

# Molecular dynamics simulation of liquid and gaseous hydrogen selenide: Cross correlation functions

M. W. Evans,<sup>a)</sup> G. C. Lie, and E. Clementi

IBM Corporation, Data Systems Division, Dept. 48B/MS 428, Neighborhood Road, Kingston, New York 12401

(Received 21 June 1988; accepted 2 August 1988)

The effect of the phase change from compressed gas to liquid in hydrogen selenide is explored in terms of cross correlation functions. There are considerable differences in amplitude and time dependence of the cross correlation functions which are recorded at several state points from the liquid just below the boiling point to the compressed gas. Results are obtained for 108 and 500 molecules in order to investigate the effect of sample size on cross correlation functions in the laboratory frame and in the frame (1,2,3) defined by the molecular moments of inertia.

## I. INTRODUCTION

Computer simulation has now developed to the stage where the fine details of molecular dynamics can be appreciated in terms of time cross correlation functions (ccfs).<sup>1-5</sup> These measure statistically the degree of correlation between different dynamical quantities in the same molecule. A complete picture of the dynamics of a molecular liquid can then be built up in terms of several different types of ccf. Their existence in the laboratory frame is determined by the basic symmetry laws of physics, including those of time reversal, parity, and reflection symmetry. In the moving frame of reference, defined by the three principal molecular moments of inertia, the existence of the ccf for  $t > 0$  depends on the point group symmetry of the molecule under consideration. The standard methods of group theory apply to the time dependence of the ccf as discussed in detail recently by Whiffen.<sup>6</sup>

By extensive use of computer simulation, many different types of ccf have recently been characterized numerically, firstly in the moving (1,2,3) frame of reference and then in the laboratory frame ( $x,y,z$ ). A theory for the laboratory frame ccfs has been developed using the concept of linked Langevin equations,<sup>7</sup> and at the expense of extra parameters is able to describe the main qualitative features of the numerical results from the computer simulation. Although the theory is able to follow the numerical data qualitatively in terms of the friction coefficient and potential energy parameter, it is not yet a predictive theory, i.e., it is still semiempirical in nature. For this reason it is necessary to use computer simulation to investigate systematically the effect of varying conditions, such as molecular geometry and thermodynamics, on the magnitude and time dependence of each cross correlation function. A systematic investigation of this kind will allow us to see which factors are most important in controlling statistical cross correlation at molecular level. One of the simplest of the class of asymmetric top molecules is hydrogen selenide, which is a simple liquid essentially free of the hydrogen bonding (H bonding).

The hydrogen selenide molecule is an asymmetric top in

which one moment of inertia is considerably smaller than the other two. The subsequent anisotropy in the molecular diffusion should therefore be greater than that in liquid water, where the replacement of selenium by oxygen introduces the well known aqueous hydrogen bonding. The dynamics should therefore be those of a simple triatomic with autocorrelation functions (ccfs) and cross correlation functions reminiscent of anisotropic diffusion in the laboratory and moving frames of reference. The moving frame of reference is defined in this paper as that of the three principal molecular moments of inertia, useful for establishing the anisotropy of the diffusion of quantities such as the cross correlation between the molecular center of mass linear velocity and the molecular angular velocity. Other ccfs of interest appear directly in the laboratory frame of reference and part of the purpose of this paper is to establish their time dependence in the compressed gaseous and liquid states of hydrogen selenide.

The amplitude and time dependence is measured in terms of number density across the phase change from compressed gas to liquid and then at different number densities in the liquid at a constant temperature just below the boiling point. The area beneath the ccf is then plotted as a function of number density, thus providing an estimate of the increasing strength of statistical cross correlation across the phase change. This is repeated for several ccfs of interest in the laboratory and moving (1,2,3) frames of reference.

## II. COMPUTER SIMULATION METHODS

The equations of motion for 108 H<sub>2</sub>Se or alternatively for 500 molecules were solved using an algorithm which integrates separately the rotational and the translational parts.<sup>8</sup> The equations of motions are integrated using a Verlet algorithm.<sup>9</sup> For each molecule in the ensemble the algorithm provides records of dynamical quantities such as linear velocity, angular momentum, orientation, rotational velocity, force, torque, and so on at each time step. This information is stored on disk and then used to compute auto and cross correlation functions as classified fully elsewhere. Each cross correlation function (ccf) was computed over 6000 time steps using a running time average after an initial equilibration period of up to 20 000 time steps.

