Statistical Mechanics of Nonequilibrium Liquids

by

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Preface

During the 1980's there have been many new developments regarding the nonequilibrium statistical mechanics of dense classical systems. These developments have had a major impact on the computer simulation methods used to model nonequilibrium fluids. Some of these new algorithms are discussed in the recent book by Allen and Tildesley, Computer Simulation of Liquids. However that book was never intended to provide a detailed statistical mechanical backdrop to the new computer algorithms. As the authors commented in their preface, their main purpose was to provide a working knowledge of computer simulation techniques. The present volume is, in part, an attempt to provide a pedagogical discussion of the statistical mechanical environment of these algorithms.

There is a symbiotic relationship between nonequilibrium statistical mechanics on the one hand and the theory and practice of computer simulation on the other. Sometimes, the initiative for progress has been with the pragmatic requirements of computer simulation and at other times, the initiative has been with the fundamental theory of nonequilibrium processes. Although progress has been rapid, the number of participants who have been involved in the exposition and development rather than with application, has been relatively small.

The formal theory is often illustrated with examples involving shear flow in liquids. Since a central theme of this volume is the nonlinear response of systems, this book could be described as a text on Theoretical Rheology. However our choice of rheology as a testbed for theory is merely a reflection of personal interest. The statistical mechanical theory that is outlined in this book is capable of far wider application.

All but two pages of this book are concerned with atomic rather than molecular fluids. This restriction is one of economy. The main purpose of this text is best served by choosing simple applications.

Many people deserve thanks for their help in developing and writing this book. Firstly we must thank our wives, Val and Jan, for putting up with our absences, our irritability and our exhaustion. We would also like to thank Dr. David MacGowan for reading sections of the manuscript. Thanks must also go to Mrs. Marie Lawrence for help with indexing. Finally special thanks must go to Professors Cohen, Hanley and Hoover for incessant argument and interest.

D. J. Evans and G. P. Morriss

Biographies

Denis Evans was born in Sydney Australia in 1951. He obtained first class honours in astrophysics at Sydney University in 1972 and gained his Ph.D. in statistical mechanics from the Australian National University (ANU) in 1975. After postdoctoral appointments at Oxford, Cornell and ANU and a Fulbright Fellowship to the National Bureau of Standards he became a Fellow in the Research School of Chemistry at ANU in 1982. He has won a number of awards including the Rennie Medal for Chemistry (1983), the Young Distinguished Chemist Award of the Federation of Asian Chemical Societies (1989) and the Frederick White Prize of the Australian Academy of Science (1990). In 1989 he was appointed as Professor of Theoretical Chemistry at ANU and currently serves as Academic Director of the ANU Supercomputer Facility.

Gary Morriss was born in Singleton, Australia in 1951. He obtained first class honours in mathematics/physics at Newcastle University in 1976 and gained his Ph.D. in statistical mechanics from Melbourne University in 1980. After postdoctoral appointments at Cornell and ANU, he became a Research Fellow and later Senior Research Fellow at ANU. In 1989 he was appointed as Lecturer in the School of Physics at the University of New South Wales.

Contents.

List of Symbols

Transport coefficients

η	shear viscosity
λ	thermal conductivity
η_V	bulk viscosity
ζ	Brownian friction coefficient
D	self diffusion coefficient

Thermodynamic fluxes

P	the pressure tensor
$\mathbf{J}_Q$	heat flux
Π	viscous pressure tensor

Thermodynamic forces

∇u	strain rate tensor
γ	shear rate $= \partial u_x / \partial y$
∇T	temperature gradient
∇.u	dilation rate
$\mathbf{u}$	streaming velocity
ε	elastic deformation
∇ ε	strain tensor
$\dot{\varepsilon}$	dilation rate = $\frac{1}{3}(\nabla.\varepsilon\ )$

Thermodynamic state variables

T	temperature
k_B	Boltzmann's Constant
β	$1/k_BT$
V	volume
p	hydrostatic pressure, = $\frac{1}{3}$ tr(P)
N	number of particles
ρ	mass density
n	number density

Thermodynamic constants

G	shear modulus
C_V	constant volume specific heat
C_p	constant pressure, specific heat
c_V	constant volume, specific heat per unit mass
c_p	constant pressure, specific heat per unit mass
D_T	isochoric thermal diffusivity

Thermodynamic potentials

E	internal energy
$U(\mathbf{r},t)$	internal energy per unit mass
S	entropy
$s(\mathbf{r},t)$	internal energy per unit volume
σ	entropy source strength = rate of spontaneous entropy production per unit volume
I	enthalpy
Q	heat

Mechanics

L	Lagrangian
H	Hamiltonian
H_0	phase variable whose average is the internal energy
I_0	phase variable whose average is the enthalpy
$J(\Gamma)$	dissipative flux
F_e	external field
α	thermostatting multiplier
iL	p-Liouvillean
iL	f-Liouvillean
$A^{\dagger}$	Hermitian adjoint of A
Λ	phase space compression factor
$\exp_R$	right time-ordered exponential
$\exp_L$	left time-ordered exponential
$U_R(t_1,t_2)$	incremental p-propagator t_1 to t_2
$U_R(t_1,t_2)^{-1}$	inverse of $U_R(t_1,t_2)$, take phase variables from t_2 to t_1, $U_R(t_2,t_1) = U_L(t_1,t_2)$
$U_R(t_1,t_2)^{\dagger}$	incremental f-propagator t_1 to t_2
T_R	right time-ordering opertator
T_L	left time-ordering opertator
$C_{AB}(t)$	equilibrium time correlation function = $\langle A(t)B^* \rangle$
$[A,B]$	commutator bracket
$\{A,B\}$	Poisson bracket
$\delta(t)$	Dirac delta function (of time)
$\delta(\mathbf{r}-\mathbf{r}_i)$	Kirkwood delta function $= 0$, $\lvert\mathbf{r}-\mathbf{r}_i\rvert >$ an *infinitesmal* macroscopic distance, l $= 1/l^3$, $\lvert\mathbf{r}-\mathbf{r}_i\rvert <$ an *infinitesmal* macroscopic distance, l
$f(\mathbf{k}) = \int d\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}} f(\mathbf{r})$	spatial Fourier transform
$f(\omega) = \int_0^{\infty} d\mathbf{r}\, e^{-i\omega t} f(t)$	spatial Fourier-Laplace trasform transform
$\mathbf{dS}$	infinitesmal vector area element
$\mathbf{J}^{\perp}$	transverse momentum current
Φ	total intermolecular potential energy
ϕ_{ij}	potential energy of particle i,j
K	total kinetic energy
f_c	canonical distribution function
f_T	isokinetic distribution function

m	particle mass
$\mathbf{r}_i$	position of particle i
$\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$	
$\mathbf{v}_i$	velocity of particle i