2.29)$$

which is known as the apse angle.

The scattering angle is finally derived as

$$\chi = \pi - 2\Theta. \quad (2.30)$$

This procedure shows that the dependence of the scattering angle on the potentials is generally pretty involved. As a general rule, however, small-impact parameters correspond to large scattering angles.

2.4.4 Distinguished Potentials

Once the atomistic potential is known, the procedure already outlined permits us to compute the scattering differential cross section σ , hence the collisional relaxation time and the mean-free path, starting from the atomistic potentials. This accomplishes the fundamental task of transferring information from the atomistic world of trajectories and intermolecular potentials to the kinetic world of statistical distributions, scattering cross sections and mean-free path.

Symbolically, the kinetic micro-meso bridge reads as follows:

$$V(r) \rightarrow \sigma(v_r) \leftrightarrow l_{\mu}. \quad (2.31)$$

Given that some specific potentials stand out for their importance, either from the mathematical point of view or for their applicability to realistic fluids, in the sequel we provide a cursory coverage of such potentials.

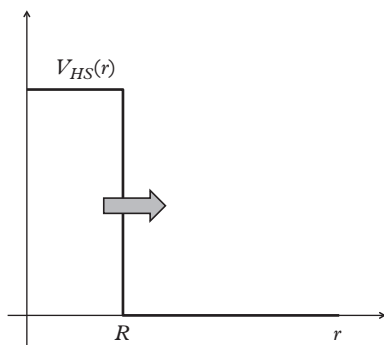


Figure 2.6 The hard-sphere potential. For graphical purpose the potential step has a finite amplitude, leading nonetheless to an infinite force (arrow) at $r = R$. This is basically a solid wall, bouncing back the molecules the molecules which impinge on it.

2.4.4.1 Hard Spheres

A particularly important and analytically solvable case is provided by the hard-sphere potential,

$$V_{HS}(r) = \begin{cases} \infty, & r \leq R \\ 0, & \text{otherwise} \end{cases} \quad (2.32)$$

where R is the sphere radius (see Fig 2.6).

Detailed calculations yield $\sigma = \pi R^2$, i.e., the geometrical area of the particle cross section, as it should be.

Despite their simplicity hard-sphere potentials have played a major role in the kinetic theory of fluids and continue to provide valuable information for molecular dynamics simulations with hard-core repulsive interactions.

2.4.4.2 Lennard-Jones potential

Another potential which plays a prominent role in the physics of non-ideal fluids, is the so-called 12–6 Lennard-Jones potential, after the British physicist John Edward Lennard-Jones (1894–1954):

$$V_{LJ}(r) = 4\epsilon[(r/R)^{-12} - (r/R)^{-6}] \quad (2.33)$$

This potential consists of a hard-core repulsion (–12 branch), plus soft-core attraction (–6 branch) (see Fig. 2.7). The former stems for the strong repulsion between incipient overlap of electronic orbitals, when nuclei get seriously close together at distances around one third of nanometer and below. The latter is due to cohesive forces arising from screened multipole electrostatic interactions (Van der Waals interactions) and plays a defining role on the thermodynamic properties of the fluid.

The competition between short-range repulsion and long-range attraction leads to a minimum of depth $-\epsilon$ at a distance $r^* = 2^{1/6}R$, which fixes the typical scale of intermolecular separation in the fluid.

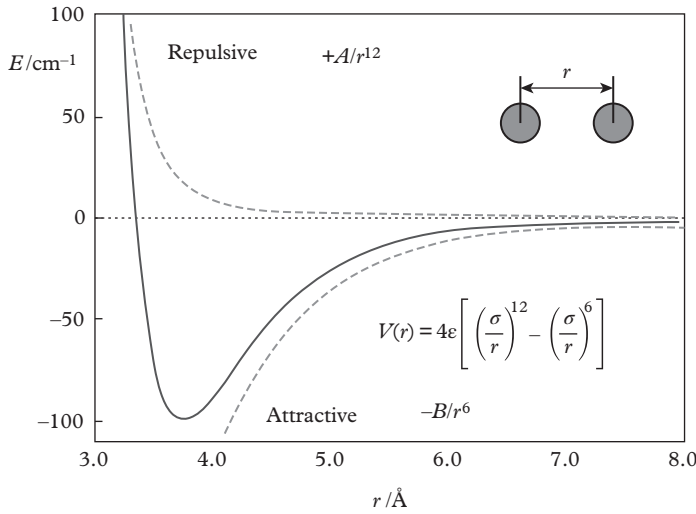


Figure 2.7 The Lennard-Jones 6 - 12 potential. In the figure, σ represents the range of interaction, called R in the text, to avoid confusion with the cross-section. From <http://chemistry.stackexchange.com/questions/34214/physical-significance-of-double-well-potential-in-quantum-bonding>.

The Lennard-Jones potential provides a microscopic basis for the celebrated van der Waals equation of state of non-ideal fluids,

$$\left(p + \frac{a}{V^2}\right)(V - b) = Nk_B T \quad (2.34)$$

where N is the number of molecules in the volume V .

The attractive branch a/V^2 echoes the soft-core tail $(r/R)^{-6}$ and the covolume b is related to the spatial scale, $b^{1/3}$, of the hard-core repulsion $(r/R)^{-12}$.

2.4.4.3 Maxwell molecules

A special case is provided by the so-called Maxwell molecules, characterized by a -4 power-law decay:

$$V_{MM}(r) \propto r^{-4}. \quad (2.35)$$

The calculations show that for such power-law potential $v_r \sigma(v_r) = \text{Const.}$, so that the collision time scale is a constant, see eqn (2.22).

This constitutes a major simplification of the Boltzmann collision integral, whence the special role of this potential in kinetic theory.

Even though Maxwell's molecules do not appear to have any realistic counterpart in the physical world, they provide nonetheless a very fruitful theoretical idealization for several mathematical developments in kinetic theory.

In particular, under appropriate simplifications, they permit us to obtain exact solutions of the Boltzmann equation.

Calculations in three spatial dimensions for inverse power-law potentials of the form

$$V(r) \sim 1/r^\alpha \quad (2.36)$$

show that

$$v_r \sigma(v_r) \sim v_r^{\frac{\alpha-4}{\alpha}}. \quad (2.37)$$

This highlights that Maxwell molecules, $\alpha = 4$, mark an qualitative borderline: for $\alpha < 4$, i.e., slower decay than for Maxwell molecules, the collision rate

$$\gamma = n v_r \sigma(v_r) \quad (2.38)$$

turns from an increasing to a decreasing function of the relative speed v_r , i.e., essentially the fluid temperature.

A moment's thought reveals that a collision frequency decreasing with the molecular speed implies that fast molecules experience less friction than the slow ones, which is clearly a portal to collective instability.

Indeed, this opens up *non-hydrodynamic* scenarios, whereby particles accelerated beyond a given critical speed by, say, a constant external field, do not experience a sufficient collisional drag to be drained back to the bulk distribution. As a result, no local equilibrium can be established and the system enters various sorts of unstable regimes, some of which are of great relevance to fusion and astrophysical plasmas and other states of matter typically governed by long-range microscopic interactions.