<sup>a)</sup> Permanent Address: Department of Physics, University College of Swansea, Singleton Park, Swansea SA2 8PP, Wales (UK) and Visiting Academic, Department of Microelectronics & Electrical Engineering, Trinity College, Dublin 2, Republic of Ireland.

The intermolecular pair potential of hydrogen selenide was approximated with a  $3 \times 3$  Lennard-Jones site-site potential with the following parameters:

$$\epsilon/k_B(\text{Se-Se}) = 350.0\text{K}; \quad \sigma(\text{Se-Se}) = 3.5\text{\AA};$$

$$\epsilon/k_B(\text{H-H}) = 54.5\text{K}; \quad \sigma(\text{H-H}) = 2.8\text{\AA}.$$

The lack of H bonding in hydrogen selenide means that the partial charges used to represent the electrostatic distribution on each atom could safely be inferred as zero.

With this model pair potential the molecular dynamics of the hydrogen selenide were simulated at several state points in the compressed gas and liquid, and the behavior of the ccf obtained as a function of number density.

### III. RESULTS AND DISCUSSION

Figure 1 illustrates the direct laboratory frame ccf between the molecular rotational velocity and the molecular center of mass linear velocity as a function of molar volume. As the molar volume is decreased from  $180 \text{ cm}^3/\text{mol}$  in the

compressed gas to  $40 \text{ cm}^3/\text{mol}$  in the liquid, the amplitude of the ccf increases by a factor of approximately 10 times, as defined by the intensity of the first peak of the ccf. The amplitude is plotted against molar volume in Fig. 2, and it is clear that at high number densities there is considerable cross correlation between rotational velocity and velocity in the condensed state of hydrogen selenide.

Figure 2(a) is a plot of the height of the first peak of the rotational velocity to velocity ccf against the molar volume, whereas Fig. 2(b) the equivalent for the orientation to velocity ccf. The transition from compressed gas to liquid is marked with a dashed line. As the gas condenses into the liquid there is a discontinuity in the dependence of the height of the first peak on the molar volume, i.e., there is a pronounced change of slope. The phase transition is measured through the fact that the total energy of the system changes from positive (compressed gas) to negative (liquid). At constant temperature (kinetic energy), the change of slope becomes apparent at a molar volume of  $150 \text{ cm}^3/\text{mol}$ , which is the point at which the total energy of the system becomes negative. In the compressed gas the total energy is positive, and in the liquid, negative to a molar volume of about  $20 \text{ cm}^3/\text{mol}$ , when it once more becomes positive due to the high external pressures (about  $250.0 \text{ kbar}$ ) needed to sustain the liquid at  $20.0 \text{ cm}^3/\text{mol}$  and a temperature of  $243 \text{ K}$  (just below the boiling point at  $1 \text{ bar}$ ). Statistical cross correlation between the molecular linear and rotational velocity is therefore sensitive to molar volume, and therefore to the mean intermolecular separation. At the phase change between the compressed gas and the liquid there is a discontinuity in the height of the first peak of the ccf as a function of molar volume which coincides with the point at which the total energy of the simulation changes from positive (compressed gas) to negative (liquid).

