Hydrodynamic Fluctuations in Fluids and Fluid Mixtures

by

José M. Ortiz de Zárate
Departamento de Física Aplicada I
Universidad Complutense, Madrid, Spain

Jan V. Sengers
Institute for Physical Science and Technology
and Burgers Program for Fluid Dynamics
University of Maryland, College Park
Maryland, USA

ELSEVIER
Amsterdam – Boston – Heidelberg – London – New York – Oxford
Paris – San Diego – San Francisco – Singapore – Sydney – Tokyo

Contents

1 **Introduction** 1

2 **Nonequilibrium thermodynamics** 5
- 2.1 Local thermodynamic properties . . . 5
  - 2.1.1 Equilibrium thermodynamics . . . 5
  - 2.1.2 Continuum hypothesis and the assumption of local equilibrium . . . 7
- 2.2 Balance laws . . . 8
  - 2.2.1 Mass balance . . . 9
  - 2.2.2 Pressure tensor . . . 11
  - 2.2.3 Momentum balance . . . 15
  - 2.2.4 Energy balance . . . 16
  - 2.2.5 Additional remarks . . . 19
- 2.3 Entropy balance, dissipative fluxes and thermodynamic forces 20
  - 2.3.1 Phenomenological relations . . . 22
  - 2.3.2 Onsager's reciprocal relations . . . 23
- 2.4 Hydrodynamic equations . . . 24
  - 2.4.1 Hydrodynamic equations for a one-component fluid . . . 24
  - 2.4.2 Hydrodynamic equations for a binary mixture . . . 28
- 2.5 Boundary conditions . . . 33
  - 2.5.1 Conditions at the interface between two continuous media . . . 33
  - 2.5.2 A flat horizontal fluid boundary . . . 36

3 **Fluctuations in fluids in thermodynamic equilibrium** 39
- 3.1 Fluctuating hydrodynamics . . . 40
- 3.2 Fluctuation-dissipation theorem for fluids and fluid mixtures 43
  - 3.2.1 Fluctuation-dissipation theorem for a one-component fluid . . . 43
  - 3.2.2 Fluctuation-dissipation theorem for a binary mixture 45
- 3.3 Hydrodynamic fluctuations in a one-component fluid . . . 46

3.3.1 Structure factor 51
3.3.2 Equal-time correlations 54
3.4 Equilibrium correlation functions and entropy probability functional 56
3.5 Extension of fluctuating hydrodynamics to nonequilibrium steady states 60

4 Thermal nonequilibrium fluctuations in one-component fluids 63
4.1 Boussinesq approximation 64
4.2 Bulk structure factor in the presence of a stationary temperature gradient 70
4.3 Nonequilibrium effects on the Brillouin doublet 76
4.4 Nonequilibrium fluctuations in heat conduction 82

5 Thermal nonequilibrium fluctuations in fluid mixtures 89
5.1 Linearized fluctuating Boussinesq equations for a binary liquid 91
5.1.1 The linear stability problem 94
5.2 Structure factor in a large-Lewis-number approximation . . 97
5.3 Comprehensive structure factor of a nonequilibrium binary mixture 102
5.4 Nonequilibrium fluctuations in isothermal free-diffusion processes 110

6 Finite-size effects in hydrodynamic fluctuations 113
6.1 The hydrodynamic operator 115
6.1.1 Structure factors 122
6.2 Hydrodynamic modes and decay rates for two free boundaries 125
6.3 Hydrodynamic modes and decay rates for two rigid boundaries 129
6.3.1 Decay rates for rigid boundaries in the limit of small $q_{\|}$ 131
6.3.2 Decay rates for rigid boundaries in the limit of large $q_{\|}$ 134
6.4 The slowest decay rate 136

7 Thermal nonequilibrium fluctuations in one-component-fluid layers 141
7.1 A fluid confined between two free boundaries 142
7.2 A fluid confined between two rigid boundaries 147
7.3 Limiting behavior of the structure factor for rigid boundaries at small and large wave numbers 152
7.4 A Galerkin approximation for two rigid boundaries 155
7.5 Correlations in real space 162
7.6 Contribution of nonequilibrium fluctuations to heat transfer 166

8 Thermal fluctuations close to the Rayleigh-Bénard instability 167
8.1 Critical slowing down of nonequilibrium fluctuations 168
8.2 The most-unstable-mode approximation 169
8.3 The Swift-Hohenberg approximation 172
8.4 Power of thermal fluctuations 175
8.5 Wave number of maximum enhancement of fluctuations . . 179
8.6 Wave number of fluctuations with maximum growth rate . . 181

9 Thermal nonequilibrium fluctuations in binary-fluid layers 185
9.1 The hydrodynamic operator for binary Boussinesq 187
9.2 A Galerkin approximation for rigid and impermeable boundary conditions 189
9.3 Evaluation of nonequilibrium structure factors 194
9.4 Structure factor in thermal equilibrium 197
9.5 Nonequilibrium fluctuations for positive separation ratio . . 198
9.5.1 Temperature fluctuations 199
9.5.2 Concentration fluctuations 204
9.6 Large-Lewis-number approximation for positive separation ratio 207
9.7 Concluding remarks 211

10 Experiments on nonequilibrium fluctuations in the Rayleigh-Bénard problem 213
10.1 Experimental techniques 214
10.1.1 Small-angle light scattering 214
10.1.2 Quantitative shadowgraph analysis 222
10.1.3 Dependence of shadowgraph images on collecting times 228
10.2 Nonequilibrium light-scattering experiments in one-component fluids 229
10.2.1 Propagating modes 229
10.2.2 Brillouin doublet 230
10.2.3 Rayleigh scattering 232
10.3 Shadowgraph experiments in one-component fluids 235
10.3.1 Divergence of critical fluctuations near the onset of convection 235
10.3.2 Critical slowing down of fluctuations near the onset of convection 237
10.4 Light scattering in binary systems 239
10.4.1 Nonequilibrium fluctuations in liquid mixtures . . . 240
10.4.2 Concentration fluctuations in dilute polymer solutions 243
10.5 Shadowgraphy in binary mixtures 246

11 Other nonequilibrium fluctuations 247
11.1 Nonequilibrium fluctuations in isothermal one-component fluids under shear 248
11.2 Nonequilibrium interface fluctuations 252
11.3 Nonequilibrium fluctuations in nematic liquid crystals . . . 253
11.4 Concentration fluctuations in reaction-diffusion problems . . 256
11.4.1 Equilibrium concentration fluctuations in reaction-diffusion 257
11.4.2 Nonequilibrium concentration fluctuations in reaction-diffusion 263

12 Epilogue 269

Bibliography 273

List of symbols and corresponding SI units 297

List of abbreviations 303

Subject index 305