SIMULATING THE PHYSICAL WORLD

The simulation of physical systems requires a simplified, hierarchical approach, which models each level from the atomistic to the macroscopic scale. From quantum mechanics to fluid dynamics, this book systematically treats the broad scope of computer modeling and simulations, describing the fundamental theory behind each level of approximation. Berendsen evaluates each stage in relation to their applications giving the reader insight into the possibilities and limitations of the models. Practical guidance for applications and sample programs in Python are provided. With a strong emphasis on molecular models in chemistry and biochemistry, this book will be suitable for advanced undergraduate and graduate courses on molecular modeling and simulation within physics, biophysics, physical chemistry and materials science. It will also be a useful reference to all those working in the field. Additional resources for this title including solutions for instructors and programs are available online at www.cambridge.org/9780521835275.

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SIMULATING THE PHYSICAL WORLD

Hierarchical Modeling from Quantum Mechanics to Fluid Dynamics

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Preface

This book was conceived as a result of many years research with students and postdocs in molecular simulation, and shaped over several courses on the subject given at the University of Groningen, the Eidgenössische Technische Hochschule (ETH) in Zürich, the University of Cambridge, UK, the University of Rome (La Sapienza), and the University of North Carolina at Chapel Hill, NC, USA. The leading theme has been the truly interdisciplinary character of molecular simulation: its gamma of methods and models encompasses the sciences ranging from advanced theoretical physics to very applied (bio)technology, and it attracts chemists and biologists with limited mathematical training as well as physicists, computer scientists and mathematicians. There is a clear hierarchy in models used for simulations, ranging from detailed (relativistic) quantum dynamics of particles, via a cascade of approximations, to the macroscopic behavior of complex systems. As the human brain cannot hold all the specialisms involved, many practical simulators specialize in their niche of interest, adopt – often unquestioned – the methods that are commonplace in their niche, read the literature selectively, and too often turn a blind eye on the limitations of their approaches.

This book tries to connect the various disciplines and expand the horizon for each field of application. The basic approach is a physical one, and an attempt is made to rationalize each necessary approximation in the light of the underlying physics. The necessary mathematics is not avoided, but hopefully remains accessible to a wide audience. It is at a level of abstraction that allows compact notation and concise reasoning, without the burden of excessive symbolism. The book consists of two parts: Part I follows the hierarchy of models for simulation from relativistic quantum mechanics to macroscopic fluid dynamics; Part II reviews the necessary mathematical, physical and chemical concepts, which are meant to provide a common background of knowledge and notation. Some of these topics may be superfluous to physicists or mathematicians, others to chemists. The chapters of Part II could be useful in courses or for self-study for those who have missed certain topics in their education; for this purpose exercises are included. Answers and further information are available on the book's website.

The subjects treated in this book, and the depth to which they are explored, necessarily reflect the personal preference and experience of the author. Within this subjective selection the literature sources are restricted to the period before January 1, 2006. The overall emphasis is on simulation of large molecular systems, such as biomolecular systems where function is related to structure and dynamics. Such systems are in the middle of the hierarchy of models: very fast motions and the fate of electronically excited states require quantum-dynamical treatment, while the sheer size of the systems and the long time span of events often require severe approximations and coarse-grained approaches. Proper and efficient sampling of the configurational space (e.g., in the prediction of protein folding and other rare events) poses special problems and requires innovative solutions. The fun of simulation methods is that they may use physically impossible pathways to reach physically possible states; thus they allow a range of innovative phantasies that are not available to experimental scientists.

This book contains sample programs for educational purposes, but it contains no programs that are optimized to run on large or complex systems. For real applications that require molecular or stochastic dynamics or energy minimization, the reader is referred to the public-domain program suite GROMACS (http://www.gromacs.org), which has been described by Van der Spoel *et al.* (2005).

Programming examples are given in Python, a public domain interpretative object-oriented language that is both simple and powerful. For those who are not familiar with Python, the example programs will still be intelligible, provided a few rules are understood:

- Indentation is essential. Consecutive statements at the same indentation level are considered as a block, as if – in C – they were placed between curly brackets.
- Python comes with many *modules*, which can be imported (or of which certain elements can be imported) into the main program. For example, after the statement *import math* the *math* module is accessible and the sine function is now known as *math.sin*. Alternatively, the sine function may be imported by *from math import sin*, after which it is known as *sin*. One may also import all the methods and attributes of the *math* module at once by the statement *from math import* $*$.

- Python variables need not be declared. Some programmers don't like this feature as errors are more easily introduced, but it makes programs a lot shorter and easier to read.