2.4.4.4 Long-range potentials

An important example of strongly non-hydrodynamic conditions is provided by long-range potentials, such as r^{-1} unscreened Coulomb electrostatics, or gravitation, formally corresponding to α .

For such potentials, the calculations provide a *divergent* cross section, due to the unbounded accumulation of many small-angle deflections (*grazing* collisions).

This is not surprising: the mean-free path is virtually zero, because owing to the infinitely long range of the acting force, the molecules are constantly interacting and the accumulation of very numerous small deflections leads to a logarithmic divergence of the cross section.

In practice, such infrared divergence is regulated by imposing a long-range cut off, typically via a so-called Debye screening, after the Dutch chemist Peter Debye (1884 – 1966):

$$\frac{1}{r} \rightarrow \frac{e^{-r/\lambda}}{r} \quad (2.39)$$

The Debye length, λ , marks the scale above which electrostatic interactions are screened out due to polarization effects, a condition typical of quasi-neutral plasmas, composed by a mixture of oppositely charged species, say ions and electrons.

The kinetic theory of such screened systems is described by a different collision operator, due to Landau and Balescu–Lenard, after the Hungarian–Belgian physicist Radu Balescu (1932–96) and the German, Philipp Lenard (one “n” only, not to be confused with Lennard-Jones!) (1862–1947) (5).

This takes the following form:

$$C_{LBL} = \partial_{\vec{v}} \cdot \int \vec{\vec{B}}(\vec{v}, \vec{v}') \cdot \left[\frac{\partial}{\partial \vec{v}} - \frac{\partial}{\partial \vec{v}'} \right] f(\vec{v}) f(\vec{v}') d\vec{v} d\vec{v}' \quad (2.40)$$

where $\vec{\vec{B}}(\vec{v}, \vec{v}')$ is a suitable-tensorial collision kernel.

This expression is obtained from the Boltzmann collision operator by expanding upon the velocity change, $\Delta \vec{v} = \vec{v}' - \vec{v}$, under the assumption of small deflections:

$$|\Delta \vec{v}| \ll v_T \quad (2.41)$$

as it is appropriate for soft-core grazing collisions.

The Balescu–Lenard collision operator belongs to the general class of Fokker–Planck kinetic equations, which we shall discuss in chapter 9. For the case of unscreened long-range interactions, say self-gravitating systems, the derivation of a suitable collision operator is still an open issue in modern statistical mechanics, with important implications in plasma physics, astrophysics, and cosmology.

2.4.5 Molecular Chaos (Stosszahlansatz)

Having discussed the details of the two-body scattering problem inherent to Boltzmann's collision operator, we next move on to consider the all-important *statistical* aspects of this operator.

In the first place, in order to derive a closed equation, one has to express the two-body distributions f'_{12} and f_{12} , in terms of the one-body ones f_1 and f_2 .

The simplest such closure, which is precisely the one taken by Boltzmann reads as follows:

$$f_{12} = f_1 f_2 \equiv f(\vec{z}_1; t) f(\vec{z}_2; t) \quad (2.42)$$

and same for $f'_{12} \equiv f_{1'2'}$.

This closure is tantamount to assuming no correlations between molecules entering a collision (*molecular chaos* or *Stosszahlansatz*).

This assumption is fairly plausible for a dilute gas with short-range interactions, in which molecules spend most of their lifetime traveling in free space, only to meet occasionally for very short lived, in fact instantaneous, interactions.

Note that molecules are assumed to be correlated only *prior* to the collision, whereas after collision, they become strongly correlated on account of mass, momentum and energy conservation.

Within this picture, the probability for two molecules that met at time t , to meet again at some subsequent time $t + \tau$, with the *same* velocities $\vec{v}_1$ and $\vec{v}_2$, decays exponentially with τ .

More precisely, this probability scales like $e^{-\tau/\tau_{int}}$ where τ_{int} is the duration of a collisional event. Since in Boltzmann's theory $\tau_{int} \sim s/v_T$ (the thermal speed v_T is taken to be a typical particle speed and s a typical effective molecular diameter) is negligibly small, so is the (auto)correlation function at time τ .

The situation is obviously completely different in a liquid, where, due to the much higher density, the molecules are in constant interaction.

Violations of Boltzmann's molecular chaos can occur due to the onset of nonlinear correlations. A most notable example are the famous long-time tails, first detected by Alder and Wainwright (6), where molecular correlations exhibit anomalous persistence due to self-sustained vortices generated by the molecular motion itself.⁴

Summarizing, in view of the molecular chaos assumption, the Boltzmann equation takes the following form:

$$\partial_t f + \vec{v} \cdot \partial_{\vec{x}} f + \frac{\vec{F}^{ext}}{m} \cdot \partial_{\vec{v}} f = \int (f_1' f_2' - f_1 f_2) v_r \sigma(v_r, \vec{\Omega}) d\vec{\Omega} d\vec{v}_2 \quad (2.43)$$

The left-hand side is a mirror of reversible Newtonian single-particle dynamics, while the right-hand side describes intermolecular interactions, under the Stosszahlansatz approximation.

2.5 Local and Global Equilibria

Given that the collision operator naturally splits into a Gain minus Loss components, it is only natural to ask under what conditions would the two antagonists come to an exact balance.

This singles out a very special distribution function, characterizing the attainment of *local equilibrium*, a notion which proves central to the purpose of deriving hydrodynamic equations from Boltzmann's kinetic theory.

Mathematically, the local equilibrium is defined by the condition

$$C(f^e, f^e) \equiv \mathcal{G}(f^e, f^e) - \mathcal{L}(f^e, f^e) = 0 \quad (2.44)$$

where superscript “e” denotes “equilibrium.”

⁴ This is amazingly reminiscent of the mechanisms invoked by Aristoteles to explain the motion of arrows in air!

The identification of Gain and Loss follow straight from the expression of the collision operator:

$$\mathcal{G} \equiv \int f_1' f_2' v_r \sigma(v_r) d\vec{v}_2 \quad (2.45)$$

$$\mathcal{L} \equiv \int f_1 f_2 v_r \sigma(v_r) d\vec{v}_2. \quad (2.46)$$

This leads to the so-called *detailed balance* condition:

$$f_1' f_2' = f_1 f_2 \quad (2.47)$$

which holds *regardless of the details of the molecular interactions*.

This is a strong statement of universality: microscopic details affect the *rate* at which local equilibrium is reached, not the equilibrium itself, which depends only on conserved quantities.

Of course, detailed balance does by no means imply that molecules sit idle, but rather that any direct (inverse) collision is dynamically balanced by an inverse (direct) partner collision.

For instance, in a room at standard temperature, with no appreciable macroscopic flow, the typical molecule moves at the speed of sound, that is, about three times faster than a Ferrari!

For a fluid at rest, along any given spatial direction, there is, on average, another molecule doing exactly the same along the opposite direction, so that no net macroscopic flow results.

The detailed balance condition has far-reaching consequences on the shape of the equilibrium distribution in velocity space.

To appreciate this, let us first take the logarithm of the eqn (2.47), to obtain

$$\log f_1' + \log f_2' = \log f_1 + \log f_2 \quad (2.48)$$

This shows that the quantity $\log f$ is an *additive collision invariant*, i.e., a microscopic additive property which does not change under the effect of collisions.

