

INTERPRETATION OF FAR INFRARED SPECTRA IN TERMS OF A COLLISION DISTRIBUTION

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Abstract. A generalized model for the description of molecular motions is discussed. Computer simulations are compared with experimental data, which are thereupon analysed in terms of model parameters. Some general trends are indicated and an interpretation in terms of molecular properties is proposed.

Résumé. L'extension d'un modèle collisionnel pour la description des mouvements moléculaires est discutée. Les simulations du calculateur sont comparées avec les données expérimentales, qui sont en conséquent analysées en fonction du modèle. Ainsi on peut dégager certaines lignes générales. On propose une interprétation en termes de propriétés moléculaires.

It is well known that the description of liquids differs greatly from the description of gases on the one hand and solids on the other. In the latter two systems it is possible to express measurable properties in terms of coordinates that have, at least in zero'th order, a simple time dependence. In liquids however this simple zero'th order starting point is lacking and therefore, although it may still be possible to specify the coordinates that are relevant for a certain property, these coordinates will be coupled so strongly to all others that their time dependence will be far from simple. Hence anyone wishing to analyse experimental data on microscopic properties of liquids will have to choose between two approaches: either take all coordinates into explicit consideration or restrict the description to one or a few coordinates and lump the coupling with all others in a coupling-(friction-)parameter which will in general be frequency dependent.

The first approach leads to molecular dynamics calculations, the second to phenomenological descriptions that find their theoretical justification in the generalized Langevin equation.

The advantage of model descriptions lies in the fact that they combine the simplicity obtained by taking only few coordinates into explicit consideration with an intuitively clear picture of the coupling of these coordinates with all others; the main disadvantage is of course the loss of rigour.

In the following we will discuss the description of some dynamical properties of liquids in terms of a molecular model in which the molecules perform rotational or translational motion interrupted by collisions.

The model description of rotational and translational diffusion is as follows: molecules are assumed to undergo infinitely short collisions while rotating or translating freely in between. In contrast to earlier models [1, 2, 3] successive collisions may be correlated i.e. the distribution of times between two consecutive collisions is not necessarily of the Poisson type. The assumption that collisions are Poisson distributed seems justified for a dilute gas but need not necessarily hold for dense systems. The reason for the incorporation of correlated collisions in the model was the hope that

it might be possible to interpret certain experimental properties characteristic of liquids in these terms.

In the model the effect of a collision may be twofold: firstly angular or linear momentum may be transferred and secondly energy transfer may take place. Two limiting cases are usually discerned:

- (1) No energy is transferred during a collision.
(For rotation this is known as *m*-diffusion.)
- (2) The size of the momentum vector is thermally averaged by every collision (in this case large energy transfer occurs).
(For rotation this is known as *J*-diffusion.)

If it is assumed that only successive collisions may be directly correlated and that the effect of successive collisions on the molecular motion is uncorrelated, the mathematical formulation of the diffusion problem may be cast in a form that has agreeable analytical properties. In this form all *n*-collision contributions can be summed explicitly and closed expressions are obtained for the autocorrelation function of the dipole moment and the angular momentum in the case of rotational diffusion and of the velocity in the case of translational diffusion [4]. These correlation functions provide a link with experiment and hence information could be obtained from comparison of model calculations with experimental data.

Experimentally obtained and computer simulated far infrared spectra due to the rotational motion of linear molecules or the translational motion of spherical molecules were thus compared to extract information from model calculations. To this end we separately studied the effect of:

- (1) Changing the ratio between energy transfer and momentum transfer (i.e. the limiting elastic and inelastic cases were compared).
- (2) Introducing a correlation between successive collisions.
- (3) Changing the net effect of one collision on the amount of momentum transferred.

Conclusions based on this procedure can only be qualitative. For a phenomenological description of physical systems this model would actually be rather inefficient due to its flexibility. More importance should be attached to conclusions stating that under certain restrictions a particular type of experimental spectrum can or cannot be simulated than to the actual values of the parameters which give the best fit.

As an example we consider the far infrared rotation spectra of linear molecules in liquids. Qualitative features that can be recognized are:

- (a) The presence or absence of rotational fine structure over the entire absorption region or part thereof [5, 6, 7].
- (b) The overall intensity distribution. (In fact a wide variety of band shapes can be found in the literature; e.g. [8, 9, 10].)

