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MOLECULAR SIMULATION
From Algorithms to Applications

second edition

分子模拟入门

第2版

Daan **Frenkel** & Berend **Smit**

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From Algorithms to Applications

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Preface to the Second Edition

Why did we write a second edition? A minor revision of the first edition would have been adequate to correct the (admittedly many) typographical mistakes. However, many of the nice comments that we received from students and colleagues alike, ended with a remark of the type: "unfortunately, you don't discuss topic *x*". And indeed, we feel that, after only five years, the simulation world has changed so much that the title of the book was no longer covered by the contents.

The first edition was written in 1995 and since then several new techniques have appeared or matured. Most (but not all) of the major changes in the second edition deal with these new developments. In particular, we have included a section on:

- Transition path sampling and diffusive barrier crossing to simulate rare events
- Dissipative particle dynamic as a course-grained simulation technique
- Novel schemes to compute the long-ranged forces
- Discussion on Hamiltonian and non-Hamiltonian dynamics in the context of constant-temperature and constant-pressure Molecular Dynamics simulations
- Multiple-time-step algorithms as an alternative for constraints
- Defects in solids
- The pruned-enriched Rosenbluth sampling, recoil growth, and concerted rotations for complex molecules
- Parallel tempering for glassy Hamiltonians

We have updated some of the examples to include also recent work. Several new Examples have been added to illustrate recent applications.

We have taught several courses on Molecular Simulation, based on the first edition of this book. As part of these courses, Dr. Thijs Vlugt prepared many *Questions, Exercises,* and *Case Studies,* most of which have been included in the present edition. Some additional exercises can be found on the Web. We are very grateful to Thijs Vlugt for the permission to reproduce this material.

Many of the advanced Molecular Dynamics techniques described in this book are derived using the Lagrangian or Hamilton formulations of classical mechanics. However, many chemistry and chemical engineering students are not familiar with these formalisms. While a full description of classical mechanics is clearly beyond the scope of the present book, we have added an Appendix that summarizes the necessary essentials of Lagrangian and Hamiltonian mechanics.

Special thanks are due to Giovanni Ciccotti, Rob Groot, Gavin Crooks, Thijs Vlugt, and Peter Bolhuis for their comments on parts of the text. In addition, we thank everyone who pointed out mistakes and typos, in particular Drs. J.B. Freund, R. Akkermans, and D. Moroni.

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Preface

This book is not a computer simulation cookbook. Our aim is to explain the physics that is behind the "recipes" of molecular simulation. Of course, we also give the recipes themselves, because otherwise the book would be too abstract to be of much practical use. The scope of this book is necessarily limited: we do not aim to discuss all aspects of computer simulation. Rather, we intend to give a unified presentation of those computational tools that are currently used to study the equilibrium properties and, in particular, the phase behavior of molecular and supramolecular substances. Moreover, we intentionally restrict the discussion to simulations of *classical* many-body systems, even though some of the techniques mentioned can be applied to quantum systems as well. And, within the context of classical many-body systems, we restrict our discussion to the modeling of systems at, or near, equilibrium.

The book is aimed at readers who are active in computer simulation or are planning to become so. Computer simulators are continuously confronted with questions concerning the choice of technique, because a bewildering variety of computational tools is available. We believe that, to make a rational choice, a good understanding of the physics behind each technique is essential. Our aim is to provide the reader with this background.

We should state at the outset that we consider some techniques to be more useful than others, and therefore our presentation is biased. In fact, we believe that the reader is well served by the fact that we do not present all techniques as equivalent. However, whenever we express our personal preference, we try to back it up with arguments based in physics, applied mathematics, or simply experience. In fact, we mix our presentation with practical examples that serve a twofold purpose: first, to show how a given technique works in practice, and second, to give the reader a flavor of the kind of phenomena that can be studied by numerical simulation.