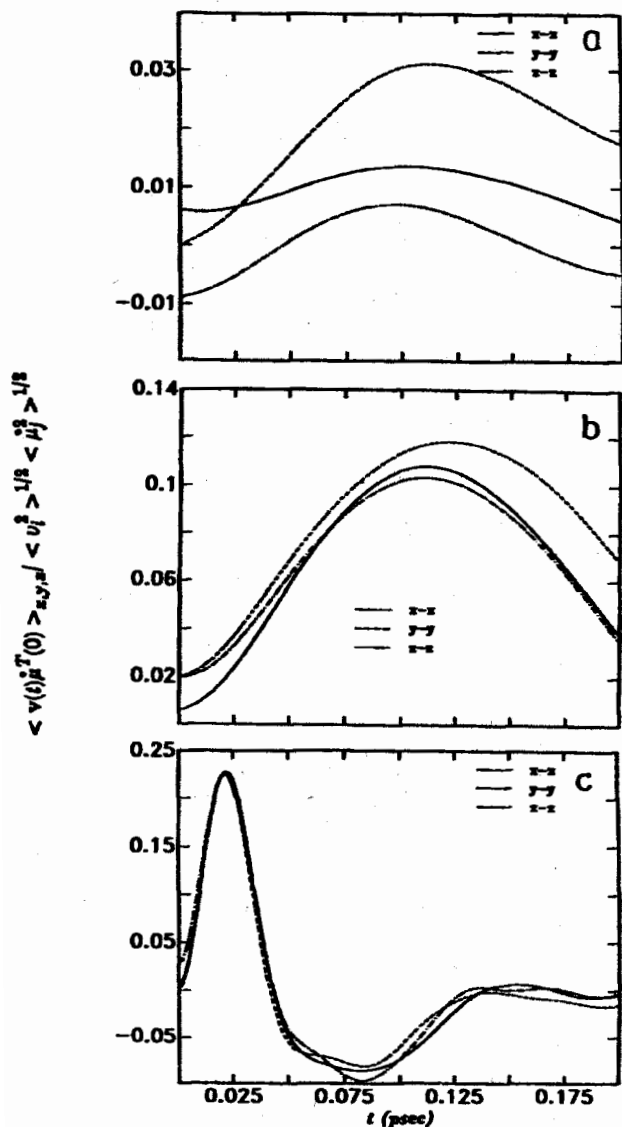


FIG. 1. Cross correlation between rotational and linear velocity for different molar volumes: (a)  $180 \text{ cm}^3/\text{mol}$ , compressed gas; (b)  $40 \text{ cm}^3/\text{mol}$ ; and (c)  $20 \text{ cm}^3/\text{mol}$ .

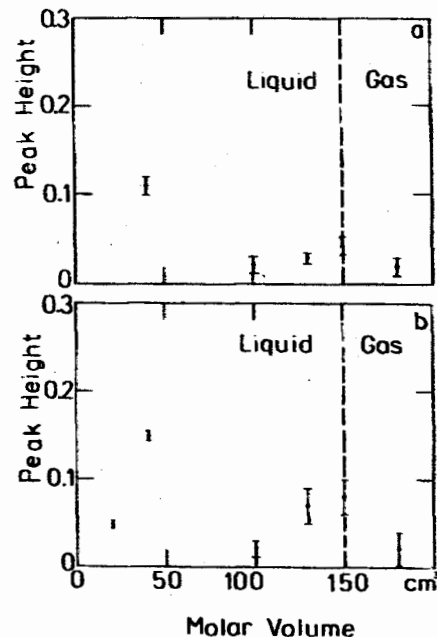


FIG. 2. (a) Amplitude of the first peak of the normalized cross correlation function  $\langle v(t) \mu^T(0) \rangle$  as a function of molar volume; (b) amplitude of the first peak of the normalized cross correlation function  $\langle v(t) \mu^T(0) \rangle$  as a function of molar volume.

The available theory, to be described shortly, would follow this effect through parameters such as the friction coefficient and the barrier height to libration. The theory is approximately capable of reproducing the simulation data in terms of these parameters, as illustrated in Fig. 3 for the friction coefficients and barrier heights of the caption.

The cross correlation function is derived theoretically by solving the itinerant oscillator equations

$$\ddot{r} + \beta \dot{r} + V(r, \mu) = \lambda_1(t),$$

$$\ddot{\mu} + \beta \dot{\mu} - V(r, \mu) = \lambda_2(t).$$

Here  $\beta$  is the Langevin friction coefficient, a special form of the more general memory function. This has been assumed to be the same for the two equations, in general the friction coefficients are different in magnitude, but this leads to mathematical complexity. The potential term  $V$  is generated by assuming that the rotational and linear velocities are not statistically independent in frame  $(x, y, z)$ . In general the dependence of  $V$  on its argument is unknown, being the outcome of inter- and intramolecular potential energy terms. It is assumed that it can be expanded in a Taylor series. The potential energy will in general have minima and maxima (potential wells and barrier heights) and it is reasonable to approximate these with an even powered Taylor series in the energy, such as a cosine. In the first approximation only the energy term in the argument squared is retained. Differentiating this gives

$$V(r, \mu) \approx -2V_0(r, \mu).$$

The terms on the right-hand side of the Langevin equations are Wiener stochastic noise terms as usual, and the equations in this form are soluble analytically using the methods recently developed by Coffey *et al.*<sup>10</sup> The results are given in terms of the friction coefficient and the barrier height  $V_0$  in Fig. 3.