The immediate consequence is that, at thermodynamic equilibrium, $\log f$ must be a function of the five collision invariants

$$\mathcal{I}(v) \equiv \{1, m\vec{v}, m\vec{v}^2/2\}$$

associated with the conservation of number (mass), momentum and energy.

This yields (repeated Latin indices, denoting spatial directions, are summed upon):

$$\log f^e(\vec{x}, \vec{v}; t) = A(\vec{x}; t) + B_a(\vec{x}; t) v_a + C(\vec{x}; t) \frac{v^2}{2} \quad (2.49)$$

where A, B_a, C are five Lagrangian multipliers, carrying the entire dependence on the space-time coordinates through the conjugate hydrodynamic fields

$$\mathcal{H} \equiv \rho(\vec{x}, t), \rho(\vec{x}, t)u_a(\vec{x}, t), \rho(\vec{x}, t)e(\vec{x}, t)$$

namely density of mass, momentum and energy.

These Lagrangian parameters can be computed by imposing conservation of mass-momentum energy:

$$\int f^e \left\{ m, mv_a \frac{mv^2}{2} \right\} d\vec{v} = \{\rho, \rho u_a, \rho e\} \quad (2.50)$$

where, $\rho = nm$ is the mass density, u_a , $a = x, y, z$, is the macroscopic flow speed and ρe is the energy density.⁵

Elementary quadrature of Gaussian integrals delivers the celebrated Maxwell-Boltzmann equilibrium distribution.

In D spatial dimensions, this reads as follows:

$$f^e = \frac{n}{(2\pi v_T^2)^{D/2}} e^{-c^2/2v_T^2} \quad (2.51)$$

where c is the magnitude of the *peculiar speed*

$$\vec{c} = \vec{v} - \vec{u} \quad (2.52)$$

namely the relative speed of the molecules with respect to the fluid, and

$$v_T = \sqrt{\frac{k_B T}{m}} \quad (2.53)$$

is the thermal speed associated with the fluid temperature T , k_B being the Boltzmann constant. With this definition, each direction carries $k_B T/2$ units of energy.

2.5.1 Local Equilibria and Equation of State

Local equilibria associate with perfect (or inviscid) fluids, i.e., fluids in which dissipative effects can be neglected.

At equilibrium, density, temperature and pressure are related through an equation of state:

$$p = p(\rho, T) \quad (2.54)$$

⁵ The Latin subscript a denotes cartesian components of a vector, so that the notation v_a is an equivalent substitute for $\vec{v}$ and shall be used interchangeably throughout the text, see Appendix on Notation.

From a kinetic point of view, the temperature is defined as the variance of the equilibrium distribution:

$$\rho D \frac{k_B T}{2} = \int f(\vec{x}, \vec{v}; t) \frac{mc^2}{2} d\vec{v} \quad (2.55)$$

where c is the magnitude of the peculiar velocity and $\rho = nm$ is the mass density.

The definition shows that temperature is basically the variance of the kinetic distribution function, or, in different terms, the peculiar kinetic energy of the molecules with respect to the mean-flow motion (see Figs. 2.8 and 2.9).

Another quantity of chief interest for hydrodynamics is the momentum-flux tensor, often called pressure tensor for short:

$$P_{ab} = m \int f v_a v_b d\vec{v} \quad (2.56)$$

The definition indicates that the component P_{ab} of the pressure tensor represents the amount of momentum mv_a along direction x_a , fluxing across the unit surface with normal oriented along direction x_b .

The ordinary pressure is given by the diagonal components of the pressure tensor, evaluated at zero-flow conditions $u_a = 0$.

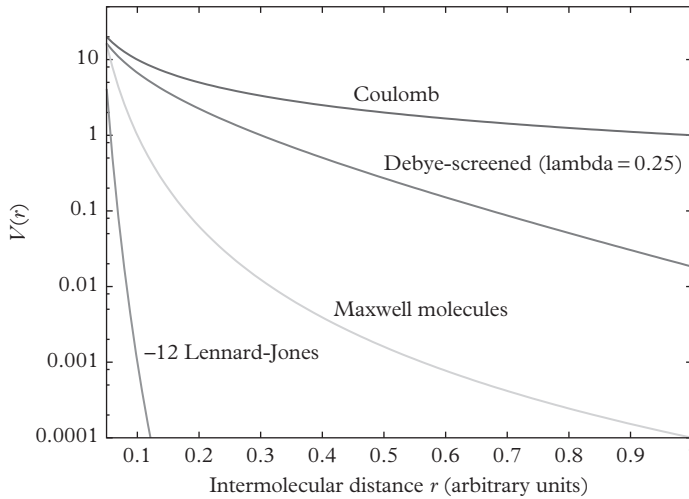


Figure 2.8 From long-range to short-range potentials: top, repulsive bare Coulomb ($1/r$), Debye-screened Coulomb ($\frac{e^{-r/\lambda}}{r}$), Maxwell molecules ($1/r^4$) and the repulsive branch of the 6–12 Lennard-Jones. The prefactors have been adjusted to keep all four potentials on the same scale.

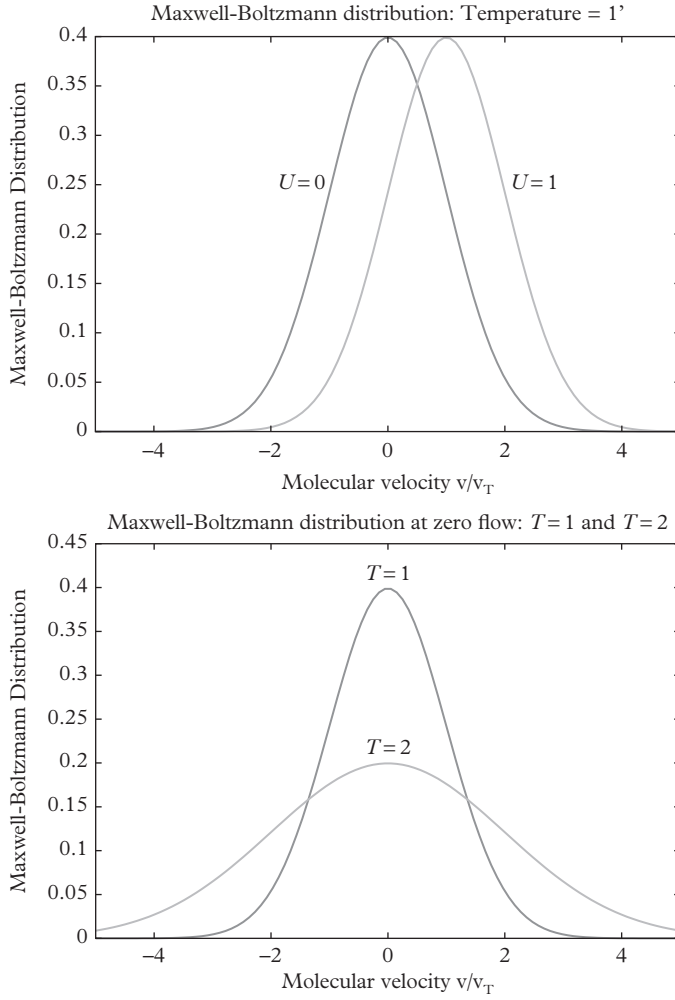


Figure 2.9 Top: Maxwell-Boltzmann distribution at unit temperature, $T = 1$, at rest, $U = 0$, and with flow, $U = 1$. Bottom: Maxwell-Boltzmann distribution at rest with $T = 1$ and $T = 2$.