- Python knows several types of sequences or *lists*, which are very versatile (they may contain a mix of different variable types) and can be manipulated. For example, if $x = [1, 2, 3]$ then $x[0] = 1$, etc. (indexing starts at 0), and $x[0:2]$ or $x[:2]$ will be the list $[1, 2]$. $x + [4, 5]$ will concatenate x with $[4, 5]$, resulting in the list $[1, 2, 3, 4, 5]$. $x * 2$ will produce the list $[1, 2, 3, 1, 2, 3]$. A multidimensional list, as $x = [[1, 2], [3, 4]]$ is accessed as $x[i][j]$, e.g., $x[0][1] = 2$. The function $range(3)$ will produce the list $[0, 1, 2]$. One can run over the elements of a list x by the statement *for i in range(len(x)): ...*

- The extra package *numpy* (numerical python) which is not included in the standard Python distribution, provides (multidimensional) arrays with fixed size and with all elements of the same type, that have fast methods or functions like matrix multiplication, linear solver, etc. The easiest way to include *numpy* and – in addition – a large number of mathematical and statistical functions, is to install the package *scipy* (scientific python). The function *arange* acts like *range*, but defines an array. An array element is accessed as $x[i, j]$. Addition, multiplication etc. now work element-wise on arrays. The package defines the very useful *universal functions* that also work on arrays. For example, if $x = array([1, 2, 3])$, $\sin(x * pi/2)$ will be $array([1., 0., -1.])$.

The reader who wishes to try out the sample programs, should install in this order: a recent version of Python (http://www.python.org), *numpy* and *scipy* (http://www.scipy.org) on his system. The use of the IDLE Python shell is recommended. For all sample programs in this book it is assumed that *scipy* has been imported:

```
from scipy import *
```

This imports universal functions as well, implying that functions like *sin* are known and need not be imported from the *math* module. The programs in this book can be downloaded from the Cambridge University Press website (http://www.cambridge.org/9780521835275) or from the author's website (http://www.hjcb.nl). These sites also offer additional Python modules that are useful in the context of this book: *plotps* for plotting data, producing postscript files, and *physcon* containing all relevant physical constants in SI units. Instructions for the installation and use of Python are also given on the author's website.

This book could not have been written without the help of many former students and collaborators. It would never have been written without the stimulating scientific environment in the Chemistry Department of the University of Groningen, the superb guidance into computer simulation methods by Aneesur Rahman (1927–1987) in the early 1970s, the pioneering atmosphere of several interdisciplinary CECAM workshops, and the fruitful collaboration with Wilfred van Gunsteren between 1976 and 1992. Many ideas discussed in this book have originated from collaborations with colleagues, often at CECAM, postdocs and graduate students, of whom I can only mention a few here: Andrew McCammon, Jan Hermans, Giovanni Ciccotti, Jean-Paul Ryckaert, Alfredo DiNola, Raúl Grigera, Johan Postma, Tjerk Straatsma, Bert Egberts, David van der Spoel, Henk Bekker, Peter Ahlström, Siewert-Jan Marrink, Andrea Amadei, Janez Mavri, Bert de Groot, Steven Hayward, Alan Mark, Humberto Saint-Martin and Berk Hess. I thank Frans van Hoesel, Tjerk Wassenaar, Farid Abraham, Alex de Vries, Agur Sevink and Florin Iancu for providing pictures.

Finally, I thank my wife Lia for her endurance and support; to her I dedicate this book.

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Symbols, units and constants

Symbols

The typographic conventions and special symbols used in this book are listed in Table 1; Latin and Greek symbols are listed in Tables 2, 3, and 4. Symbols that are listed as vectors (bold italic, e.g., $\boldsymbol{r}$) may occur in their roman italic version ($r = |\boldsymbol{r}|$) signifying the norm (absolute value or magnitude) of the vector, or in their roman bold version ($\mathbf{r}$) signifying a one-column matrix of vector components. The reader should be aware that occasionally the same symbol has a different meaning when used in a different context. Symbols that represent general quantities as a, unknowns as x, functions as $f(x)$, or numbers as i, j, n are not listed.

Units

This book adopts the SI system of units (Table 5). The SI units (Système International d'Unités) were agreed in 1960 by the CGPM, the Conférence Générale des Poids et Mesures. The CGPM is the general conference of countries that are members of the *Metre Convention*. Virtually every country in the world is a member or associate, including the USA, but not all member countries have strict laws enforcing the use of SI units in trade and commerce.[1] Certain units that are (still) popular in the USA, such as inch (2.54 cm), Ångström (10^{-10} m), kcal (4.184 kJ), dyne (10^{-5} N), erg (10^{-7} J), bar (10^{5} Pa), atm (101 325 Pa), electrostatic units, and Gauss units, in principle have no place in this book. Some of these, such as the Å and bar, which are decimally related to SI units, will occasionally be used. Another exception that will occasionally be used is the still popular Debye for dipole moment ($10^{-29}/2.997\,924\,58$ Cm); the Debye relates decimally

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[1] A European Union directive on the enforcement of SI units, issued in 1979, has been incorporated in the national laws of most EU countries, including England in 1995.

