

## Translational component of the interaction-induced dipole correlation functions in dense fluids

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The translational dynamics of pairs of interacting molecules plays an important role in the theory of interaction-induced phenomena. For the isotropic fluid the quantity of interest is the correlation function  $C_{tr}^{(l)}(t)$  ( $l = 1, 2, 3, \dots$ ),

$$C_{tr}^{(l)}(t) = \langle [R(t)R(0)]^{-(l+2)} P_{l+1}(\cos \theta(t)) \cdot P(\mathbf{R}_0, \mathbf{R}, t) \rangle \quad (1)$$

$$\sim \int d^3\mathbf{R} d^3\mathbf{R}_0 (R_0 R)^{-(l+2)} \cdot P_{l+1}(\cos \theta(t)) \cdot P(\mathbf{R}_0, \mathbf{R}, t),$$

where  $P(\mathbf{R}_0, \mathbf{R}, t)$  is the conditional probability that the intermolecular vector  $\mathbf{r}_{12}$  has the value  $\mathbf{R}$  at the time  $t$  if it has the value  $\mathbf{R}_0$  at  $t=0$ . In the Legendre polynomial  $P_{l+1}[\cos \theta(t)]$ ,  $\theta(t)$  is the angle between the vectors  $\mathbf{R}_0$  and  $\mathbf{R}$ .

In Ref. 1 we have calculated  $C_{tr}^{(l)}(t)$  assuming independent diffusion of each molecule (noninteracting or "force-free" hard spheres) and neglecting the problem of impenetrability of molecular spheres in the course of a trajectory; however, as pointed out by Hwang and Freed<sup>2</sup> and Ayant *et al.*,<sup>3</sup> the reflecting wall boundary condition at the distance of the closest approach  $d$  of two molecules:

$$\left. \frac{\partial P(\mathbf{R}_0, \mathbf{R}, t)}{\partial R} \right|_{R=d} = 0 \quad (2)$$

ensures that the molecular spheres do not penetrate each other in the course of a trajectory.

As noted in Ref. 2, the appropriate solution to the force-free diffusion equation

$$\frac{\partial P(\mathbf{R}_0, \mathbf{R}, t)}{\partial t} = D \nabla^2 P(\mathbf{R}_0, \mathbf{R}, t), \quad (3)$$

where  $\nabla = \partial/\partial R$ , with the reflecting wall boundary condition at  $R = d$  [Eq. (2)] is given by Carslaw and Jaeger,<sup>4</sup>

$$P(\mathbf{R}_0, \mathbf{R}, t) = \frac{1}{\sqrt{RR_0} 4\pi} \sum_0^\infty (2l+1) P_l[\cos \theta(t)] \times \int_0^\infty d\kappa \kappa e^{-D\kappa^2 t} F_{l+1/2}(\kappa R) F_{l+1/2}(\kappa R_0), \quad (4)$$

$$F_{l+1/2}(\kappa R) = \left( \frac{2\kappa R}{\pi} \right)^{1/2} \frac{[j_l(\kappa R) y'_l(\kappa d) - y_l(\kappa R) j'_l(\kappa d)]}{\{ [j'_l(\kappa d)]^2 + [y'_l(\kappa d)]^2 \}^{1/2}}, \quad (5)$$

where  $j_l(x)$  and  $y_l(x)$  are the  $l$ th order spherical Bessel functions of the first and second kind, respectively,  $j'_l(x)$  and  $y'_l(x)$  are their derivatives, and  $D$  is relative diffusion coefficient. Substituting  $P(\mathbf{R}_0, \mathbf{R}, t)$  of Eq. (4) into Eq. (1) and performing calculations similar to those in Refs. 1 and 2 one can obtain, after some algebra,

$$C_{tr}^{(l)}(t) \approx \int_0^\infty d\kappa \kappa e^{-D\kappa^2 t} \times \left[ \int_d^\infty dR F_{l+3/2}(\kappa R) R^{-(l+1/2)} \right]^2. \quad (6)$$

The case of Eq. (6) with  $l = 1$  (dipolar interaction) has been discussed in detail by Hwang and Freed,<sup>2</sup> and in a different form by Ayant *et al.*,<sup>3</sup> in the context of NMR spectroscopy. The molecular dynamics simulation of  $C_{tr}^{(l)}(t)$  in liquids are available for  $N_2$ <sup>5</sup> and  $CS_2$ .<sup>6</sup> The dominant induction mechanism is quadrupolar both in  $N_2$  and  $CS_2$ , so  $l = 2$  is involved.