For an isotropic fluid at rest ($u_a = 0$), each component gives the same result, namely

$$p = P_{xx} = P_{yy} = P_{zz} \quad (2.57)$$

It is now instructive to compute the value of the macroscopic quantities corresponding to the local equilibrium distribution.

Elementary gaussian integration yields

$$\rho^e = \rho, \quad u_a^e = u_a, \quad T^e = T, \quad P_{ab}^e = \rho v_T^2 \delta_{ab} \quad (2.58)$$

This shows that local equilibrium only supports diagonal components of the pressure tensor, with a corresponding ideal equation of state

$$p = \rho v_T^2 = nk_B T$$

It is also of interest to note that, under such conditions, the thermal speed corresponds exactly to the sound speed, defined as the derivative of the pressure with respect to the density at a constant temperature, namely

$$c_s^2 = \left. \frac{\partial p}{\partial \rho} \right|_T. \quad (2.59)$$

Knowledge of the ratio of thermal to sound speed, $\theta \equiv \frac{v_T}{c_s}$, as a function of density and temperature is just another way of specifying the equation of state of the fluid, $\theta = 1$ denoting the ideal gas.

2.5.2 The Evershifting Battle

As shown in Section 2.5.1, local Maxwell equilibria are the result of a statistical balance between forward and backward collisions.

This balance between gain and loss terms annihilates the effect of the collision operator on the distribution function.

Quite remarkably, such balance holds true independently of whether or not the macroscopic fields exhibit a variation in space and/or time (whence the label “local”), as long as such variation occurs on scales longer than the mean-free path.

This property stems directly from the assumption that collisions take place in the limit $s \rightarrow 0$, or, more precisely, $s/l_\mu \rightarrow 0$.

A natural, and indeed often-asked question is:

Do local equilibria annihilate the effects of the streaming operator too?

A moment's thought reveals that this is *not* the case, unless the macroscopic fields are totally flat, i.e., constant in space and time, a condition which defines *global* equilibria, hence equilibrium thermodynamics.

To appreciate the point in a little more detail, let us compute the effect of the streaming operator on local equilibria.

A simple application of the chain rule yields

$$\frac{df^e}{dt} = \frac{\partial f^e}{\partial \rho} \frac{d\rho}{dt} + \frac{\partial f^e}{\partial \vec{u}} \cdot \frac{d\vec{u}}{dt} + \frac{\partial f^e}{\partial T} \frac{dT}{dt}. \quad (2.60)$$

By evaluating the partial derivatives of f^e with respect to ρ , $\vec{u}$ and T , simple algebra delivers

$$\frac{d \log f^e}{dt} = \frac{d \log \rho}{dt} + \vec{\xi} \cdot \frac{d\vec{u}}{dt} + \left(1 - \frac{\xi^2}{2}\right) \frac{d \log T}{dt} \quad (2.61)$$

where

$$\vec{\xi} \equiv \frac{\vec{v} - \vec{u}}{v_T} \quad (2.62)$$

is the peculiar speed in units of the thermal speed.

Expression (2.62) clearly shows that, by construction, local equilibria are not preserved upon streaming, i.e., they can only be conserved if all macroscopic fields are constant in space and time, which, by definition means they are no longer local, but global ones.

Of course, this is all but a coincidence. The broken-invariance of local equilibria upon streaming, reflects a profound physical mechanism: *space-time inhomogeneity is the source of non-equilibrium*.

Differently restated, collisions act so as to achieve detailed balance, thereby couching the distribution function into the universal local Maxwell–Boltzmann distribution.

Streaming, on the other hand, works exactly in the opposite direction; it destroys the delicate (detailed) balance established by collisions, and revives non-equilibrium through inhomogeneity.

This is the famous “evershifting battle” between equilibrium and non-equilibrium, as evoked by Boltzmann, a battle which is not over until a featureless uniform macroscopic scenario is attained.

For those versed in philosophical aspects of science, the evershifting battle between equilibrium and non-equilibrium can be seen as a sort of metaphor of Life itself, which depends crucially on the ability to function far from equilibrium in local and temporary elusion of the Second Law (“life on borrowed time”).

It is sometimes heard that the depth of any given equation is measured by the conceptual distance between its left- and right-hand side. If such criterion is anything to go by, there is little doubt that the Boltzmann equation scores very highly indeed.

Back to the ground. Broken invariance of local equilibria under streaming reflects the broken symmetries of classical mechanics. To this purpose, we note that Maxwellian equilibria inherit two basic symmetries of Newtonian mechanics, namely (7):

— *Space and time translational invariance*

$$\begin{cases} x'_a = x_a - \lambda_a \\ t' = t - \tau \end{cases} \quad (2.63)$$

where τ and λ_a are arbitrary constants.

The invariance under such transformation reflects the homogeneity of space and time. For the case where $\lambda_a = V_a \tau$, V_a being a constant velocity, (2.63) reflect invariance under Galilean transformations.

— *Rotational invariance*

$$x'_a = \sum_{b=1}^D R_{ab} x_b \quad (2.64)$$

where R_{ab} is a symmetric, unitary (norm-preserving) rotation matrix.

Rotational invariance, which applies to the particle velocities as well, is ensured by the fact that the peculiar speed $\vec{c}$ appears through its magnitude alone, so that any sense of preferential direction is erased.

These symmetries are built-in in continuum kinetic theory, but it would be a gross mistake to take them for granted also when space time and velocity are made discrete.

Actually, this is the leading theme of Discrete Kinetic Theory.

The hydrodynamic probe of rotational symmetry is the *momentum-flux tensor* P_{ab} , which plays a pivotal role in Discrete Kinetic Theory and most notably in Lattice Gas Cellular Automata and Lattice Boltzmann theories.

2.6 Summary

Summarizing, Boltzmann kinetic theory describes the dynamics of dilute gases in terms of a probability distribution function including, besides space and time, molecular velocities. The result is a complicated quadratic integro-differential equation describing the competition between free streaming and interparticle collisions. For sufficiently well-behaved (short-ranged) atomistic potentials, such competition ultimately ends up into a universal local equilibrium, which depends only on the local conserved fluid quantities, mass, momentum and energy. This local equilibrium plays a crucial role in the derivation of hydrodynamics from Boltzmann's kinetic theory.

REFERENCES

1. L. Boltzmann, *Lectures on Gas Theory*, University of California Press, California, 1964.
2. C. Cercignani, *Theory and Application of the Boltzmann Equation*, Elsevier, New York, 1975.
3. C. Cercignani, *Mathematical Methods in Kinetic Theory*, Plenum Press, New York, 1969.
4. K. Huang, *Statistical Mechanics*, Wiley, New York, 1987.
5. R. Balescu, *Equilibrium and non equilibrium statistical mechanics*, John Wiley and sons, New York, 1975.
6. B. Alder and J. Wainwright, Decay of the velocity autocorrelation function, *Phys. Rev.*, **A 1**, 18, 1970.
7. S. Goldstein, *Classical Mechanics*, Addison-Wesley, London, 1959.