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to the obsolete electrostatic units. Electrostatic and electromagnetic equations involve the vacuum permittivity (now called the *electric constant*) ε_0 and vacuum permeability (now called the *magnetic constant*) μ_0; the velocity of light does not enter explicitly into the equations connecting electric and magnetic quantities. The SI system is *rationalized*, meaning that electric and magnetic potentials, but also energies, fields and forces, are derived from their sources (charge density ρ, current density $\boldsymbol{j}$) with a multiplicative factor $1/(4\pi\varepsilon_0)$, resp. $\mu_0/4\pi$:

$$\Phi(r) = \frac{1}{4\pi\varepsilon_0}\int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\,d\boldsymbol{r}', \tag{1}$$

$$\boldsymbol{A}(\boldsymbol{r}) = \frac{\mu_0}{4\pi}\int \frac{\boldsymbol{j}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\,d\boldsymbol{r}', \tag{2}$$

while in differential form the 4π vanishes:

$$\mathrm{div}\,\boldsymbol{E} = -\,\mathrm{div}\,\mathbf{grad}\,\Phi = \rho/\varepsilon_0, \tag{3}$$

$$\mathbf{curl}\,\boldsymbol{B} = \mathbf{curl}\,\mathbf{curl}\,\boldsymbol{A} = \mu_0\boldsymbol{j}. \tag{4}$$

In *non-rationalized* systems without a multiplicative factor in the integrated forms (as in the obsolete electrostatic and Gauss systems, *but also in atomic units*), an extra factor 4π occurs in the integrated forms:

$$\mathrm{div}\,\boldsymbol{E} = 4\pi\rho, \tag{5}$$

$$\mathbf{curl}\,\boldsymbol{B} = 4\pi\boldsymbol{j}. \tag{6}$$

Consistent use of the SI system avoids ambiguities, especially in the use of electric and magnetic units, but the reader who has been educated with *non-rationalized* units (electrostatic and Gauss units) should not fall into one of the common traps. For example, the magnetic susceptibility χ_m, which is the ratio between induced magnetic polarization $\boldsymbol{M}$ (dipole moment per unit volume) and applied magnetic intensity $\boldsymbol{H}$, is a dimensionless quantity, which nevertheless differs by a factor of 4π between rationalized and non-rationalized systems of units. Another quantity that may cause confusion is the *polarizability* $\boldsymbol{\alpha}$, which is a tensor defined by the relation $\boldsymbol{\mu} = \boldsymbol{\alpha}\boldsymbol{E}$ between induced dipole moment and electric field. Its SI unit is F m^2, but its non-rationalized unit is a volume. To be able to compare α with a volume, the quantity $\alpha' = \alpha/(4\pi\varepsilon_0)$ may be defined, the SI unit of which is m^3.

Technical units are often based on the force exerted by standard gravity (9.806 65 m s^{-2}) on a mass of a kilogram or a pound avoirdupois [lb = 0.453 592 37 kg (exact)], yielding a kilogramforce (kgf) = 9.806 65 N, or a poundforce (lbf) = 4.448 22 N. The US technical unit for pressure psi (pound

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per square inch) amounts to 6894.76 Pa. Such non-SI units are avoided in this book.

When dealing with electrons, atoms and molecules, SI units are not very practical. For treating quantum problems with electrons, as in quantum chemistry, *atomic units* (a.u.) are often used (see Table 7). In a.u. the electron mass and charge and Dirac's constant all have the value 1. For treating molecules, a very convenient system of units, related to the SI system, uses nm for length, u (unified atomic mass unit) for mass, and ps for time. We call these *molecular units* (m.u.). Both systems are detailed below.

SI Units

SI units are defined by the basic units *length*, *mass*, *time*, *electric current*, *thermodynamic temperature*, *quantity of matter* and *intensity of light*. Units for angle and solid angle are the dimensionless *radian* and *steradian*. See Table 5 for the defined SI units. All other units are derived from these basic units (Table 6).

While the *Système International* also defines the *mole* (with unit *mol*), being a number of entities (such as molecules) large enough to bring its total mass into the range of grams, one may express quantities of molecular size also per mole rather than per molecule. For macroscopic system sizes one then obtains more convenient numbers closer to unity. In chemical thermodynamics molar quantities are commonly used. Molar constants as the Faraday F (molar elementary charge), the gas constant R (molar Boltzmann constant) and the molar standard ideal gas volume V_m (273.15 K, 10^5 Pa) are specified in SI units (see Table 9).

Atomic units

Atomic units (a.u.) are based on electron mass $m_\mathrm{e} = 1$, Dirac's constant $\hbar = 1$, elementary charge $e = 1$ and $4\pi\varepsilon_0 = 1$. These choices determine the units of other quantities, such as

$$\text{a.u. of length (Bohr radius) } a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_\mathrm{e}e^2} = \frac{\hbar}{\alpha m_\mathrm{e}c}, \tag{7}$$

$$\text{a.u. of time} = \frac{(4\pi\varepsilon_0)^2\hbar^3}{m_\mathrm{e}e^4} = \frac{m_\mathrm{e}a_0^2}{\hbar}, \tag{8}$$

$$\text{a.u. of velocity} = \hbar/(m_\mathrm{e}a_0) = \alpha c, \tag{9}$$

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$$\text{a.u. of energy (hartree) } E_{\rm h} = \frac{m_{\rm e}e^4}{(4\pi\varepsilon_0)^2\hbar^2} = \frac{\alpha^2 c^2 m_{\rm e}}{\hbar^2}. \tag{10}$$

Here, $\alpha = e^2/(4\pi\varepsilon_0\hbar c)$ is the dimensionless *fine-structure constant*. The system is *non-rationalized* and in electromagnetic equations $\varepsilon_0 = 1/(4\pi)$ and $\mu_0 = 4\pi\alpha^2$. The latter is equivalent to $\mu_0 = 1/(\varepsilon_0 c^2)$, with both quantities expressed in a.u. Table 7 lists the values of the basic atomic units in terms of SI units.

