Ultrafast dielectric relaxation response of polar liquids

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In this paper we calculate the complex dielectric constant of polar liquids for microwave and far-infrared range of frequencies. We use the formalism of extended irreversible thermodynamics (EIT) to obtain the autocorrelation function of the polarization vector. To this end, we introduce the local variation of the polarization flow as an independent variable, which allows for the description of collective interacting effects into the formalism. The results obtained here are compared with previous work in the so-called three-variable theory based on the Mori-Zwanzig projection operator technique. This comparison provides an interpretation of EIT in terms of a microscopic theory from which the role of the new independent variable can be established. Using the result of the complex dielectric constant presented here, we show that the fitting of experimental data in polar fluids can be improved in the far infrared frequencies. © 1997 American Institute of Physics.

I. INTRODUCTION

Some results of dielectric relaxation experiments on dense polar liquids remain unexplained. The involved effects are related to the well known dielectric friction mechanism produced by fluctuations of the dipole-dipole interactions. The theoretical explanation of the experimental data in terms of the three-variable theory of Kivelson et al.1,2 based on the Mori-Zwanzig formalism fits the observed spectrum over a limited frequency range (1 MHz–900 GHz) and does not work well for the high frequency range (900–6000 GHz).1

The three-variable theory in the form of a third order continued fraction expansion describes effects of the dynamic variables which are related to the molecular collective orientation, the angular velocity and the intermolecular torques.2 On the other hand, in a treatment of these effects using extended irreversible thermodynamics (EIT), as we will see later, one may include the direct effects as mentioned before, as well as the cross-coupling between them. The comparison between EIT results and the three-variable theory can be done directly, since the results of EIT may be brought into the form of a third order continued fraction expansion.3

In this paper we want to stress two points. The first one lies in the fact that this is the first time that a system that previously has been treated using the projector operator technique of Mori and Zwanzig is explicitly compared with EIT. In particular, the phenomenological coefficients appearing in the equations derived from this theory are interpreted with a microscopic model, here, the three-variable theory. The second one is that, as we shall see below, the phenomenological theory here developed is more general than the three-variable theory. In fact, a new coefficient may be chosen to improve the experimental data on dense polar fluids in the high frequency range.

The theoretical background of this paper is the following. Nee and Zwanzig4 showed that the dielectric relaxation response is modified by the presence of a retarded reaction field in an “Onsager cavity” or a memory effect in the dielectric friction mechanism. This allows for a further development in the description of dipolaron plasma modes in dense fluids where the inertial effect was considered by Lobo, Robinson and Rodriguez.5 Pollak and Alder6 showed numerically that the transverse and longitudinal collective motions are different in character and confirmed that the dipolaron frequency is determined by the longitudinal modes. Using Mori-Zwanzig’s operator formalism Kivelson and Keyes,2 Kivelson and Madden7 and Gershel8 have described many of the observed dynamical properties of organic liquids. Madden and Kivelson1 have studied the nature of the hindered rotation of dipole librational oscillations in collective dipole-dipole interactions. The autocorrelation function may be put in the form of a continued fraction where the terms appearing in the fractions “cascade” can be expressed as successive moments of the autocorrelation function given by the corresponding sum rules. The three-variable theory is a conclusion of many theoretical efforts done by several authors using the projector operator approach to explain the experimental data in polar and organic liquids.

The main point in this discussion is that, the elements of the memory kernel matrix of this approach are indeed integral representations of the full N-body dynamics and there is no systematic way to identify the specific dependence of these parameters with the microscopic ones. Besides, the simplest assumption is to consider the uncoupled dynamics of different collective molecular variables as direct effects. This is the basic assumption behind the three-variable theory. Several solvable models have been presented9,10 to remove this assumption. However, those reports do not work out the comparison with the large number of observations performed on organic liquids. Here, we use extended irreversible thermodynamic (EIT) in order to improve the three-variable