EXERCISES

1. Prove the relation (2.15).
2. Prove the Maxwellian expression (2.51).
3. What fraction of molecules move faster than $2v_T$ in a local Maxwellian? And how many at $5v_T$?

Approach to Equilibrium, the H -Theorem and Irreversibility

Like most of the greatest equations in science, the Boltzmann equation is not only beautiful but also generous. Indeed, it delivers a great deal of information without imposing a detailed knowledge of its solutions. In fact, Boltzmann himself derived most, if not all, of his main results without ever showing that his equation did admit rigorous solutions. In this chapter, we shall illustrate one of the most profound contributions of Boltzmann, namely the famous H -theorem, providing the first quantitative bridge between the irreversible evolution of the macroscopic world and the reversible laws of the underlying microdynamics.

(We cannot stop the arrow of time, but perhaps we can try to fight with it)

It is amazing to observe how much information can be extracted from a great equation, without even knowing whether its solution(s) exist in the first place, but simply assuming they do. In fact, one might argue that the greatness of an equation is to a large extent measured precisely by its *generosity*, i.e., the amount of knowledge it delivers with no requirements of explicit knowledge of its solution. There is hardly any doubt that the Boltzmann equation is one of the greatest equations of all time; less known than the famous Einstein's $E = mc^2$, or Schrödinger's wave equation, its practical and philosophical implications are by no means any less. The Boltzmann equation tells us about profound and universal ideas, which concern all of us, such as the connection between the invisible micro and the tangible macro, a story intimately related to the nature of time and the way macrosystems evolve toward their equilibrium states, if any. The main import of the H -theorem is to place such deep questions onto a systematic mathematical basis.

3.1 Approach to Equilibrium: the Second Principle of Thermodynamics

Heat flows from hot to cold bodies, we all know this. The question is why? At skim value, one could simply observe that if it were otherwise, hot bodies would become increasingly hot, and cold bodies increasingly cold, so that no equilibrium could ever be attained. Thus, heat flow from hot to cold bodies is basically an instance of stability. Note that not all systems behave like this, the financial market being a much debated example in point these days. The way heat moves in space and time (Thermodynamics) was a major concern to nineteenth-century scientists, primarily Nicolas Sadi Carnot (1796–1832) in France and Rudolf Clausius in Germany (1822–88).

These scientists were eager to understand how to possibly optimize the “moving force of heat,” i.e., the amazing ability of heat to convert into useful mechanical work (those were the heydays of the industrial revolution). In the course of such studies, they realized that while the heat exchanged between two bodies, name it δQ , depends on the specific process in point, say constant pressure, or constant volume, the *ratio* $\delta Q/T$ is process independent, i.e., depends only on the initial and final states. In the above, T denotes the temperature at which the heat exchange takes place. Such a ratio defines the change of entropy in the process, i.e., $dS = \delta Q/T$, S being the entropy of the system. The symbol dS stands for a true differential, one which depends only on the initial and final states, as opposed to δ , which denotes a process-dependent change. The inquisitive reader might have noticed that we are using a common temperature T for the hot and cold bodies, which formally contradicts the very notion of hot and cold in the first place. The point is that the heat exchange is supposed to take place under conditions where the difference between the two temperatures is much smaller than any of the two. Having clarified the point, the change of entropy in a process where a quantity δQ of heat flows from the hot body at temperature T_H to the cold body at temperature T_C is simply given by the sum of the two, namely

$$\Delta S = -\frac{\delta Q}{T_H} + \frac{\delta Q}{T_C} \quad (3.1)$$

where the minus sign indicates that the hot body loses entropy, while the cold one gains it. The very fact that, by definition, $T_H > T_C$ implies that

$$\Delta S \geq 0 \quad (3.2)$$

In other words, entropy can only increase in the process, and stays the same only once the two bodies come to a common temperature, for instance $(T_H + T_C)/2$ (see Fig. 3.1).

This defines the condition of thermal equilibrium. The inequality (3.2) is the mathematically expression of the Second Law of Thermodynamics, allegedly one of the most universal and inescapable constraints of the natural world, as we know it. Entropy is inexorably growing in time, a literal aging process which ends up in the bleak “thermal death” picture. Viewed from this side, it is easy to see why entropy was immediately connected with the most enigmatic concept of all, Time, and colorfully named the “arrow of time” by Sir Arthur Eddington (1882–1944).

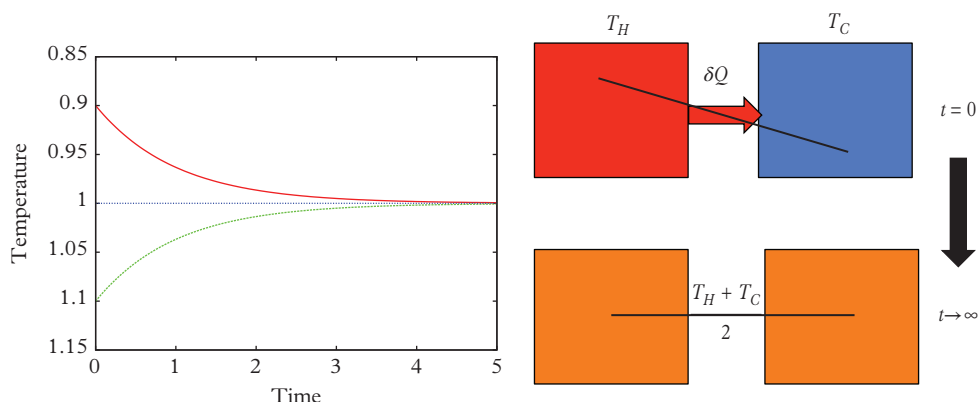


Figure 3.1 Thermal equilibration: the hot body (upper curve) lowers its temperature by transferring heat to the cold body (lower curve). This process drives the system (hot body plus cold body) toward thermal equilibrium characterized by the same temperature for the two bodies. Time-reversal symmetry is clearly broken, the hallmark of irreversibility. The opposite process, spontaneous heat flow from cold to hot bodies, albeit not forbidden by Newton's laws, is not observed in the macroscopic world other than under the effect of thermal instabilities.

It should be noted that the Second Principle makes no reference whatsoever to microscopic states of matter; as a matter of fact, in those days, the very existence of atoms was far from being accepted, a controversy which costed Boltzmann much anxiety and, according to some, might even have played a role in his tragic decision to take his life.

Leaving these fascinating matters to the historians of science, we next proceed to sketch the way that Boltzmann managed to lay down a mathematical bridge between the irreversible laws of Thermodynamics and the reversible equations of the underlying Newtonian mechanics.

3.2 Approach to Equilibrium, the H-Theorem

Thermal equilibria speak a language of dull uniformity, no room for heterogeneity. We have noted that at the level of *global* uniform equilibria, the fluid density ρ , the mean-flow speed $\vec{u}$ and temperature T must be constant throughout the physical domain. We have also noted that this restriction stems from the streaming operator, which has no effect once global uniformity is attained.

