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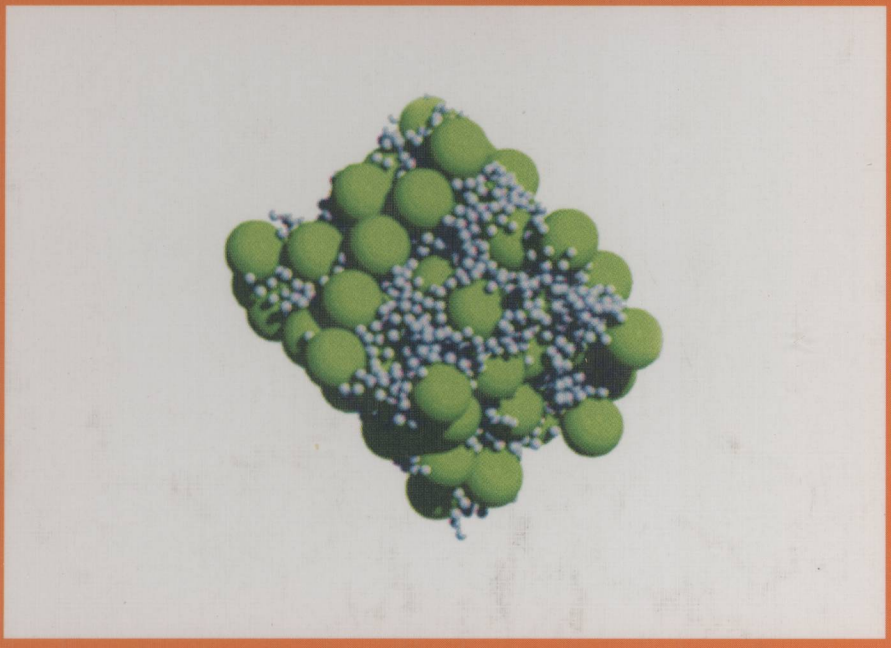

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# The Langevin and Generalised Langevin Approach to the Dynamics of Atomic, Polymeric and Colloidal Systems

*I dedicate this book to my mother Joan, my wife Marie and my children Stuart, Graeme, Tamara and Simon*

# Preface

The stochastic description of the dynamics of a many-body system consisting of a single, large particle, suspended in a fluid made up of an enormous number of much smaller, molecular-sized particles was a major advance in Physics. This approach to describe Brownian motion was pioneered by Einstein [1] and Langevin [2], and their work marks the beginning of a new way to treat the dynamics of many-body systems where a dynamical variable of interest (in this case the velocity of the large particle) is singled out and some other aspects of the problem are treated by the theory of random processes. This treatment is in contrast with the more traditional, kinetic-theory approach of considering the explicit dynamics of all the particles in the system.

Since this early work these stochastic methods have been generalised and refined into a field of major significance. Many areas of research have been influenced by this Brownian approach and stochastic methods have been applied to problems in such diverse areas of physics, chemistry, biology and engineering [3–5]. One of the main uses of these methods in the theory of matter is to treat many-body systems in which different degrees of freedom operate on very different time scales. This is because this approach allows the separation of these very different degrees of freedom and the treatment of each of them by different methods. This separation is achieved by averaging over some variables, which results in equations of motion for only the chosen variables. This approach to singling out particular variables is, however, quite general and not restricted to situations where there is a clear distinction between "fast" and "slow" variables, and can be applied to any system whose dynamics is described by equations of motion such as Newton's equations. The equations resulting from this alternative approach are exact and equivalent to the starting equations from which they are derived and, thus, may be used to provide an exact, but alternative description of the time evolution of any dynamical variable. However, the form of these new equations of motion also enables certain variables to be treated approximately and simply, while allowing the remaining variables to be treated in greater detail. Many methods of this type have been developed under the heading of generalised Langevin methods (GLE) and have provided insight into the properties of many-body systems ranging from atomic liquids, atoms on surfaces and polymeric solutions to colloidal suspensions.

