Translation–Rotation of Rough Spheres

Far Infrared–Microwave Estimation of the Binary Collision Approximation

BY MYRON W. EVANS*

Edward Davies Chemical Laboratories, University College of Wales,
Aberystwyth SY33 INE

AND GRAHAM J. DAVIES

Post Office Telecommunications H.Q., Martlesham Heath, Ipswich IP9 7RE

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The rotation–translation of rough spheres, developed recently by Berne and Montgomery, is considered in relation to microwave and far infrared data on 2-chloro-2-nitropropane in the liquid phase. When there is no momentum transfer between the incoming radiation and the molecules in the liquid, the B-M model reduces to rotational J-diffusion. This fails to match the characteristic frequency shift between gas and liquid of the far infrared power absorption peak. By considering the coupled Langevin equations for translation and rotation *in the diffusion limit* it becomes clear that for mixed translation/rotation it is not possible for *any* type of autocorrelation function associated with observable power spectra to remain a single exponential. The results of Berne and Montgomery's calculations on rough sphere fluids should therefore be regarded with caution when dealing with liquids made up of dipolar molecules.

In this paper we discuss the role of translation–rotation coupling in determining the dynamics of a rough sphere fluid.[1-3] We compare the results for the orientational autocorrelation function with the dielectric–far-infrared spectrum of a dipolar molecular (pseudo-spherical) fluid. This is a subtle topic in which there has been a resurgence of interest since the discovery by Rytov of the zero frequency splitting in the depolarised Rayleigh band. This is due to the interaction between the second rank orientational density and the velocity field. Clearly there should be observable the same kind of phenomenon in the dielectric–far-infrared region, *i.e.*, a coupling between the first rank orientational density and the velocity field. The far-infrared–dielectric spectrum therefore cannot be treated in terms merely of rotational molecular motion, be this collective or otherwise. The rough sphere fluid is one where the auto-correlation functions are calculable analytically.

In their recent treatment of rototranslations in rough spheres Berne and Montgomery [2] used the exponential diffusion approximation so that the calculated power absorption spectrum remains at a physically unrealistic plateau level to infinite frequency. The spectral moments are all infinite because of the physically unrealistic linear t term in the Taylor expansion of the autocorrelation function. We modify the theory to define the first spectral moment thus enabling us to compare the theoretical results with those from the far infrared and dielectric data available for 2-chloro-2-nitropropane. The basic inability of the J-diffusion mechanism used by Berne and Montgomery to follow the large shift away from the gas phase value of the far infrared peak frequency of the liquid then becomes apparent.

THEORETICAL SYNOPSIS

The relevant rototranslational autocorrelation function for the description of spectral distributions of Rayleigh light scattering, far infrared absorption and neutron scattering from spheres is:

$$C_l(\boldsymbol{q}, t) = \langle P_l[\boldsymbol{u}(t)\cdot\boldsymbol{u}(0)]\exp[i\boldsymbol{q}\cdot\Delta\boldsymbol{r}(t)]\rangle \tag{1}$$

where P_l is the Legendre polynomial of order l, $\boldsymbol{u}$ is a unit vector embedded in the sphere along the dipole axis, $\Delta\boldsymbol{r}(t) = \boldsymbol{r}(t)-\boldsymbol{r}(0)$ is the displacement of a molecule in time t and $\boldsymbol{q}$ is the wave-vector. If rotation and translation have no mutual influence then eqn (1) factorises:

$$\begin{aligned} C_l^{(\mathrm{unc})}(Q, t) &= C_l(O, t)C_0(Q, t) \qquad (2)\\ &\equiv \langle P_l[\boldsymbol{u}(t)\cdot\boldsymbol{u}(0)]\rangle\langle\exp[i\boldsymbol{q}\cdot\Delta\boldsymbol{r}(t)]\rangle \end{aligned}$$

In the $\boldsymbol{q}\to\boldsymbol{O}$ limit (dielectric spectroscopy) both equations reduce to

$$C_l(\boldsymbol{q}, t) = \langle P_l[\boldsymbol{u}(t)\cdot\boldsymbol{u}(0)]\rangle.$$

Here, $\boldsymbol{Q}$ is $\boldsymbol{q}$ normalised so as to be dimensionless. This does *not* imply that translation/rotation interaction is no longer important since $P_l\langle[\boldsymbol{u}(t)\cdot\boldsymbol{u}(0)\rangle$ may still be directly influenced by translational, rototranslational, and transrotational factors. For example, if we write down the Langevin equations for spherical top rotation/translation diffusion:

$$m\dot{\boldsymbol{v}} = -m\gamma_t\boldsymbol{v}-\gamma_{tr}I\boldsymbol{\omega}+\boldsymbol{F} \tag{3}$$

$$I\dot{\boldsymbol{\omega}} = -I\gamma_r\boldsymbol{\omega}-\gamma_{rt}m\boldsymbol{v}+\boldsymbol{T} \tag{4}$$