The collision operator, being local in space and time, does not place any such restriction on the spacetime dependence of the flow density, speed and temperature, with the only caveat that such dependence must occur on scales much longer than the molecular mean-free path. Whenever such slow spatial dependence is allowed in the local thermodynamic fields, one speaks of *local* hydrodynamic equilibria, namely states which attain thermodynamic equilibrium only on a local scale. Thus, the system supports a

variety of local equilibria, each with its own local values of density, velocity and temperature. On a longer timescale, global equilibration does then take place through the flux of mass, momentum and energy across the different regions of the system (transport phenomena).

This connects to the length scales l_μ , the particle *mean-free path*, the mean distance traveled by molecules between two subsequent collisions and l_M the typical scale of variation of macroscopic fields. Local equilibration takes places on a timescale $\tau_\mu \sim l_\mu/v_T$, whereas global equilibration requires much longer times, of the order of several $\tau_M = l_M/u_M$, u_M being a macroscopic velocity, or l_M^2/D , D being a typical diffusivity of the system. This identifies the *transport* regime in which hydrodynamic quantities diffuse and advect along macroscopic distances within the fluid domain. It is of course a regime of great practical relevance, since most real-life devices—to be of any use at all—must work away from thermodynamic equilibrium, and, sometimes, even very far from it.

Transport is naturally associated with the notion of *dissipation*, hence to the elusive concept of *irreversibility*, the subtle thread behind the Second Law of Thermodynamics. As hinted earlier on, one of the most profound contributions of Boltzmann to statistical mechanics rests with his discovery of a quantitative measure of irreversibility. We refer to the celebrated *H*-function and the attendant *H*-theorem.

Boltzmann showed that the following functional (*H*-function)

$$H(t) = - \int f(\vec{x}, \vec{v}; t) \log f(\vec{x}, \vec{v}; t) d\vec{v} d\vec{x} \quad (3.3)$$

is a monotonically increasing function of time, regardless of the underlying microscopic potential.

In equations

$$\frac{dH}{dt} \geq 0 \quad (3.4)$$

the equality sign holding at global equilibrium, when the evolutionary potential of the system is exhausted and the *entropy* of the system (basically *H* itself) is maximal.

The role of $H(t)$ as an evolutionary potential (the “time arrow”) is adamant and its intellectual magic hardly escaped.

A full proof of the *H*-theorem can be found in most textbooks of kinetic theory. Therefore, for the mere sake of self-containedness, in the following we only sketch the main guidelines.

3.2.1 Sketch of the Proof of the *H*-Theorem

Let us begin by considering the force-free Boltzmann equation in the uniform case ($\nabla_x f_1 = 0$):

$$\partial_t f_1 = \int (f'_1 f'_2 - f_1 f_2) v_r \sigma(v_r, \vec{\Omega}) d\vec{\Omega} d\vec{v}_2 \quad (3.5)$$

where $f_1 \equiv f$ is the one-body distribution function.

Define a local H functional as

$$H(t) = - \int f_1 \log f_1 d\vec{v}_1 \quad (3.6)$$

where space dependence is removed because of the uniformity assumption.

Let us multiply both sides of eqn (3.5) by $1 + \log f_1$ and integrate upon $\vec{v}_1$. The left-hand side yields

$$\int (1 + \log f_1) \partial_t f_1 d\vec{v}_1 = \int \partial_t (f_1 \log f_1) d\vec{v}_1 \equiv -dH/dt$$

As a result, by equating the left- and right-hand side, we obtain

$$-\frac{dH}{dt} = \int (1 + \log f_1) (f'_1 f'_2 - f_1 f_2) v_r \sigma(v_r, \vec{\Omega}) d\vec{\Omega} d\vec{v}_1 d\vec{v}_2 \quad (3.7)$$

Since the previous expression does not change upon swapping the dummy subscripts $1 \leftrightarrow 2$, we can further write

$$-\frac{dH}{dt} = \int (1 + \log f_2) (f'_2 f'_1 - f_2 f_1) v_r \sigma(v_r, \vec{\Omega}) d\vec{\Omega} d\vec{v}_2 d\vec{v}_1 \quad (3.8)$$

By summing (3.7) and (3.8) and dividing by a factor 2:

$$-\frac{dH}{dt} = \frac{1}{2} \int [2 + \log(f_1 f_2)] (f'_2 f'_1 - f_2 f_1) v_r \sigma(v_r, \vec{\Omega}) d\vec{\Omega} d\vec{v}_2 d\vec{v}_1 \quad (3.9)$$

By the same token, we can swap primed and unprimed quantities to obtain

$$-\frac{dH}{dt} = -\frac{1}{2} \int [2 + \log(f'_1 f'_2)] (f'_2 f'_1 - f_2 f_1) v'_r \sigma(v'_r, \vec{\Omega}) d\vec{\Omega} d\vec{v}'_2 d\vec{v}'_1 \quad (3.10)$$

Upon summing (3.10) and (3.9) and dividing again by 2, we finally obtain

$$-\frac{dH}{dt} = -\frac{1}{4} \int \log \left(\frac{f'_1 f'_2}{f_1 f_2} \right) (f'_2 f'_1 - f_2 f_1) v_r \sigma(v_r, \vec{\Omega}) d\vec{\Omega} d\vec{v}_2 d\vec{v}_1 \quad (3.11)$$

where we have made use of the kinematic properties $d\vec{v}'_1 d\vec{v}'_2 = d\vec{v}_1 d\vec{v}_2$ and $v'_r = v_r$, whence $\sigma(v_r) = \sigma(v'_r)$.

By calling $X \equiv f_1 f_2$ and $X' \equiv f'_1 f'_2$, we next observe that the function $(X' - X) \log(X'/X)$ cannot be negative for any value of its arguments X and X' being both non-negative, since it is the product of two equally signed functions. In fact, this function attains its minimum, zero, at $X' = X$.

As a result, one finally concludes that

$$\frac{dH}{dt} \geq 0 \quad (3.12)$$

q.e.d. The identification of H with entropy S immediately delivers the second law of thermodynamics, namely

$$\frac{dS}{dt} \geq 0 \quad (3.13)$$

This proof relies upon a few ingenious tricks based on the symmetries of the Boltzmann equation, as combined with the kinematic properties of the two-body problem underlying the collision operator. Remarkably, it does *not* depend on the details of the molecular interactions, but only on the general conservation properties and symmetries of the Boltzmann equation.

The extension to the non-uniform case takes the form of a conservative equation for the local H -function $h(\vec{x}; t)$,

$$\partial_t h + \nabla \cdot \vec{J}_h = S_h(\vec{x}; t) \quad (3.14)$$

where $\vec{J}_h = -\int f \log f \vec{v} d\vec{v}$ is the entropy flux and S_h is the entropy production due to the collisions.