Theories of this type have been considered by many authors from a variety of different points of view ranging from atomic to macroscopic and many excellent treatises and review articles are available (see for example references to Chapters 2 and 3) that deal with specialist aspects of these methods, for example, time correlation functions of atomic and molecular systems. By contrast this treatise attempts to unify this approach to a large number of areas encountered in condensed-matter theory. Explicitly, his book is primarily intended as a fundamental treatment of the background and derivation of GLE's and Langevin equations of use in the interpretation of the dynamics and dynamical properties of many-body systems governed by Classical Mechanics. Such systems may be atomic, molecular, colloidal or polymeric. The attempt is to provide a reasonably rigorous and

complete text, which starts from first principles and provides detailed derivations and discussions of these fundamentals. No attempt is made to cover all applications, but only a few typical applications are discussed in order to illustrate these fundamentals. However, the references given should enable the reader to get a reasonable idea of applications to various areas.

Discussions of the use of approximations are given which should help the reader to make use of approximate schemes to calculate and interpret time-correlation functions. Furthermore, we have included methods to construct numerical GLE algorithms to assist researchers to carry out computer simulations of the dynamical properties of atomic, colloidal and polymeric systems using "Brownian Dynamics" methods. To help in this, details are also given of relevant macroscopic hydrodynamics, which is needed to treat the dynamics of colloidal suspensions. In addition, some Fortran programs are included in Appendix O and references to where other computer programs and routines may be found in order to help the interested reader produce their own results and, hopefully, to aid some people in their research.

Finally, I would like to thank some of the many people who have helped me in this area over the years and attempted to educate me about specific aspects of the theory covered in this book. In no particular order I would like to thank, Bill van Megen, Peter Daivis, Kevin Gaylor, Bob Watts, Brendan O'Malley, Ed Smith, Peter Pusey, Heiner Versmold, Ubo Felderholf, Denis Evans, Rudolf Klein, Kurt Binder, Mike Towler and Ron Otterwill. I would also like to thank my young colleagues who helped me with some aspects of this book, Nicole Benedek, Manolo Per, Tanya Kairn, Mat McPhie, Stephen Williams and Rob Rees.

## REFERENCES

1. A. Einstein, *Investigations on the Theory of Brownian Movement*, Dover, New York, USA, 1956.
2. P. Langevin, *Comp. Rendus*, **146**, 530 (1908).
3. S. Chandrasekhar, Stochastic problems in physics and astronomy, *Rev. Mod. Phys.*, **15,** 1–91 (1943).
4. N. Wax (Ed.), Selected papers on noise and stochastic processes, Dover, New York, 1954.
5. N.G. Van Kampen, *Stochastic processes in physics and chemistry*, North-Holland, Amsterdam, 1992.

# Notation

The following notation, definitions and symbols have been used throughout this book.

## A. POTENTIAL ENERGY FUNCTIONS

*Hard Sphere Potential*

$$u(r) = \infty, \quad r \leq d$$
$$= 0, \quad r > d$$

*Lennard-Jones 12-6 (or LJ12-6) potential*

$$u_{ij}(r) = 4\varepsilon_{ij}\left\{(\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^{6}\right\}$$

or with a core,

$$u_{ij}(r) = 4\varepsilon_{ij}\left[\left\{\sigma_{ij}/(r - d_{ij})\right\}^{12} - \left\{\sigma_{ij}/(r - d_{ij})\right\}^{6}\right]$$