It turns out that qualitatively all these different shapes can be accounted for by adjusting the variables within the model. A systematic study of the effect of the variation of the different parameters on the simulated spectra led us to the following generalizations:

For liquids showing spectra with rotational fine structure rotational energy transfer is relatively slow whereas angular momentum is readily exchanged. These systems are best described by an m -diffusion model; it seems unnecessary to assume any correlation between successive collisions.

Liquids giving rise to strong absorption at higher than pure rotational frequencies (Poley absorption) have considerable coupling of their rotational coordinates to translational coordinates in the fluid. Because of the large torques acting on the molecules the rotational energy is not even approximately a constant of motion and rotation tends to libration which is of course strongly coupled to translational modes of about the same frequency. In terms of model parameters this strongly coupled motion is best described by a J -diffusion model with correlated collisions that tend to reverse the direction of the angular momentum (thus giving rise to a librational type of diffusive motion).

Figure 1 shows a series of simulated far infrared spectra with rotational fine structure. (If the moment of inertia that appears in the reduced frequency units is chosen to be the moment of inertia of hydrogen chloride, the temperature corresponds to 100 K; by appropriate scaling these simulations may be made to apply to other systems.) For each set of parameters the spectrum is calculated twice; one simulation corresponding to the elastic (m -diffusion) limit, the other to the inelastic (J -diffusion) limit. Two parameters are varied independently:

- (1) The average time between collisions (t_{BC}).
- (2) The average cosine of the angle through which the angular momentum is rotated during a collision ($\overline{\cos \gamma}$).

Successive collisions are assumed to be uncorrelated. Clearly the dependence of the rotational fine structure on $\overline{\cos \gamma}$ is only slight in the J -diffusion case compared to m -diffusion. In contrast the dependence on t_{BC} is much stronger; so much in fact that if t_{BC} (in units I/h) is less than one all rotational fine structure disappears in the J -diffusion case. Furthermore the overall spectral intensity distribution for J -diffusion tends to lower frequencies than the corresponding m -diffusion calculations.

Figure 2 shows a series of simulated far infrared spectra without rotational fine structure. Again for each set of parameters an m - and J -diffusion calculation was done. To obtain a spectral intensity distribution resembling Poley absorption it is necessary to assume that $\overline{\cos \gamma} < 0$ (i.e. the sense of rotation is on the average reversed during a collision). This condition is necessary but not sufficient; a distinct correlation between successive collisions is required to shift the maximum of absorption to higher frequencies. This latter effect is shown in the figure in which corresponding simulations with uncorrelated collisions (A) and strongly correlated collisions (B) are plotted. The position of the maximum of absorption is mainly determined by the time at which the deviation from uncorrelated behaviour in the collision distribution is largest. Clearly the behaviour of m - and J -diffusion simulations is similar; however the shape of the spectra simulated with the J -diffusion model fits experimental spectra better, particularly in the low frequency region.

For the description of translational diffusion in liquids a similar analysis can be