The reader will also notice that two topics are discussed in great detail, namely simulation techniques to study first-order phase transitions, and various aspects of the configurational-bias Monte Carlo method. The reason why we devote so much space to these topics is not that we consider them to be more important than other subjects that get less coverage, but rather because we feel that, at present, the discussion of both topics in the literature is rather fragmented.

The present introduction is written for the nonexpert. We have done so on purpose. The community of people who perform computer simulations is rapidly expanding as computer experiments become a general research tool. Many of the new simulators will use computer simulation as a tool and will not be primarily interested in techniques. Yet, we hope to convince those readers who consider a computer simulation program a *black box*, that the inside of the black box is interesting and, more importantly, that a better understanding of the working of a simulation program may greatly improve the efficiency with which the black box is used.

In addition to the theoretical framework, we discuss some of the practical tricks and rules of thumb that have become "common" knowledge in the simulation community and are routinely used in a simulation. Often, it is difficult to trace back the original motivation behind these rules. As a result, some "tricks" can be very useful in one case yet result in inefficient programs in others. In this book, we discuss the rationale behind the various tricks, in order to place them in a proper context. In the main text of the book we describe the theoretical framework of the various techniques. To illustrate how these ideas are used in practice we provide Algorithms, Case Studies and Examples.

Algorithms

The description of an algorithm forms an essential part of this book. Such a description, however, does not provide much information on how to implement the algorithm efficiently. Of course, details about the implementation of an algorithm can be obtained from a listing of the complete program. However, even in a well-structured program, the code contains many lines that, although necessary to obtain a working program, tend to obscure the essentials of the algorithm that they express. As a compromise solution, we provide a pseudo-code for each algorithm. These pseudo-codes contain only those aspects of the implementation directly related to the particular algorithm under discussion. This implies that some aspects that are essential for using this pseudo-code in an actual program have to be added. For example, the pseudo-codes consider only the x directions; similar lines have to be added for the y and z direction if the code is going to be used in a simulation. Furthermore, we have omitted the initialization of most variables.

Case Studies

In the Case Studies , the algorithms discussed in the main text are combined in a complete program. These programs are used to illustrate some elementary aspects of simulations. Some Case Studies focus on the problems that can occur in a simulation or on the errors that are sometimes made. The complete listing of the FORTRAN codes that we have used for the Case Studies is accessible to the reader through the Internet.[1]

Examples

In the Examples, we demonstrate how the techniques discussed in the main text are used in an application. We have tried to refer as much as possible to research topics of current interest. In this way, the reader may get some feeling for the type of systems that can be studied with simulations. In addition, we have tried to illustrate in these examples how simulations can contribute to the solution of "real" experimental or theoretical problems.

Many of the topics that we discuss in this book have appeared previously in the open literature. However, the Examples and Case Studies were prepared specifically for this book. In writing this material, we could not resist including a few computational tricks that, to our knowledge, have not been reported in the literature.

In computer science it is generally assumed that any source code over 200 lines contains at least one error. The source codes of the Case Studies contain over 25,000 lines of code. Assuming we are no worse than the average programmer this implies that we have made at least 125 errors in the source code. If you spot these errors and send them to us, we will try to correct them (we can not promise this!). It also implies that, before you use part of the code yourself, you should convince yourself that the code is doing what you expect it to do.

In the light of the previous paragraph, we must add the following disclaimer:

> We make no warranties, express or implied, that the programs contained in this work are free of error, or that they will meet your requirements for any particular application. They should not be relied on for solving problems whose incorrect solution could result in injury, damage, or loss of property. The authors and publishers disclaim all liability for direct or consequential damages resulting from your use of the programs.

Although this book and the included programs are copyrighted, we authorize the readers of this book to use parts of the programs for their own use, provided that proper acknowledgment is made.