The correlation function  $\hat{C}_{tr}^{(2)}(t) = C_{tr}^{(2)}(t)/C_{tr}^{(2)}(0)$  for  $N_2$  with  $D = 4.5 \cdot 10^{-5} \text{ m}^2/\text{s}$ ,  $d = 3.315 \text{ \AA}$  and for  $CS_2$  with  $D = 8.0 \cdot 10^{-3} \text{ cm}^2/\text{s}$ ,  $d = 5.5 \text{ \AA}$  obtained both from molecular dynamics simulation and the present model are given in Figs. 1 and 2, respectively. Overall, the agreement is good, given the simplicity of the discussed model. Note, that including the reflecting wall boundary condition at  $R = d$  corrects the short-time behavior of the previously calculated functions  $\hat{C}_{tr}^{(2)}(t)$ .<sup>1</sup> It would be interesting to perform more MD simulations in order to check the validity of and eventually to improve the discussed model.

Further improvement on other molecular liquids

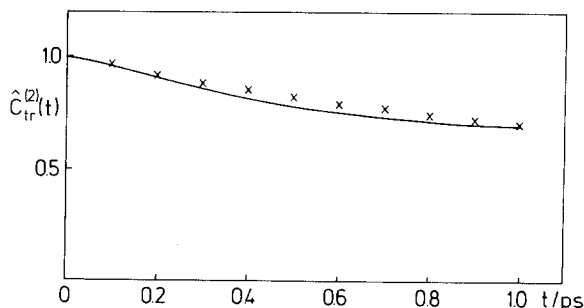


FIG. 1. Comparison of the simulated (---; Ref. 5) and theoretical [ $\times$ , Eq. (5)] translational correlation function  $C_{tr}^{(2)}(t)$  for liquid nitrogen at  $T = 75 \text{ K}$  and density  $\rho_0 = 0.814 \text{ g/cm}^3$ .

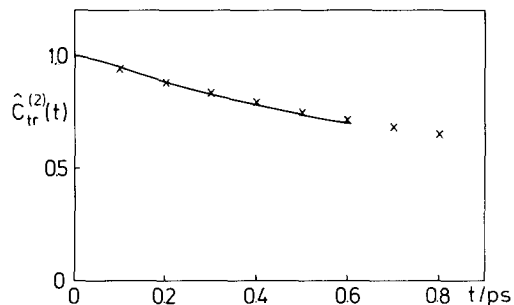


FIG. 2. Comparison of the simulated (---; Ref. 6) and theoretical translational correlation function  $C_{tr}^{(2)}(t)$  for liquid  $CS_2$  at  $T = 298$  K and  $\rho_0 = 1.29$  g/cm<sup>3</sup>.

should include the mean force term in the diffusion equation (3), as suggested in Refs. 2, 7, and 8.

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<sup>2</sup>L. Hwang and J. Freed, *J. Chem. Phys.* **63**, 118 (1975).

<sup>3</sup>Y. Ayant, E. Belorizky, J. Alizon, and J. Gallice, *J. Phys.* **36**, 991 (1975).

<sup>4</sup>H. S. Carslaw and J. VC. Jaeger, *Conduction of Heat in Solids*, 2nd ed. (Oxford University, Oxford, 1959), p. 382. For the definition of  $\kappa$  see Ref. 1.

<sup>5</sup>W. A. Steele, *Mol. Phys.* **56**, 415 (1985).

<sup>6</sup>J. Samios, U. Mittag, and T. Dorf Müller, *Mol. Phys.* **59**, 65 (1986).

<sup>7</sup>L. P. Hwang and J. Freed, *J. Chem. Phys.* **63**, 4017 (1975).

<sup>8</sup>M. Moraldi and R. Vallauri, *Chem. Phys. Lett.* **114**, 82 (1984).