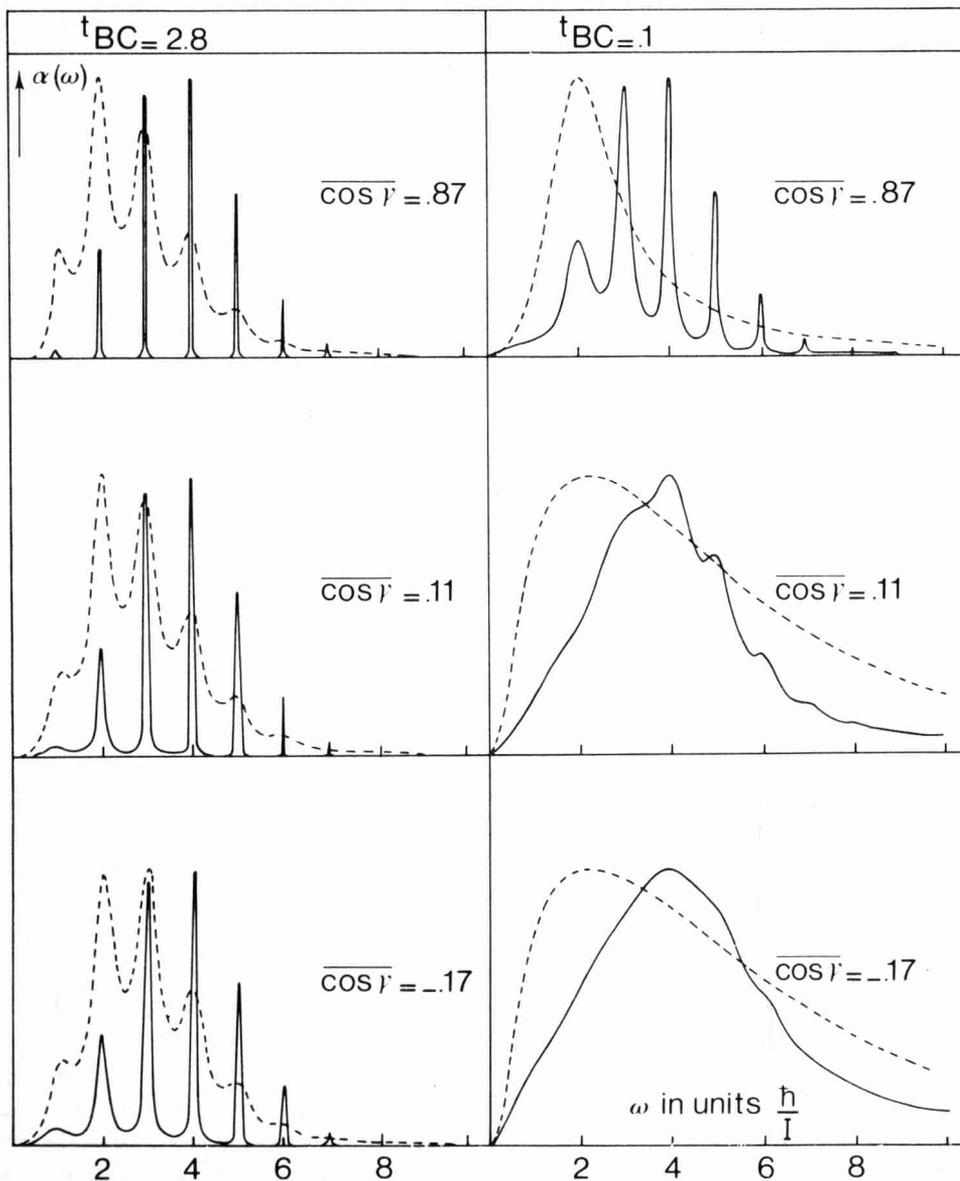


Fig. 1. Dependence of simulated far infrared spectra with rotational fine structure on t_{BC} and $\overline{\cos \gamma}$. Collisions are assumed to be Poisson distributed. Reduced temperature $\theta_R = (2IkT/\hbar^2) = 6.7$; extinction in arbitrary units. m -diffusion simulation = (—); J -diffusion simulation = (-----).

made. The appearance of a hump in the power spectrum of the velocity autocorrelation function of simple liquids at a characteristic frequency is well known [11]. Translational energy transfer depends on the mass ratio of the colliding particles (in a Lorentz gas collisions are completely elastic, for a system of identical particles the

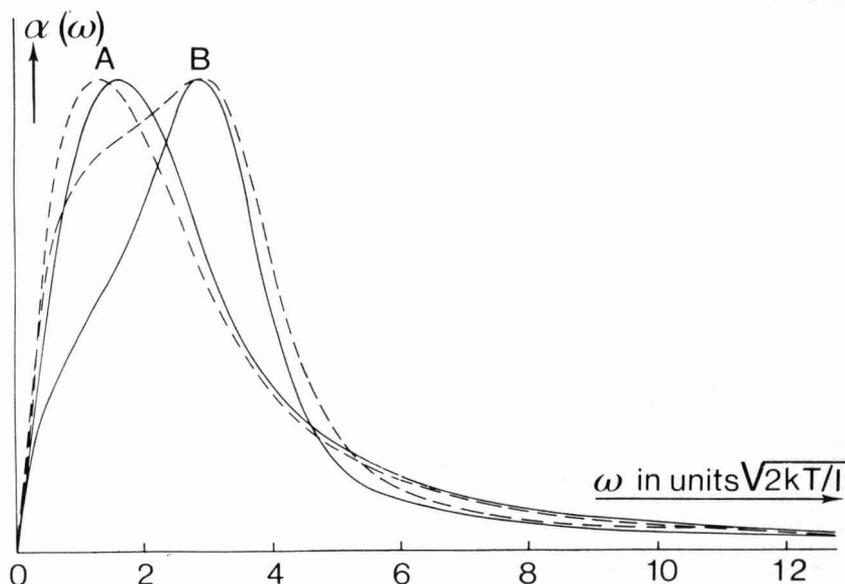


Fig. 2. Simulated far infrared spectra calculated with uncorrelated (*A*) and strongly correlated (*B*) collisions. Reduced temperature $\theta_R = (2IkT/h^2) = 680$, $\overline{\cos \gamma} = -0.88$; extinction in arbitrary units. *m*-diffusion simulation = (—); *J*-diffusion simulation = (-----).