These units employ physical constants, which are not so constant as the name suggests; they depend on the definition of basic units and on the improving precision of measurements. The numbers given here refer to constants published in 2002 by CODATA (Mohr and Taylor, 2005). Standard errors in the last decimals are given between parentheses.

Molecular units

Convenient units for molecular simulations are based on nm for length, u (unified atomic mass units) for mass, ps for time, and the elementary charge e for charge. The unified atomic mass unit is defined as 1/12 of the mass of a ^{12}C atom, which makes 1 u equal to 1 gram divided by Avogadro's number. The unit of energy now appears to be 1 kJ/mol = 1 $\text{u}\,\text{nm}^2\,\text{ps}^{-2}$. There is an *electric factor* $f_{\rm el} = (4\pi\varepsilon_0)^{-1} = 138.935\,4574(14)$ $\text{kJ}\,\text{mol}^{-1}\,\text{nm}\,\text{e}^{-2}$ when calculating energy and forces from charges, as in $V_{\rm pot} = f_{\rm el}\, q^2/r$. While these units are convenient, the unit of pressure ($\text{kJ}\,\text{mol}^{-1}\,\text{nm}^{-3}$) becomes a bit awkward, being equal to 1.666 053 886(28) MPa or 16.66 … bar.

Warning: One may not change kJ/mol into kcal/mol and nm into Å (the usual units for some simulation packages) without punishment. When keeping the u for mass, the unit of time then becomes $0.1/\sqrt{4.184}$ ps = 48.888 821 … fs. Keeping the e for charge, the electric factor must be expressed in $\text{kcal}\,\text{mol}^{-1}\,\text{Å}\,\text{e}^{-2}$ with a value of 332.063 7127(33). The unit of pressure becomes 69 707.6946(12) bar! These units also form a consistent system, but we do not recommend their use.

Physical constants

In Table 9 some relevant physical constants are given in SI units; the values are those published by CODATA in 2002.[2] The same constants are given in Table 10 in atomic and molecular units. Note that in the latter table

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[2] See Mohr and Taylor (2005) and http://physics.nist.gov/cuu/. A Python module containing a variety of physical constants, *physcon.py*, may be downloaded from this book's or the author's website.

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molar quantities are not listed: It does not make sense to list quantities in molecular-sized units per mole of material, because values in the order of 10^{23} would be obtained. The whole purpose of atomic and molecular units is to obtain “normal” values for atomic and molecular quantities.

Table 1 *Typographic conventions and special symbols*

Element	Example	Meaning
$*$	c^*	complex conjugate $c^* = a - bi$ if $c = a + bi$
$\ddagger$	$\Delta G^\ddagger$	transition state label
hat	$\hat{H}$	operator
overline	$\overline{u}$	(1) quantity per unit mass, (2) time average
dot	$\dot{v}$	time derivative
$\langle\rangle$	$\langle x \rangle$	average over ensemble
bold italic (l.c.)	$\boldsymbol{r}$	vector
bold italic (u.c.)	$\boldsymbol{Q}$	tensor of rank ≥ 2
bold roman (l.c.)	$\mathbf{r}$	one-column matrix, e.g., representing vector components
bold roman (u.c.)	$\mathbf{Q}$	matrix, e.g., representing tensor components
overline	$\overline{u}$	quantity per unit mass
overline	$\overline{M}$	multipole definition
superscript T	$\mathbf{b}^\mathsf{T}$	transpose of a column matrix (a row matrix)
	$\mathbf{A}^\mathsf{T}$	transpose of a rank-2 matrix $(A^\mathsf{T})_{ij} = A_{ji}$
superscript $\dagger$	$\mathbf{H}^\dagger$	Hermitian conjugate $(\mathbf{H}^\dagger)_{ij} = H^*_{ji}$
d	df/dx	derivative function of f
∂	$\partial f/\partial x$	partial derivative
D	D/Dt	Lagrangian derivative $\partial/\partial t + \boldsymbol{u} \cdot \boldsymbol{\nabla}$
δ	$\delta A/\delta \rho$	functional derivative
centered dot	$\boldsymbol{v} \cdot \boldsymbol{w}$	dot product of two vectors $\mathbf{v}^\mathsf{T}\mathbf{w}$
$\times$	$\boldsymbol{v} \times \boldsymbol{w}$	vector product of two vectors
∇		nabla vector operator $(\partial/\partial x, \partial/\partial y, \partial/\partial z)$
grad	$\nabla \phi$	gradient $(\partial\phi/\partial x, \partial\phi/\partial y, \partial\phi/\partial z)$
div	$\nabla \cdot \boldsymbol{v}$	divergence $(\partial v_x/\partial x + \partial v_y/\partial y + \partial v_z/\partial z)$
grad	$\nabla \boldsymbol{v}$	gradient of a vector (tensor of rank 2) $(\nabla\boldsymbol{v})_{xy} = \partial v_y/\partial x$
curl	$\nabla \times \boldsymbol{v}$	$\mathbf{curl}\,\boldsymbol{v}$; $(\nabla \times \boldsymbol{v})_x = \partial v_z/\partial y - \partial v_y/\partial z$
∇^2	$\nabla^2\Phi$	Laplacian: nabla-square or Laplace operator $(\partial^2\Phi/\partial x^2 + \partial^2\Phi/\partial y^2 + \partial^2\Phi/\partial z^2)$
$\nabla\nabla$	$\nabla\nabla\Phi$	Hessian (tensor) $(\nabla\nabla\Phi)_{xy} = \partial^2\Phi/\partial x\partial y$
tr	$\mathrm{tr}\,\mathbf{Q}$	trace of a matrix (sum of diagonal elements)
calligraphic	$\mathcal{C}$	set, domain or contour
$\mathbb{Z}$		set of all integers $(0, \pm 1, \pm 2, \ldots)$
$\mathbb{R}$		set of all real numbers
$\mathbb{C}$		set of all complex numbers
$\Re$	$\Re z$	real part of complex z
$\Im$	$\Im z$	imaginary part of complex z
$\mathbf{1}$		diagonal unit matrix or tensor