*Chandler–Weeks–Andersen (or CWA) potential*

$$u_{ij}(r) = 4\varepsilon_{ij}\left\{(\sigma_{ij}/r)^{12} - (r/\sigma_{ij})^{6}\right\} + \varepsilon, \mathrm{r} \leq \mathrm{r}_{0ij}$$

$$= 0, \quad r > r_{0ij}$$

or with a core,

$$u_{ij}(r) = 4\varepsilon_{ij}\left[\left\{\sigma_{ij}/(r - d_{ij})\right\}^{12} - \left\{\sigma_{ij}/(r - d_{ij})\right\}^{6}\right] + \varepsilon_{ij}, \quad r \leq r_{0ij}$$

$$= 0, \quad r > r_{0ij}$$

where $\varepsilon_{ij}$ is the well depth, $\sigma_{ij}$ the value of $r$ for which $u(r) = 0$, $r_0$ is the position of the well, i.e., $u_{ij}(r_0) = -\varepsilon_{ij}$ and $d_{ij}$ is the core diameter

*Soft-sphere potential*

$$u(r) = 4\varepsilon_{ij}(\sigma_{ij}/r)^{n}$$

where $n$ is an integer.

## B. SYMBOLS USED

| | |
|---|---|
| $A, A_{ij}$ | a scalar |
| $\underline{A}$ | a vector, |
| $\mathbf{A}_{ij}$ | a tensor |
| $\mathbf{A}$ | an operator |

## C. OPERATIONS

$$\underline{A} \bullet \underline{B} = A_x B_x + A_y B_y + A_z B_z$$

$$\mathbf{A_{ij}} : \mathbf{B_{ij}} = \Sigma\Sigma A_{ij}\ B_{ji} = A_{ij}\ B_{ji}$$

# Contents

# – 1 –

# Background, Mechanics and Statistical Mechanics

In order to fully appreciate how to calculate and use generalised Langevin equations (GLEs) it is first necessary to review the mechanics upon which these GLEs are based and the statistical mechanics which is used in order to calculate bulk properties from the information which these equations generate.

## 1.1 BACKGROUND

The instantaneous mechanical state of system described by classical mechanics requires only the specification of a set of positions and momenta of the particles making up the system and provided that these particles are "heavy enough" this classical mechanical approach will provide an accurate description of the physical state of a many-body system. In practice this applies to systems consisting of most atoms under normal physical conditions, except for hydrogen and helium. Then the common approach to describing the time evolution of this mechanical state of such a many-body system, its dynamics, is by use of a coupled set of differential equations, for example, Newton's equations of motion, which describes the detailed, individual dynamics of all the particles in the system. In the study of molecular systems this approach has led to the development of the widely used numerical technique called molecular dynamics (MD). This method has provided numerous insights into the behaviour of molecular systems and there is now an extensive literature on the method and its application.

However an alternative approach to describing dynamics is to use equations of motion that describe the dynamics of only some, selected particles moving in the presence of the other particles in the system which are now regarded as a background or bath whose detailed dynamics is not treated. Thus, we select out a typical particle or set of particles in which we are interested and find an equation which describes the dynamics of these chosen particles in the presence of the other particles. The classical example of this is the Langevin equation (LE) developed in a heuristic way by Paul Langevin to describe the Brownian motion of a large particle suspended in a fluid consisting of an enormously large number of lighter particles.

The LE is an equation of motion for the velocity $\underline{V}_B$ of a single Brownian (B) particle of mass $M_B$ suspended in a "bath" consisting of an enormous number, $N_b$, of particles of much smaller mass $m$ and is

$$M_B\left(\frac{d}{dt}\right)\underline{V}_B = -\zeta\underline{V}_B + \underline{F}_B^R(t) \tag{1.1}$$

where $\zeta$ is the friction factor, $-\zeta\underline{V}_B$ the drag force due to the bath particles and $\underline{F}_B^R(t)$ the random force due to random thermal motion of the bath particles. Thus, instead of a description of the dynamics of the system by writing down the coupled set of Newton equations for the total system of particles consisting of the B particle and all the $N_b$ background particles, we write down an equation for the dynamics of only the B particle in a background of the small particles. The effect of the small particles on the dynamics of the B particle now only appears via the drag force $-\zeta\underline{V}_B$ and the random force , a description of their detailed dynamics no longer is needed nor, in fact, is possible in this treatment. Further, the drag force $-\zeta\underline{V}_B$ is calculated by the theory of macroscopic hydrodynamics and the random force is assumed to be a Gaussian random variable, that is, is treated stochastically and only its statistical properties are needed. Thus, we have reduced the description of the dynamics of an $N_b + 1$ body problem to that of a one-body problem. However, we have lost information as we now no longer are able using this approach to follow the dynamics of the $N_b$ bath particles as we have averaged-out or coarse-grained over their motion.