thermalization of translational energy is effected in a few collisions). The completely elastic and strongly inelastic models therefore describe limiting cases. To obtain the characteristic frequency in the power spectrum of the velocity autocorrelation function one must assume that successive collisions are correlated and reverse on the average the direction of the particle velocity. Earlier models for the description of translational diffusion in liquids have been given [12, 13] in which the diffusion is described as a combination of translatory and oscillatory motions. To fit known power spectra of velocity autocorrelation functions of liquids one has to attribute considerable oscillatory character to the diffusional motion; this is commonly interpreted in terms of collective motions that are present in the liquid. Increasing the oscillatory character of the motion in such a description has much the same effect on the power spectrum of the velocity autocorrelation function as the introduction of correlated collisions in the collision model. This indicates a relation between correlated collisions in the model and collective motions in the system described.

Conclusions

Using a collision model for the description of rotational and translational diffusion of molecules certain qualitative conclusions may be drawn about the dynamical behaviour of systems studied experimentally. The relevant parameters in terms of which the experimental data may be interpreted are the amount of energy and momentum transfer during collisions and the possible correlation between successive collisions. The

interpretation of experimental far infrared spectra of linear dipole molecules suggests that correlated collisions and large energy transfer appear together for rotation. As it is known that translational energy transfer depends strongly on the mass ratio of the interacting particles it is tempting to offer an interpretation for the rotational case that makes use of an analogous concept.

Molecules that give rise to spectra with rotational fine structure in the liquid phase mainly interact with the surrounding medium through relatively long range forces. These forces couple the rotation to a large number of molecules and this can be considered as an interaction with a pseudoparticle with large effective moment of inertia (this would favor elastic angular momentum transfer, in particular if energy transfer to the relative center of mass motion is small). The precise time dependence of the torques is determined by a large number of coordinates which will all have different time dependences; the coupling to any one of these coordinates separately is weak. Under these circumstances the autocorrelation function of the random torque will tend to δ -function behaviour, hence the autocorrelation function of the angular momentum will become exponential which corresponds to rotational motion modulated by uncorrelated collisions.

Molecules that give rise to Poley absorption mainly couple their rotational coordinates to the fluid through the short range non-central part of the potential. This short range interaction couples the rotation to only a few particles; therefore, using once more the analogy with translation, rotational energy is readily transferred. Furthermore the torques depend mainly on the coordinates of the nearest neighbours. These coordinates are strongly coupled to the coordinates of the rotating molecule itself and therefore the autocorrelation function of the random torque will persist relatively long; the angular momentum will not decay exponentially but exhibit the more or less oscillatory behaviour characteristic of the presence of correlated collisions in the model.

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DISCUSSION

Laulicht: Could you suggest what will be the order of magnitude of τ_{BC} for real molecules in liquids?

Frenkel: Calculated τ_{BC} values are of the order of 1×10^{-13} to 5×10^{-13} s, for not too large molecules.

Friedman: In your collision correlations, do you only have a correlation of the interval between successive collisions or do you also have correlations in the energy and momentum transfers of successive collisions?

Frenkel: In this model only correlation between successive collisions has been taken into account.

Comment by M. R. Hoare

I agree entirely, in the spirit of previous remarks, that one must look for tractable models which go beyond the oversimplified *J* and *M*-diffusion cases.

In considering these, however, I think one must draw certain distinctions in the way in which the term 'correlation' is used, bearing in mind particularly the subtle difference between the idea of chains of correlation in the probabilities of, say, rotational states before and after collisions and the idea that 'collisions' themselves may be correlated. If there is (first-order) Markovian behaviour, all 'memory-effects' will be statistically determined by the immediately-previous collision, nevertheless correlations in states – in this case the *persistence of angular velocity* – may still propagate over many collision-times.

More immediately, though, I must object to the assertion that the distribution of waiting-times for collisions in a freely-translating gas is Poisson in form. The collision-number function for hard-spheres is naturally velocity-dependent and contains a Gaussian and an error-function term. (See Chapman and Cowling.) A Poisson distribution of waiting-times only applies if one selects a sub-set of spheres with fixed translational velocity. In view of this it seems difficult to understand your statement that deviation from simple Poisson behaviour implies a correlation between successive collisions.