Equation (3.14) shows that the local value $h(\vec{x}; t)$ has no definite sign, since the positive contribution of the collisions can always be outbalanced by the flux term. However, the second law is still recovered by integrating all over the spatial domain,

$$\frac{dH}{dt} = \int S_h(\vec{x}; t) d\vec{x} \geq 0 \quad (3.15)$$

The inequality (3.15) stems from the fact that the right-hand side is negative definite and the flux term does not contribute, since we have assumed zero flux at the boundaries of the spatial domain (isolated system).

3.2.2 H -theorem and Irreversibility

The H -theorem provides a formal basis for the emergence of macroscopic irreversibility: the streaming is reversible, i.e., invariant under time reversal, while collisions are not.

In mathematical terms, time reversal is defined by the *time-parity* (T) transformation:

$$t \rightarrow t' = -t \quad (3.16)$$

We can think of t and t' as of forward and backward times, respectively (see Fig. 3.2). Note that since only time is inverted, while space remains untouched, the velocities are also reversed under the T transformation:

$$\vec{v} \rightarrow \vec{v}' = -\vec{v} \quad (3.17)$$

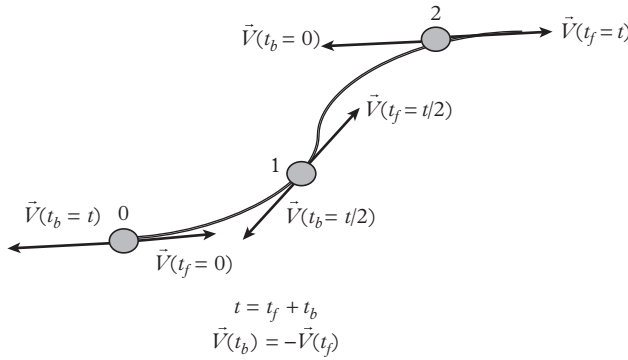


Figure 3.2 Geometrical representation of microscopic-time reversal. The time loop consists of a forward branch ($0 \rightarrow 1 \rightarrow 2$) and a backward one ($2 \rightarrow 1 \rightarrow 0$). Both forward and backward times lie in the range $[0, t]$ and each point along the trajectory carries both forward and backward time labels, with the constraint $t = t_f + t_b$. One might think of each trajectory as two-time sided. The time-parity transformation at $t_f = t \leftrightarrow t_b = 0$ implies the condition $\vec{V}(t_f) = -\vec{V}(t_b)$ along the entire trajectory. This is a formal statement of microscopic-time reversibility.

The physical meaning of time-reversal transformation is quite transparent. By streaming a particle trajectory from $\vec{x}(0)$ at time $t = 0$ to $\vec{x}(t)$ at time t and then streaming back from t to $t - t = 0$, with inverted velocity $\vec{v}(t) \rightarrow -\vec{v}(t)$, the particle regains exactly its initial position $\vec{x}(0)$, with inverted velocity $-\vec{v}(0)$.

Exactly, here means literally exactly: no information is lost in the time loop: streaming is reversible, a mirror of Newtonian mechanics. Collisions, on the other hand, do break such symmetry, as they keep acting in the same direction, i.e., pull the local distribution function back to a local Maxwellian, regardless of whether the system is in the forward or backward branch of the time loop. The information lost in the loop is the one associated with the initial conditions.

The H -theorem provides an elegant and powerful formalization of the fundamental competition between reversible streaming (non-equilibrium) and irreversible collisions (equilibrium).

Yet, the H -theorem presents one of the most debated and controversial issues in the history of theoretical physics. We will not delve here into the details of the various paradoxes which were raised against the H -theorem as a bridge between micro- and macrodynamics. Beautiful accounts can be found in the literature (1; 2). Nor shall we comment on the fact that Boltzmann derived his theorem without demonstrating that his equation, a complicated integro-differential initial-value problem, does indeed have

solutions in a rigorous mathematical sense.⁶ While leaving rigor somehow behind, the H -theorem showed for the first time the way to the unification between two fundamental and previously disconnected domains of science: Mechanics and Thermodynamics.

Even though none of the original paradoxes raised against the H -theorem could stand the test of time, one should always keep in mind that Boltzmann's H -theorem was derived under very specific conditions, namely diluteness as discussed in Chapter 2. Such conditions rule out many important states of matter, such as dense fluids and liquids, not to mention more complex materials such as glasses, which exhibit anomalous (very long) relaxation to equilibrium. Even though the Boltzmann equation in its original form does not apply to the previous problems, suitable generalizations thereof (effective Boltzmann equations) are indeed capable of providing useful insights into the physics of complex states of matter out of equilibrium. This makes a very fascinating subject of modern non-equilibrium statistical mechanics, to which we shall turn considerable attention in the "Beyond Navier–Stokes" part of this book.

3.3 Collisionless Vlasov Equilibria

It should be mentioned that there exists a class of local equilibria which can be attained through purely reversible motion, i.e., in the total absence of collisional processes. These are called Vlasov equilibria, and play an important role in many contexts of statistical mechanics, such as astrophysics and plasma physics.

By definition, Vlasov equilibria annihilate the streaming operator:

$$\vec{v} \cdot \nabla_{\vec{x}} f^{e,V} + \vec{a} \cdot \nabla_{\vec{v}} f^{e,V} = 0 \quad (3.18)$$

Under the assumption that the force field derives from a potential, $\vec{F} \equiv m\vec{a} = -\nabla_{\vec{x}} V(\vec{x})$, a simple quadrature yields the following separable solution:

$$f^{e,V}(\vec{x}, \vec{v}) = A n_0 e^{-\beta V(\vec{x})} e^{-\beta \frac{mv^2}{2}} \quad (3.19)$$

where $\beta = 1/k_B T$ and $A = (\beta/2\pi)^{D/2}$ is the normalization constant. As one can appreciate, Vlasov equilibria are a specific instance of the *canonical* distribution $Z^{-1}(\beta) e^{-\beta H}$, where $H = \frac{mv^2}{2} + V(\vec{x})$ is the Hamiltonian and Z the partition function.

Here, they are most conveniently regarded as global Maxwellian equilibria in velocity space, prefactored by a space-dependent density, the space dependence being dictated by the potential, $n(\vec{x}) = n_0 e^{-\beta V(\vec{x})}$.

These equilibria do not require any collisional relaxation and cannot exist in ordinary configuration and momentum space separately, but only as the result of a dynamic balance of the two in the double-dimensional phase space. The molecules flowing in the

⁶ Rigorous proofs of the existence of solutions of the Boltzmann equation have made a rampant surge in modern mathematics, earning two Fields Medals, arguably the highest honor in mathematical research, to Pierre Louis Lions (1994) and Cedric Villani (2010).