If the simple assumption is made that the friction coefficient  $\beta$  is inversely proportional to the molar volume then an attempt can be made theoretically to reproduce the results of Fig. 2, i.e., the height of the first peak of the cross correlation function vs number density. The friction coefficient and barrier height cannot be defined unambiguously, but the three dashed curves in Fig. 3 represent combinations of the two

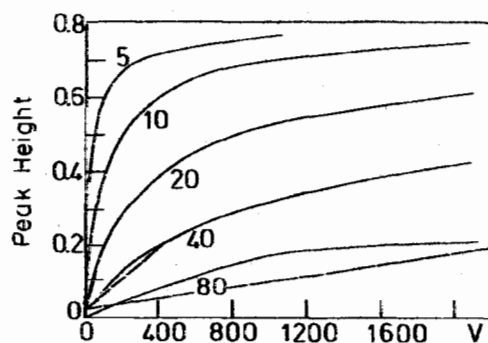


FIG. 3. Theoretical representation of the height of the first peak of the normalized cross correlation function  $\langle v(t)\mu^T(0) \rangle$  from the linked Langevin equations of the text. The height of the first peak is plotted against the potential  $V$  for different friction coefficients recorded on the figure. The significance of the dashed lines is explained in the text.

parameters which lead to approximately the same dependence of peak height on molar volume as appears in Fig. 2 to the phase transition. The theoretical results of Fig. 3 do not succeed in reproducing the discontinuity at the phase transition itself. Langevin equations in general do not have the capability of reproducing phase transitions and associated discontinuities. Note that the equivalent diffusion equations with rotational velocity replaced by angular velocity will not be a valid description of the molecular diffusion process because they would give a finite result for the cross correlation function between angular and linear velocity. In fact this ccf vanishes due to the different parity symmetry of molecular angular velocity and linear center of mass velocity in the laboratory frame  $(x, y, z)$ .

The theory can be solved self-consistently for other auto and cross correlation functions of interest, as described elsewhere in greater detail.<sup>11</sup>

The computer simulation can also be used to generate the cross correlation between orientation and linear velocity. The resulting first peaks as a function of the molar volume is described in Fig. 2(b). The overall pattern for this laboratory frame ccf is similar to that between the rotational velocity and the molecular linear velocity, i.e., the amplitude increases as a function of pressure (or with decreasing molar volume). This implies that the existing theories of molecular diffusion become less and less valid with decreasing molar volume for an asymmetric top triatomic such as hydrogen selenide (molecular point group  $C_{2v}$ ). This is because there is a lack of statistical cross correlation built in to these theories.

In the moving frame of reference defined by the principal molecular moments of inertia, the cross correlation between linear and angular velocity has two nonvanishing elements whose amplitude depends inversely on the molar volume. There is no self-consistent theory available yet for both the moving and laboratory frame cross correlation functions cited in this paper, and computer simulation is therefore the only means of obtaining the complete range of data on the important statistical correlations in hydrogen selenide (liquid and gas). In this respect the work of this paper shows clearly that the fundamental molecular dynamics of hydrogen selenide are heavily influenced by cross correlation, which becomes stronger with decreasing molar volume.

The range of cross correlation functions of this paper was recomputed with a sample of 500 molecules, and no substantial effects of box size were found. This means that the cross correlation functions reported in this paper are essentially speaking a realistic representation of statistical interrelations in liquid hydrogen selenide for the given pair potential.

#### ACKNOWLEDGMENTS

M.W.E. would like to thank the IBM Corporation for financial support.

<sup>1</sup>J. P. Ryckaert, A. Bellens, and G. Cicotti, *Mol. Phys.* **44**, 979 (1981).

<sup>2</sup>M. W. Evans, *Phys. Rev. Lett.* **55**, 1551 (1985).

<sup>3</sup>M. W. Evans and G. J. Evans, *Phys. Rev. A* **34**, 468 (1986).

<sup>4</sup>M. W. Evans, *J. Chem. Soc. Faraday Trans. 2* **82**, 650 (1986).

<sup>5</sup>M. W. Evans, K. Refton, K. N. Swamy, G. C. Lie, and E. Clementi, *Phys. Rev. A* **36**, 3935 (1987).

<sup>6</sup>D. H. Whiffen (private correspondence).

<sup>7</sup>M. W. Evans, G. C. Lie, and E. Clementi, *J. Chem. Phys.* **87**, 6040 (1987).

<sup>8</sup>M. W. Evans, *J. Chem. Soc., Faraday Trans. 2* **79**, 1811 (1983).

<sup>9</sup>L. Verlet, *Phys. Rev.* **159**, 98 (1967).

<sup>10</sup>W. T. Coffey, P. Corcoran, and M. W. Evans, *Proc. Roy. Soc. London Ser. A* **410**, 61 (1967).

<sup>11</sup>M. W. Evans, G. C. Lie, and E. Clementi, *J. Chem. Phys.* **88**, 5157 (1988).