Finally, we gratefully acknowledge the help and collaboration of many of our colleagues. In fact, many dozens of our colleagues collaborated with us on topics described in the text. Rather than listing them all here, we mention their names at the appropriate place in the text. Yet, we do wish to express our gratitude for their input. Moreover, Daan Frenkel should like to acknowledge numerous stimulating discussions with colleagues at the FOM Institute for Atomic and Molecular Physics in Amsterdam and at the van 't Hoff Laboratory of Utrecht University, while Berend Smit gratefully acknowledges discussions with colleagues at the University of Amsterdam and Shell. In addition, several colleagues helped us directly with the preparation of the manuscript, by reading the text or part thereof. They are Giovanni Ciccotti, Mike Deem, Simon de Leeuw, Toine Schlijper, Stefano Ruffo, Maria-Jose Ruiz, Guy Verbist and Thijs Vlugt. In addition, we thank Klaas Esselink and Sami Karaborni for the cover figure. We thank them all for their efforts. In addition we thank the many readers who have drawn our attention to errors and omissions in the first print. But we stress that the responsibility for the remainder of errors in the text is ours alone.

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[1] `http://molsim.chem.uva.nl/frenkel_smit`

List of Symbols

A	dynamical variable	(2.2.6)
$\text{acc}(o \to n)$	acceptance probability of a move from o to n	
$\mathbf{b}$	trial position or orientation	
c	concentration	
c_i	concentration of species i	
C_V	specific heat at constant volume	(4.4.3)
d	dimensionality	
D	diffusion coefficient	
E	total energy	
f	number of degrees of freedom	
f_i	fugacity component i	(9.1.9)
$\mathbf{f}_i$	force on particle i	
F	Helmholtz free energy	(2.1.15)
$g(r)$	radial distribution function	
G	Gibbs free energy	(5.4.9)
$h = 2\pi\hbar$	Planck's constant	
$\mathcal{H}(\mathbf{p}, \mathbf{r})$	Hamiltonian	
$\mathbf{j}_i$	flux of species i	
$\mathbf{k}$	wave vector	
k_B	Boltzmann's constant	
K	kinetic energy	
$K(o \to n)$	flow of configurations from o to n	
L	box length	
$\mathcal{L}(\mathbf{q}, \dot{\mathbf{q}})$	Lagrangian	(A.1.2)
ℓ	total number of (pseudo-)atoms in a molecule (chain length)	
n	new configuration or conformation	
m	mass	
M	total number of Monte Carlo samples	
N	number of particles	
$\mathcal{N}(o)$	prob. density to find a system in configuration o	
$\mathcal{N}_{N,V,T}$	prob. density for canonical ensemble	(5.2.2)
$\mathcal{N}_{N,P,T}$	prob. density for isobaric-isothermal ensemble	(5.4.8)
$\mathcal{N}_{\mu,V,T}$	prob. density for grand-canonical ensemble	(5.6.6)
o	old configuration or conformation	
$\mathcal{O}(x^n)$	terms of order x^n or smaller	

$\mathbf{p}$	momentum of a particle	
P	pressure	
$\mathbf{P}$	total linear momentum	
q_i	electric charge on particle i	
$\mathbf{q}$	generalized coordinates	
Q	mass associated with time scaling coordinate s	(6.1.3)
$Q(N,V,T)$	canonical partition function	(5.2.1)
$Q(N,P,T)$	isothermal-isobaric partition function	(5.4.7)
$Q(\mu,V,T)$	grand-canonical partition function	(5.6.5)
$\mathbf{r}_i$	Cartesian coordinate of particle i	
r_c	cut-off radius of the potential	
Ranf	random number uniform in [0, 1]	
s	time-scaling coordinate in Nose scheme	(6.1.3)
$\mathbf{s}_i$	scaled coordinate of particle i	(5.4.2)
S	entropy	
t	time	
T	temperature	
$\mathcal{U}(o)$	potential energy of configuration o	
u_i	potential energy per particle	
$u(r)$	pair potential	
$\mathbf{v}_i$	Cartesian velocity of particle i	
V	volume	
vir	virial	(3.4.2)
w_i	Rosenbluth factor of (pseudo-)atom i	
$W(o)$	total Rosenbluth factor configuration o	
$\mathcal{W}(o)$	normalized total Rosenbluth factor configuration o	
Z	configurational part of the partition function	
$\alpha(o \to n)$	probability of generating conf. n starting from o	(3.1.14)
β	reciprocal temperature $(1/k_B T)$	
Δt	Molecular Dynamics time step	
Γ	coordinate in phase space	
ϵ	characteristic energy in pair potential	
η	shear viscosity	(4.4.12)
μ	chemical potential	
λ_T	thermal conductivity	(4.4.14)
Λ	thermal de Broglie wavelength	(5.4.1)
$\pi(o \to n)$	transition probability from o to n	(3.1.13)
ρ	number density	
σ	characteristic distance in pair potential	
σ_e	electrical conductivity	(4.4.16)
$\sigma_{\alpha\beta}$	$\alpha\beta$ component of the stress tensor	(4.4.13)
σ_A^2	variance in dynamical variable A	
ξ	thermodynamic friction coefficient	(6.1.25)
ξ_i	fugacity coefficient of component i	(9.1.15)
$\Omega(E)$	quantum: degeneracy of energy level E	(2.1.1)
	classical: phase space subvolume with energy E	(2.2.9)