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Table 2 *List of lower case Latin symbols*

symbol	meaning
a	activity
a_0	Bohr radius
c	(1) speed of light, (2) concentration (molar density)
d	infinitesimal increment, as in dx
e	(1) elementary charge, (2) number 2.1828 ...
f_{el}	electric factor $(4\pi\varepsilon_0)^{-1}$
g	metric tensor
h	(1) Planck's constant, (2) molar enthalpy
$\hbar$	Dirac's constant ($h/2\pi$)
i	$\sqrt{-1}$ (j in Python programs)
$\boldsymbol{j}$	current density
k	(1) rate constant, (2) harmonic force constant
$\boldsymbol{k}$	wave vector
k_{B}	Boltzmann's constant
n	(1) total quantity of moles in a mixture, (2) number density
m	mass of a particle
p	(1) pressure, (2) momentum, (3) probability density
$\boldsymbol{p}$	(1) n-dimensional generalized momentum vector, (2) momentum vector $m\boldsymbol{v}$ (3D or $3N$-D)
q	(1) heat, mostly as dq, (2) generalized position, (3) charge
$[q]$	$[q_0, q_1, q_2, q_3] = [q, \boldsymbol{Q}]$ quaternions
$\boldsymbol{q}$	n-dimensional generalized position vector
$\boldsymbol{r}$	cartesian radius vector of point in space (3D or $3N$-D)
s	molar entropy
t	time
u	molar internal energy
u	symbol for unified atomic mass unit (1/12 of mass ^{12}C atom)
$\boldsymbol{u}$	fluid velocity vector (3D)
v	molar volume
$\boldsymbol{v}$	cartesian velocity vector (3D or $3N$-D)
w	(1) probability density, (2) work, mostly as dw
z	ionic charge in units of e
$\mathbf{z}$	point in phase space $\{\boldsymbol{q}, \boldsymbol{p}\}$

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Table 3 *List of upper case Latin symbols*

Symbol	Meaning
A	Helmholtz function or Helmholtz free energy
$\boldsymbol{A}$	vector potential
B_2	second virial coefficient
$\boldsymbol{B}$	magnetic field vector
D	diffusion coefficient
$\boldsymbol{D}$	dielectric displacement vector
E	energy
$\boldsymbol{E}$	electric field vector
F	Faraday constant ($N_\mathrm{A}\, e = 96\,485$ C)
$\boldsymbol{F}$	force vector
G	(1) Gibbs function or Gibbs free energy, (2) Green's function
H	(1) Hamiltonian, (2) enthalpy
$\boldsymbol{H}$	magnetic intensity
$\boldsymbol{I}$	moment of inertia tensor
J	Jacobian of a transformation
$\boldsymbol{J}$	flux density vector (quantity flowing through unit area per unit time)
K	kinetic energy
L	Onsager coefficients
$\mathcal{L}$	(1) Liouville operator, (2) Lagrangian
$\boldsymbol{L}$	angular momentum
M	(1) total mass, (2) transport coefficient
$\boldsymbol{M}$	(1) mass tensor, (2) multipole tensor (3) magnetic polarization (magnetic moment per unit volume)
N	number of particles in system
N_A	Avogadro's number
P	probability density
$\boldsymbol{P}$	(1) pressure tensor, (2) electric polarization (dipole moment per unit volume)
Q	canonical partition function
$\boldsymbol{Q}$	quadrupole tensor
R	gas constant ($N_\mathrm{A}\, k_\mathrm{B}$)
$\mathbf{R}$	rotation matrix
S	(1) entropy, (2) action
$d\boldsymbol{S}$	surface element (vector perpendicular to surface)
$\mathbf{S}$	overlap matrix
T	absolute temperature
$\boldsymbol{T}$	torque vector
U	(1) internal energy, (2) interaction energy
V	(1) volume, (2) potential energy
W	(1) electromagnetic energy density
$W_{\rightarrow}$	transition probability
$\boldsymbol{X}$	thermodynamic driving force vector