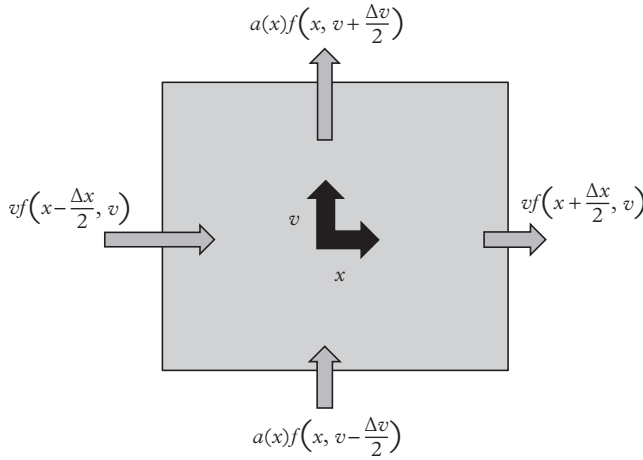


Figure 3.3 *Vlasov equilibria result from a flux balance in phase space. The flux gained(lost) along the spatial coordinate is lost(gained) along the velocity coordinate. This can only happen if the force derives from a potential.*

phase-space element centered about $(\vec{x}, \vec{v})$ via free-streaming in real space are exactly balanced by the molecules streaming away in velocity space under the effect of the external force (see Fig. 3.3). Note that such delicate balance can only occur if the force derives from a potential.

It should be noted that Vlasov equilibria are generally incompatible with local Boltzmann equilibria.

More precisely, they are compatible only for the velocities perpendicular to the flow velocity $\vec{u}$, as one can readily check by decomposing the molecular velocity into a longitudinal component $\vec{v}_l$, aligned with the local-flow velocity $\vec{u}$ and a transverse component $\vec{v}_t$, perpendicular to it. Upon such decomposition, one writes $(\vec{v} - \vec{u}) \cdot (\vec{v} - \vec{u}) = v_t^2 + u^2 + v_l^2 - 2v_l u$, which shows that the kinetic energy u^2 serves as a Vlasov potential for the transverse component of the equilibrium distribution function. Along the longitudinal direction, on the other hand, such splitting into a kinetic and potential energy is no longer possible. Vlasov equilibria play an important role in plasma physics and astrophysics where they offer the only mechanism to attain equilibria which would otherwise be impossible due to the paucity of collisions.

3.4 The Boltzmann Equation in Modern Mathematics

We shall soon focus mainly on the *practical* use of the Boltzmann equation, namely its capability to compute transport parameters, such as diffusivity, viscosity, and thermal conductivity, which characterize the approach to equilibrium on a macroscopic scale.

Before doing so, a few comments on more general issues related to the existence of solutions of the Boltzmann equations are in order.

The Boltzmann equation is not an easy piece of math: a nonlinear integro-differential equation living in $6 + 1$ dimensions! No surprise that analytical solutions of such an equation do not abound in the literature, the few available being sort of precious flowers in the desert. Some of these precious flowers are listed in (3), as well as in (4).

In the sequel, we shall spend a few comments on a different sort of analytical work, the one which does not preoccupy itself so much with the identification of specific solutions of the Boltzmann equation, but rather with the general questions regarding its basic properties, such as existence, regularity and time-asymptotic convergence (5). These deep questions are the traditional hunting ground of pure mathematicians, with no implications of “impurity” for the applied ones (does such distinction make really sense?). Indeed the highest-caliber modern math has turned a close eye to the general properties of the Boltzmann’s equation.

Forced by the author’s lack of specific competence, here we only convey a few minimal ideas on this elegant and sophisticated topic, not because it would bear any direct connection to Lattice Boltzmann theory, but as a homage to its inherent beauty, in the hope of stimulating the math-minded reader to find perhaps some for the future.

The tool of the trade is *functional analysis*, i.e., the mathematics of objects inhabiting infinite-dimensional spaces. In such functional spaces, the distribution function f is most conveniently regarded as a vector (sometimes called *ray*) with an infinite number of components. This may sound like a very thin-air notion, but it is actually a most concrete and operational idea. Indeed, similarly to the way an ordinary vector in three-dimensional space is decomposed into three components along the x, y, z directions, a function in (suitable) infinite-dimensional spaces can be expanded as an infinite series:

$$f(v) = \sum_{n=1}^{\infty} f_n H_n(v) \quad (3.20)$$

In (3.20), each $H_n(v)$ represents a suitable “basis function” in Hilbert space, the analog of unit vectors in ordinary space, and f_n are the corresponding components of the “vector” $f(v)$ along the direction associated with $H_n(v)$. For a fully phase-space dependent $f(x, v; t)$, the basis functions remain the same and the space-time dependence is wholly picked up by the coefficients $f_n(x; t)$. It is as if at each spatial location x , one would attach a time-dependent infinite-dimensional vector.

In abstract notation, the Boltzmann equation reads as follows:

$$\partial_t f = \hat{B}f \quad (3.21)$$

where the Boltzmann evolution operator is formally given by

$$\hat{B} = \hat{C} - \hat{S} \quad (3.22)$$

In (3.22), $\hat{S}f \equiv \vec{v} \cdot \nabla_{\mathbf{x}} f + \vec{a} \cdot \nabla_{\mathbf{v}} f$ defines the streaming operator and $\hat{C}f \equiv C(f, f)$ stands for the collision operator.

The formal solution of (3.21) is

$$f_t = e^{\hat{B}t} f_0 \quad (3.23)$$

where f_0 is the initial condition and f_t is its image under the action of the Boltzmann propagator

$$\hat{P}_t = e^{\hat{B}t} \quad (3.24)$$

over a time span $[0, t]$.

Such propagator obeys the following commutative and additive relations, also known as *semi-group* properties:

$$\hat{P}_{t_1} \cdot \hat{P}_{t_2} = \hat{P}_{t_2} \cdot \hat{P}_{t_1} = \hat{P}_{t_1+t_2} \quad (3.25)$$

for any $t_1, t_2 \geq 0$.

It also obeys $\hat{P}_0 = I$, I being the identity.

Note that t_1, t_2 are restricted to non-negative numbers. Indeed, the group is only *semi* because it does not obey the time-reversal property $\hat{P}_{-t} \hat{P}_t = I$, which would imply

$$\hat{P}_{-t} = \hat{P}_t^{-1} \quad (3.26)$$

This latter is a mathematical statement of reversibility; by rolling time backward, the image f_t maps exactly back into the starting point f_0 , which implies the non-singularity of $\hat{P}_t$. For the case of irreversible evolution, the operator $\hat{P}_t$ cancels information, which cannot be retrieved by rolling time backward, whence its singularity. The “culprit” is, of course, the collision operator and the previous semigroup property is a formal echo of the *H*-theorem.

A major mathematical question concerns the main properties of the image f_t , say existence, finiteness, positivity, smoothness and so on, for any given class of initial conditions f_0 .

As a first step in the rigorous study of such kind of questions, one has to define the proper functional space to work with. Such functional space is typically *metric*, i.e., equipped with a measure of the distance between its elements, for otherwise one could hardly address questions of convergence to any given limit.

In analogy with Euclidean space, a typical distance between two elements, say f and g , takes the form

$$d(f, g) = \left[\int_{R^3} |f(\vec{v}) - g(\vec{v})|^2 d\vec{v} \right]^{1/2} \quad (3.27)$$

This defines $\|\phi\|_2$, the norm of the displacement, $\phi \equiv f - g$, in Hilbert’s space L_2 (the space of square-integrable functions).

In the case of kinetic theory, a more natural norm is Hilbert’s L_1 defined by $\|f\|_1 = \int_{R^3} |f| d\vec{v}$. This space includes all distributions supporting a finite density.