On the Description of Atomic Motions in Dense Fluids by the Generalized Langevin Equation: Statistical Properties of Random Forces

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The suitability of the generalized Langevin equation (GLE) for a realistic description of the behavior of a system of interacting particles in solution is discussed. This study is focused on the GLE for a system of non-Brownian particles, i.e., the masses and the sizes of the solute particles are similar to those of the bath particles. The random and frictional forces on the atoms of the solute due to their collisions with the solvent atoms are characterized from molecular dynamics simulations of simple dense liquid mixtures. The required effective memory functions, which are dependent on the concentration of solute, are obtained by solving a generalized Volterra equation. The validity of the usual assumptions on the statistical properties of the random forces is carefully analyzed, paying special attention to their Gaussianity. The reliability of stochastic simulations based on the GLE is also discussed.

KEY WORDS: Generalized Langevin equation; random forces; time-dependent memory functions; molecular dynamics simulation; time correlation functions; computer experiments.

1. INTRODUCTION

The Langevin (LE) and generalized Langevin (GLE) equations are widely used in the statistical mechanical treatment of time-dependent phenomena in fluids. When applied to liquid solutions they allow us to replace the dynamical effects of the solvent on the solute by random and friction forces. The LE and GLE may also be used as substitutes for the classical Newton
equation in computer simulations\(^{1,2}\) at the McMillan–Mayer level of description,\(^3\) i.e., when only the particles of solute are explicitly considered. These stochastic simulation methods—termed Langevin dynamics (LD) or generalized Langevin dynamics (GLD), depending on whether the LE or GLE is assumed—are very helpful when studying the atomic behavior of multicomponent systems, since the need for very expensive computational resources is obviated.

Although the LE was originally introduced from phenomenological arguments, its molecular foundations and ranges of validity are carefully analyzed in several papers.\(^4\) The use of the LE is only justified when we deal with Brownian particles whose masses are much larger than those of the particles of the bath. If solute and solvent particles have similar sizes and masses, memory effects become important and a GLE must be considered. A simple derivation of the GLE for a single particle is achieved by applying the Mori projection method\(^5,6\) to the components of the velocity. This formalism also provides a rigorous statistical mechanical definition of the different terms of the GLE. The random force \(R(t)\) is the part of the total force that is initially orthogonal to the velocity and remains uncorrelated to \(v(0)\) at all subsequent times, and the memory function \(M(t)\) is defined from \(R(t)\) according to the fluctuation-dissipation theorem.\(^6\) In many cases (e.g., in LD or GLD simulations), more information about the random forces is required to characterize them and it is very usual to assume, as an additional hypothesis, a Gaussian distribution for \(R(t)\). One of the aims of this paper is to assess the reliability of this hypothesis.

The derivation of the GLE for a system of interacting solute particles is not so simple. The application of the Mori projection technique to this case results in a GLE where the random forces have lost some of their characteristic properties and the memory functions are so complex that they are not easily modeled and used in computer simulation.\(^7\) Moreover, in this derivation the forces among the solute particles would be due to the bare interactions, whereas in both theoretical studies and computer simulations of solutions at the McMillan–Mayer level of description the inter-solute forces are ordinarily obtained from solvent averaged potentials \(W(r)\). (A derivation of the GLE for a pair of solute particles interacting through a mean force potential is given elsewhere.\(^8\) Alternatively, one can make the assumption that the effect of the solute–solute interactions is accounted for by merely adding a force term to the GLE.\(^9\) The ability of GLD simulations to reproduce some of the solute properties (e.g., the radial distribution functions, the velocity autocorrelation functions, the self-diffusion coefficients, the shape of the atomic trajectories, etc.) when suitable memory functions and interaction potentials are used is discussed in previous works.\(^10\)–\(^13\) In this paper we analyze the GLE by studying the