Table 4 *List of Greek symbols*

Symbol	Meaning
α	(1) fine structure constant, (2) thermal expansion coefficient, (3) electric polarizability
α'	polarizability volume $\alpha/(4\pi\varepsilon_0)$
β	(1) compressibility, (2) $(k_BT)^{-1}$
γ	(1) friction coefficient as in $\dot{v} = -\gamma v$, (2) activity coefficient
Γ	interfacial surface tension
δ	(1) delta function, (2) Kronecker delta: δ_{ij}
Δ	small increment, as in Δx
ε	(1) dielectric constant, (2) Lennard Jones energy parameter
ε_0	vacuum permittivity
ε_r	relative dielectric constant $\varepsilon/\varepsilon_0$
η	viscosity coefficient
ζ	(1) bulk viscosity coefficient, (2) friction coefficient
κ	(1) inverse Debye length, (2) compressibility
λ	(1) wavelength, (2) heat conductivity coefficient, (3) coupling parameter
μ	(1) thermodynamic potential, (2) magnetic permeability, (3) mean of distribution
$\boldsymbol{\mu}$	dipole moment vector
μ_0	vacuum permeability
ν	(1) frequency, (2) stoichiometric coefficient
π	number $\pi = 3.1415\ldots$
Π	product over terms
$\mathbf{\Pi}$	momentum flux density
ρ	(1) mass density, (2) number density, (3) charge density
σ	(1) Lennard–Jones size parameter, (2) variance of distribution (3) irreversible entropy production per unit volume
$\boldsymbol{\sigma}$	stress tensor
$\sum$	sum over terms
$\mathbf{\Sigma}$	Poynting vector (wave energy flux density)
τ	generalized time
$\boldsymbol{\tau}$	viscous stress tensor
ϕ	wave function (generally basis function)
Φ	(1) wave function, (2) electric potential, (3) delta-response function
ψ	wave function
Ψ	wave function, generally time dependent
χ	susceptibility: electric (χ_e) or magnetic (χ_m)
χ^2	chi-square probability function
Ξ	(1) grand-canonical partition function, (2) virial
ω	angular frequency ($2\pi\nu$)
$\boldsymbol{\omega}$	angular velocity vector
Ω	microcanonical partition function

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Table 5 *Defined SI units*

Quantity	Name	Symbol	Definition (year adopted by CGPM)
length	**meter**	m	distance traveled by light in vacuum in 1/299 792 458 s (1983)
mass	**kilogram**	kg	mass of international prototype kilogram in Paris (1889)
time	**second**	s	duration of 9 192 631 770 periods of hyperfine transition in ^{133}Cs atoms [at rest at 0 K, in zero magnetic field] (1967)
current	**ampere**	A	current in two infinitely long and thin conductors at 1 m distance that exert a mutual force of 2×10^{-7} N/m (1948)
temperature	**kelvin**	K	1/273.16 of thermodynamic temperature of triple point of water (1967)
quantity	**mole**	mol	quantity of matter with as many specified elementary entities as there are atoms in 0.012 kg pure ^{12}C (1971)
light intensity	**candela**	cd	intensity of light source emitting 1/683 W/sr radiation with frequency 540×10^{12} Hz (1979)

Table 6 *Derived named SI units*

Quantity	Symbol	Name	Unit
planar angle	$\alpha, \ldots$	**radian**	rad (circle = 2π)
solid angle	ω, Ω	**steradian**	sr (sphere= 4π)
frequency	ν, f	**hertz**	$\mathrm{Hz} = \mathrm{s}^{-1}$
force	F	**newton**	$\mathrm{N} = \mathrm{kg\,m\,s}^{-2}$
pressure	p	**pascal**	$\mathrm{Pa} = \mathrm{N/m}^2$
energy	E, U, w	**joule**	$\mathrm{J} = \mathrm{N\,m} = \mathrm{kg\,m}^2\,\mathrm{s}^{-2}$
power	P, W	**watt**	$\mathrm{J\,s} = \mathrm{kg\,m}^2\,\mathrm{s}^{-1}$
charge	q, Q	**coulomb**	$\mathrm{C} = \mathrm{A\,s}$
electric potential	V, Φ	**volt**	$\mathrm{V} = \mathrm{J/C}$
capacity	C	**farad**	$\mathrm{F} = \mathrm{C/V}$
resistance	R	**ohm**	$\Omega = \mathrm{V/A}$
conductance	G	**siemens**	$\mathrm{S} = \Omega^{-1}$
inductance	L	**henry**	$\mathrm{H} = \mathrm{Wb/A}$
magnetic flux	Φ	**weber**	$\mathrm{Wb} = \mathrm{V\,s}$
magnetic field	B	**tesla**	$\mathrm{T} = \mathrm{Wb/m}^2$

