

Chapter 5

Conclusions and Recommendations

The results we present in this work and in the literature [Mar99, Mar00, Mar01a, Mar01b, Mar01c, Mar01d] demonstrate that three-body interactions play an important role in the overall interatomic interactions of noble gases. This is demonstrated by the good agreement between our simulation results and the experimental data for both equilibrium and non-equilibrium systems. It is our opinion that the inclusion of the three-body forces in molecular simulations attempting to reproduce accurately experimental data is worthwhile and necessary. This practice would be beneficial since it would provide new insight into the three-body effects. In fact, it may be inferred that in other atomic and molecular systems three-body forces have an equivalent importance. It is desirable to investigate this more extensively. Studying three-body potentials in complex systems requires a significant effort in terms of experimental development, theoretical approaches and computational costs [Elr94]. Nevertheless, we strongly believe that it is an important area worthy of continued investigation.

The use of effective pair potentials is obviously justified if applied either to corroborate a theory or to compare two similar molecular simulation techniques. For example the attempt, in earlier work, to validate the predictions of mode coupling theory [Kaw73] using the Lennard-Jones potential or even more simplistic potentials was reasonable. In fact, mode coupling theory predicts the general behaviour of the

viscosity and pressure vs. the strain rate, and is consequently not restricted to realistic potentials. On the other hand, the reproduction of experimental data with high accuracy and for a wide range of state points may be a prohibitive task with effective pair potentials. However, the intent to predict the experimental results with sufficient accuracy using effective pair potentials without incurring excessive computational costs is understandable and apparently feasible. There are indications that three-body effects in different properties may be accounted via mean field models [Ege88]. This approach consists in considering the many-body forces experienced by the molecules as a uniform background. The total intermolecular interactions are then considered pair-additive since they are given by a realistic pair potential corrected with this background contribution. Mean field potentials are usually temperature independent and density dependent. Their predictions are more accurate for bulk properties. Estimates on microscopic properties show some deficiencies [Ege88].

The relationship in Eq. (3.3) represents a density dependent pair potential, and it may be envisaged as an effective potential. It has the feature to have been derived from full two-body + three-body calculations. The correction term appearing in Eq. (3.3) may be considered as a background contribution due to three-body effects. The relationship was not the result of a mean field derivation, but it may represent evidence that a mean field model can be applied for the systems studied.

It is noteworthy to point out that the relationship in Eq. (3.3) is not supposed to provide high accuracy and, strictly speaking, it should be used in the range of densities and temperatures in which it was derived. To the best of our knowledge, this is the first time that such a relationship has been derived using simulation data from full two-body + three-body potential simulations. We believe that this procedure can be used to derive similar effective potentials for other systems.

In this work we did not apply three-body short-range potentials. Our results seem to demonstrate that, at least for the systems and the state points studied, these potentials should not give a significant contribution. Naturally, ours is just an *a posteriori* inference. But, very recent findings from Bukowsky and Szalewicz [Buk01] concerning the cancellations between three-body short-range potentials also strongly indicate that the triple-dipole potential is an excellent approximation of the total three-body energy. Further theoretical investigations in this direction are necessary.

A further deficiency in the literature is the investigation of the third order distribution function, $g(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$. From a molecular simulation viewpoint the calculation of $g(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ is feasible, even if it is considerably more time consuming than that of the pair distribution function. The knowledge of $g(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ enables one to choose more correctly the three-body cut-off and to test accurately the superposition approximation [Bar71a] used for long range corrections. A more precise calculation of the liquid state pressure may be a beneficial consequence of such an investigation. As pointed out in Chapter 3, the total pressure is the sum of the kinetic and potential contributions. These are of the same magnitude and opposite sign. The contribution from the three-body long-range corrections may be crucial in order to match the experimental data for the liquid state.

In the past, some simulations with three-body potentials used 108-atom systems [Mur71, Bar71a, Lee94]. The size of such systems may not be compatible with an accurate determination of the three-body effects. In our work we used a 500-atom system, which was demonstrated to provide a good accuracy. However, investigations on possible scale effects may be beneficial. This is true also for mean field theory. In fact, there is the suspicion that many-body potentials show mean field behaviour because of the short cut-off applied in the simulations [Ege88].

The results for vapour-liquid coexisting phases encourage performing further computer simulations with realistic potentials. This may improve the prediction of quantities like critical temperature and density, in particular of substances for which these properties are difficult to obtain from experiment. It also very interesting to pursue the suggestion of Frenkel and Smit [Fre96] to use direct molecular dynamics techniques to investigate coexisting phases, since nowadays the increasing computer speed and use of parallel computers can allow such attempts.

We have demonstrated that use of accurate two- and three-body potentials for shearing liquid argon and xenon displays significant departure from the expected strain rate dependencies of the pressure, energy and shear viscosity. For the first time, the pressure is convincingly observed to vary linearly with an apparent analytic $\dot{\mathbf{g}}^2$ dependence, in contrast to the predicted $\dot{\mathbf{g}}^{3/2}$ dependence of mode-coupling theory. This dependence results primarily from the two-body potential. The 3-body term only serves to raise the magnitude of the total pressure. Recent work using a Lennard-Jones potential found a similar deviation from mode-coupling theory [Mat00, GeJ01]. In particular, they found deviations from mode coupling theory predictions away from the triple point. Further work is required to understand this behaviour. The shear viscosity is also seen not to be a simple function of $\dot{\mathbf{g}}^{1/2}$, and our data are in general agreement with recent work of other authors [Tra98]. Our best extrapolation of the zero-shear viscosity for argon gives excellent agreement (within 1%) with the known experimental data. From the best of our knowledge, this the first time that such accuracy has been achieved with NEMD simulations. Once again, this encourages performing simulations with accurate potentials for transport properties.