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ω	orientation of a molecule

$\langle\cdots\rangle$	ensemble average
$\langle\cdots\rangle_{\text{sub}}$	average under condition indicated by sub

Super- and subscripts

$*$	reduced units (default, usually omitted)
$\mathbf{r}_\alpha$	α component of vector $\mathbf{r}$
$\mathbf{r}_i$	vector $\mathbf{r}$ associated with particle i
f^{ex}	excess part of quantity f
f^{id}	ideal gas part of quantity f
$\hat{\mathbf{u}}$	unit vector $\mathbf{u}$

Symbol List: Algorithms

`b(j)`	trial orientation/position j
`beta`	reciprocal temperature ($1/k_BT$)
`box`	simulation box length
`delx`	maximum displacement
`dt`	time step in an MD simulation
`ell`	chain length
`eni`	energy of atom i
`enn`	energy of the new configuration
`eno`	energy of the old configuration
`etot`	total energy of the system
`f`	force
`k`	total number of trial orientations/position
`kv`	bond vibration energy constant
`l`	bond length
`n`	selected trial position
`ncycle`	total number of MC cycles
`nhis`	number of bins in a histogram
`NINT`	nearest integer
`npart`	total number of particles
`nsamp`	number of MC cycles of MD steps between two samples
`o`	particle number of the old configuration
`p`	pressure
`phi`	bond-bending angle
`pi`	$\pi = 3.14159$
`r2`	distance squared between two atoms
`ranf()`	random number $\in [0, 1]$
`rho`	density
`rc2`	cutoff radius squared (of the potential)
`switch`	= 0 initialization; = 1 sample; = 2 print result

`t`	time in a MD simulation
`temp`	temperature
`tempa`	instantaneous temperature, from kinetic energy
`theta`	torsional angle
`tmax`	maximum simulation time
`tors`	torsion energy
`v(i)`	velocity of atom i
`vmax`	maximum displacement volume
`vol`	volume simulation box
`w`	Rosenbluth factor (new or old)
`wn, wo`	Rosenbluth factor n(ew)/o(ld) configuration
`x(i)`	position of atom i
`xm(i)`	position of atom i at previous time step
`xn`	new configuration of a particle
`xn(i)`	positions of atoms that have been grown
`xo`	old configuration of a particle
`xt(j)`	jth trial position for a given atom
`ubb`	bond-bending energy
`utors`	torsion energy

•	vector dot product
×	vector cross product
|···|	length of the vector

`a.le.b`	test: true if a is less than or equal to b
`a.lt.b`	test: true if a is less than b
`a.ge.b`	test: true if a is greater than or equal to b
`a.gt.b`	test: true if a is greater than b
`a.and.b`	test: true if both a and b are true
`a.or.b`	test: true if a or b are true

`+`	continuation symbol
`*`	multiplication
`**`	to the power
`/`	division
`sqrt`	square root

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