Table 7 *Atomic units (a.u.)*

Quantity	Symbol	Value in SI unit
mass	m_e	$9.109\,3826(16) \times 10^{-31}$ kg
length	a_0	$5.291\,772\,108(18) \times 10^{-11}$ m
time	$m_\mathrm{e}a_0^2/\hbar$	$2.418\,884\,326505(16) \times 10^{-17}$ s,
velocity	αc	$2.187\,691\,2633(73) \times 10^{6}$ m/s
energy	$\hbar^2/(m_\mathrm{e}a_0^2)$ (E_h) (hartree)	$4.359\,744\,17(75) \times 10^{-18}$ J $= 27.211\,3845(23)$ eV $= 2\,625.499\,63(45)$ kJ/mol $= 627.509\,47(11)$ kcal/mol
force	E_h/a_0	$8.238\,7225(14) \times 10^{-8}$ N
charge	e	$1.602\,176\,53(14) \times 10^{-19}$ C,
current	a.u.	$6.623\,617\,82(57) \times 10^{-3}$ A
electric potential	a.u.	$27.211\,3845(23)$ V
electric field	a.u.	$5.142\,206\,42(44) \times 10^{11}$ V/m
electric field gradient	a.u.	$9.717\,361\,82(83) \times 10^{21}$ V m^{-2}
dipole moment	a.u.	$8.478\,353\,09(73) \times 10^{-30}$ C m $= 2.541\,746\,31(22)$ Debye
quadrupole moment	a.u.	$4.486\,551\,24(39) \times 10^{-40}$ C m^2
electric polarizability	a.u.	$1.648\,777\,274(16) \times 10^{-41}$ F m^2
$\alpha' = \alpha/(4\pi\varepsilon_0)$	a.u.	$a_0^3 = 1.481\,847\,114(15) \times 10^{-31}$ m^3

Table 8 *Molecular units (m.u.)*

quantity	symbol	value in SI unit
mass	u	$1.66053886(28) \times 10^{-27}$ kg
length	nm	1×10^{-9} m
time	ps	1×10^{-12} s,
velocity	nm/ps	1000 m/s
energy	kJ/mol	$1.660\,538\,86(28) \times 10^{-21}$ J $= 0.010\,364\,268\,99(85)$ eV $= 0.239\,005\,736\ldots$ kcal/mol
force	kJ mol^{-1} nm^{-1}	$1.660\,538\,86(28) \times 10^{-12}$ N
charge	e	$1.602\,176\,53(14) \times 10^{-19}$ C,
current	e/ps	$1.602\,176\,53(14) \times 10^{-7}$ A
electric potential	kJ mol^{-1} e^{-1}	$0.010\,364\,268\,99(85)$ V
electric field	kJ mol^{-1} e^{-1} nm^{-1}	$1.036\,426\,899(85) \times 10^{7}$ V/m
electric field gradient	kJ mol^{-1} e^{-1} nm^{-2}	$1.036\,426\,899(85) \times 10^{16}$ V m^{-2}
dipole moment	e nm	$1.602\,176\,53(14) \times 10^{-28}$ C m $= 48.032\,0440(42)$ Debye
quadrupole moment	e nm^2	$1.602\,176\,53(14) \times 10^{-37}$ C m^2
electric polarizability	e^2 nm^2 kJ^{-1} mol	$1.545\,865\,44(26) \times 10^{-35}$ F m^2
$\alpha' = \alpha/(4\pi\varepsilon_0)$	nm^3	1×10^{-27} m^3

