1. Introductory remarks on the theory for dynamics of simple liquids

The study of collective excitations (collective density fluctuations) in molecular liquids has been a subject of intense investigations through experiments [1, 2, 3] and molecular dynamics simulations [4-9] in the past decade. These investigations have established that there are at least two different kinds of collective excitations in molecular fluids: the ‘acoustic’ mode which originates from the center-of-mass motions of constituent molecules and the ‘optical’ mode which is rooted in the rotational (librational) motions. The appearance of the optical mode is a distinctive feature in the dynamics of polyatomic fluids: it does not show up in liquids consisting of spherical particles. Since the rotational motions give rise to the local charge-density fluctuations, the optical mode is also responsible for the dielectric properties of polar liquids. A detailed understanding of these collective excitations at a microscopic level is prerequisite for understanding a variety of time-dependent phenomena occurring in polar liquids, such as solvation dynamics and solvent dynamical effects on charge transfer reactions in solutions [10-17].

In this chapter we review a recently developed microscopic theory to study such collective excitations in molecular liquids based on the interaction-site representation. As an application we also present a molecular theory for dynamics of solvated ion, in which the ionic dynamics is described in terms of the response of the solvent collective excitations to the solute perturbation. But before embarking on the main subject, let us make a brief survey of the historical developments of the theory.
for dynamics of simple liquids since our theory for molecular liquids is a natural extension along these developments.

Throughout this chapter we consider a homogeneous and isotropic fluid composed of $N$ rigid molecules (or spherical particles) in a volume $V$ at the inverse temperature $\beta = 1/k_B T$, and the thermodynamic limit with density $\rho = N/V$ is implied.

1.1 Memory-function formalism

The study of liquid-state dynamics is an important branch of non-equilibrium statistical physics. Over the past 40 years this active field of research has seen new and important developments. These developments, however, are largely limited to a system of spherical particles, and are not directly applicable to the description of dynamics of molecular systems. Nonetheless, ideas and concepts acquired during the growth of a modern theory constitute the bases in constructing molecular-liquid theories, and in the following main features of those developments for simple liquids are briefly surveyed.

Let us begin with the description of the general framework which constitutes a convenient starting point of any microscopic theory for liquid dynamics. The time evolution of a dynamical variable (or a set of dynamical variables), which we denote as a row vector $A$ (an example is given in Eq. (5.22)), is in general described by the Liouville equation

$$\frac{dA(t)}{dt} = i\mathcal{L}A(t), \quad (5.1)$$

where $\mathcal{L}$ denotes the Liouville operator [18, 19, 20]. This equation can be formally integrated to give

$$A(t) = \exp(i\mathcal{L}t)A. \quad (5.2)$$

(Hereafter the absence of any indication for time $t$ in dynamical variables means that the latter are evaluated at $t = 0$.) However, for a strongly interacting system, the formal solution (5.2) is useless in practice. An exception is the case in which the system can naturally be characterized by a certain ‘small parameter’ whose presence would suggest a perturbative treatment of the part of $\mathcal{L}$ which is effectively small. Unfortunately, this convenient framework does not work in dense (i.e., strongly interacting) systems such as liquids, where no obvious small parameter exists which could be used as an expansion parameter.

In such a situation a frequently adopted strategy is to rephrase the problem in a different way, still avoiding any approximation. Although this new description is again formal and no real progress has apparently