This approach pioneered by Langevin[1] has been made formal, vastly extended, and has been shown to be applicable to any dynamical variable. The basic ideas used to generalise the traditional Langevin equation are:

1. First define the dynamical variables of interest, for example, the velocities of particles.
2. Write down a set of coupled equations of motion for these variables in operator form, for example, for the velocities of some particles of the system.
3. Rewrite these equations of motion so as to project out the variables in which we are interested by use of projection operators.

This projecting out averages over the motion of the other particles in the system and is a coarse graining of the equations of motion which provides a description only of the variables which are not averaged over, thus, losing information about the dynamics of the system. Furthermore, this averaging or projection leaves us with terms, "random forces" in the resulting equations of motion for the desired variables which we only have limited information about. These terms are deterministic in the sense that, if we were to go back to the full equations of motion we would know them exactly but this would defeat the purpose of deriving the projected equations of motion. Thus, the "random forces" must, of necessity, be treated in practice as stochastic or random variables about which we only know their statistical properties.

The result of this process is as in the LE approach, one equation for each dynamical variable chosen rather than many coupled equations with which we started. There may still, of

course, be many coupled equations but many fewer than we started with and which explicitly involve many less variables than we started with. For example in the Mori–Zwanzig approach[2] we may derive a single, exact equation for the velocity of a typical particle of each species and not one equation for every particle in the system that would constitute the normal kinetic theory approach. However, it should be emphasised that the resulting equations are still exactly equivalent to the original coupled equations on which they are based and we have not eliminated the coupling of the dynamics of each particle. This coupling will be shown to be represented by a Kernel (or memory function) and a "random force" appearing in these equations. Thus, until we are able to calculate or approximate these two terms we have not achieved a solution to the problem of describing the dynamical properties of the system and their time evolution.

There are, however, advantages to this approach some of which are

1. There is one equation per "species" to be solved.
2. These equations are exact and entirely equivalent to the original equations of motion.
3. These equations may be readily used to construct approximate equations of motion.
4. Equations of motion for time-correlation functions, which can be used to calculate linear transport coefficients and scattering functions, may be directly derived from these basic equations.
5. The form of the memory function often gives us physical insight into the processes involved in the relaxation of a variable to equilibrium.

In order to carry out the above derivations we must first give an outline of the classical mechanical description of dynamics mentioned above and then establish the basis for deriving the generalised Langevin description. For completeness we will also provide an outline of how such dynamical information may be used to calculate the mechanical and non-mechanical properties of a many-body system. In subsequent chapters equations of the GLE type will be derived, basic applications given and numerical schemes outlined for solving them which are analogous to the MD method based on Newton's equations of motion.

## 1.2 THE MECHANICAL DESCRIPTION OF A SYSTEM OF PARTICLES

The classical mechanical description of the instantaneous mechanical state of system only requires the specification of the set of positions and momenta for all the $N$ particles in the system. Then the common approach to describing the time evolution of these variables, the dynamics, of such a many-body system is by use of a coupled set of differential equations describing the detailed time evolution of the position and momentum of each particle. Usually this time evolution is described by Newton's equations of motion written in terms of Cartesian co-ordinates but other equations of motion may be used such as the Lagrange or Hamilton equations and various co-ordinate and momenta schemes used as appropriate. However, we will not give a detailed description of these aspects of mechanics as they are very well known.[3] It does, however, seem wise to comment on the description of a many-body system as given by this classical treatment, show how its output may be used to