Table 9 *Some physical constants in SI units (CODATA 2002)*

Constant		Equivalent	Value in SI units
magnetic constant[a]	μ_0		$4\pi \times 10^{-7}$ (ex) N/A^2
electric constant[b]	ε_0	$(\mu_0 c^2)^{-1}$	$8.854\,187\,818... \times 10^{-12}$ F/m
electric factor[c]	f_{el}	$(4\pi\varepsilon_0)^{-1}$	$8.987\,551\,787... \times 10^{9}$ m/F
velocity of light	c	def	$299\,792\,458$(ex) m/s
gravitation constant[d]	G	fund	$6.6742(10) \times 10^{-11}$ m^3 kg^{-1} s^{-1}
Planck constant	h	fund	$6.626\,0693(11) \times 10^{-34}$ J s
Dirac constant	$\hbar$	$h/2\pi$	$1.054\,571\,68(18) \times 10^{-34}$ J s
electron mass	m_{e}	fund	$9.109\,3826(16) \times 10^{-31}$ kg
elementary charge	e	fund	$1.602\,176\,53(14) \times 10^{-19}$ C
unified a.m.u.[e]	u	fund	$1.66053886(28) \times 10^{-27}$ kg
proton mass	m_{p}	fund	$1.672\,621\,71(29) \times 10^{-27}$ kg
neutron mass	m_{n}	fund	$1.674\,927\,28(29) \times 10^{-27}$ kg
deuteron mass	m_{d}	fund	$3.343\,583\,35(57) \times 10^{-27}$ kg
muon mass	m_{μ}	fund	$1.883\,531\,40(33) \times 10^{-28}$ kg
^{1}H atom mass	m_{H}	fund	$1.673\,532\,60(29) \times 10^{-27}$ kg
fine-structure const.	α	$e^2/(2\varepsilon_0 hc)$	$7.297\,352\,568(24) \times 10^{-3}$
—, inverse	α^{-1}	$2\varepsilon_0 hc/e^2$	$137.035\,999\,11(46)$
Bohr radius	a_0	$\hbar/(\alpha c m_{\mathrm{e}})$	$5.291\,772\,108(18) \times 10^{-11}$ m
Rydberg constant[f]	R_∞	$\alpha^2 m_{\mathrm{e}} c/2h$	$1.097\,373\,156\,8525(73) \times 10^{7}$ m^{-1}
Bohr magneton	μ_{B}	$e\hbar/2m_{\mathrm{e}}$	$9.274\,009\,49(80) \times 10^{-24}$ J/T
Boltzmann constant	k_{B}		$1.380\,6505(24) \times 10^{-23}$ J/K
ideal gas volume[g]	v_{m}^0	$k_{\mathrm{B}}T^0/p^0$	$3.771\,2467(66) \times 10^{-26}$ m^3
Avogadro constant	N_{A}	0.001 kg/u	$6.022\,1415(10) \times 10^{23}$ mol^{-1}
Faraday constant	F	$N_{\mathrm{A}} e$	$96\,485.3383(83)$ C/mol
molar gas constant	R	$N_{\mathrm{A}} k_{\mathrm{B}}$	$8.314\,472(15)$ J mol^{-1} K^{-1}
molar gas volume[h]	V_{m}^0	RT^0/p^0	$22.710\,981(40) \times 10^{-3}$ m^3/mol

[a] also called *vacuum permeability*.
[b] also called *vacuum permittivity* or *vacuum dielectric constant*.
[c] as in $F = f_{\mathrm{el}} q_1 q_2 / r^2$.
[d] as in $F = G m_1 m_2 / r^2$.
[e] atomic mass unit, defined as 1/12 of the mass of a ^{12}C atom
[f] very accurately known: relative uncertainty is 6.6×10^{-12}.
[g] volume per molecule of an ideal gas at a temperature of $T^0 = 273.15$ K and a pressure of $p^0 = 10^5$ Pa. An alternative, but now outdated, standard pressure is 101 325 Pa.
[h] volume per mole of ideal gas under standard conditions; see previous note.

Table 10 *Physical constants in atomic units and "molecular units"*

Symbol	Value in a.u.	Value in m.u.
μ_0	$6.691\,762\,564(44) \times 10^{-4}$	$1.942\,591\,810(19) \times 10^{-8}$
ε_0	$1/(4\pi)$	$5.727\,657\,506(58) \times 10^{-4}$
f_{el}	1(ex)	$138.935\,4574(14)$
c	$137.035\,99911(46)$	$299\,792.458$(ex)
G	$4.222\,18(63) \times 10^{-32}$	$1.108\,28(17) \times 10^{-34}$
h	2π	$0.399\,031\,2716(27)$
$\hbar$	1(ex)	$0.063\,507\,799\,32(43)$
m_{e}	1(ex)	$5.485\,799\,0945(24) \times 10^{-4}$
e	1(ex)	1(ex)
u	$1\,822.888\,484\,93(80)$	1(ex)
m_{p}	$1\,836.152\,672\,61(85)$	$1.007\,276\,46688(13)$
m_{n}	$1\,838.683\,6598(13)$	$1.008\,664\,915\,60(55)$
m_{d}	$3\,670.482\,9652(18)$	$2.013\,553\,212\,70(35)$
m_{μ}	$206.768\,2838(54)$	$0.113\,428\,9264(30)$
m_{H}	$1\,837.152\,645\,89(85)$	$1.007\,825\,032\,13(13)$
α	$7.297\,352\,568(24) \times 10^{-3}$	$7.297\,352\,568(24) \times 10^{-3}$
α^{-1}	$137.035\,999\,11(46)$	$137.035\,999\,11(46)$
a_0	1 (ex)	$5.291\,772\,108(18) \times 10^{-2}$
R_∞	0.5(ex)	$0.010\,973\,731\,568\,525(73)$
μ_{B}	0.5(ex)	$57.883\,818\,04(39)$
k_{B}	$3.166\,8154(55) \times 10^{-6}$	$0.008\,314\,472(15)$
v_{m}^0	$254\,496.34(44)$	$37.712\,467(66)$