both $\langle\boldsymbol{v}(t)\cdot\boldsymbol{v}(0)\rangle$ and $\langle\boldsymbol{\omega}(t)\cdot\boldsymbol{\omega}(0)\rangle$ are defined in terms of *four* friction coefficients $\gamma_t, \gamma_r, \gamma_{tr}, \gamma_{rt}$ and therefore so is the autocorrelation function of orientation $\langle\boldsymbol{u}(t)\cdot\boldsymbol{u}(0)\rangle$. It is fundamentally important that the far infrared Poley absorption may then be defined, even in the diffusion limit, merely by considering the mixing of rotation and translation. This will be the subject of future papers. Furthermore by considering the full translation/rotation dynamics it is no longer possible for the velocity or angular velocity correlation functions to be purely exponential in nature, so that the diffusion model assumed by Berne and Montgomery is not strictly valid.

The fundamental equation of the rough sphere rototranslation is:

$$\tilde{C}_l(Q, p) = \frac{\tilde{C}_l^{(0)}[Q, p+\beta_l(Q)]}{1-\beta(Q)\tilde{C}_l^{(0)}[Q, p+\beta_l(Q)]} \tag{5}$$

Here Q is the wavevector, p is the dimensionless Laplace variable, $\beta_l(Q)$ is the dimensionless characteristic frequency of the first memory function of $C_l(Q, t)$, and $C_l^{(0)}$ is the autocorrelation function of an ensemble of non-interacting rough spheres freely rotating and translating. To second order this is defined as:

$$\tilde{C}_l^{(0)}[Q, p+\beta_l(Q)] = \frac{1}{p+\beta_l(Q)}-\frac{l(l+1)+Q^2}{[p+\beta_l(Q)]^3} \tag{6}$$

so that we have

$$\tilde{C}_l(Q, p) = \frac{p^2+2\beta_l(Q)p+(\beta_l^2(Q)-l(l+1)-Q^2)}{p^3+2\beta_l(Q)p^2+\beta_l^2(Q)p+\beta_l(Q)[Q^2+l(l+1)]}. \tag{7}$$

The microwave–far-infrared spectrum is recovered by setting $\boldsymbol{Q} \rightarrow \boldsymbol{O}$ in eqn (4) replacing p by $-\mathrm{i}\omega$:

$$\varepsilon'' = (\varepsilon_0-\varepsilon_\omega)\omega \,\mathrm{Re}\,[\tilde{C}_1(\boldsymbol{O}, \mathrm{i}\omega)] \tag{8}$$

$$\varepsilon' = \varepsilon_0-(\varepsilon_0-\varepsilon_\omega)\omega \,\mathrm{Im}\,[\tilde{C}_1(\boldsymbol{O}, \mathrm{i}\omega)] \tag{9}$$

$$\alpha(\bar{\nu}) = 2\sqrt{2}\pi\varepsilon''\bar{\nu}/[(\varepsilon''^2+\varepsilon'^2)^{\frac{1}{2}}+\varepsilon']^{\frac{1}{2}} \tag{10}$$

where $\alpha(\bar{\nu})$ is the power absorption coefficient, ε'' is the loss and ε' is the dispersion.

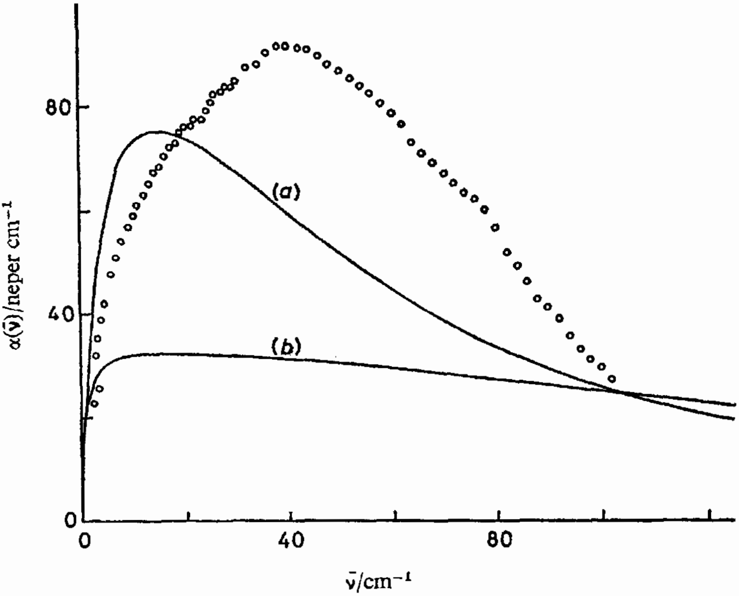

FIG. 1.—Plot of $\alpha(\bar{\nu})$, the experimental absorption coefficient (in neper cm^{-1}) against wavenumber ($\bar{\nu}$) for the pseudo spherical molecule 2-chloro-2-nitropropane in the liquid at 296 K. (—) (*a*) Least mean squares best fit of eqn (10) to the experimental data. The optimum value of β_ω is 11.7 in reduced units. (—) (*b*) Curve obtained by a least mean squares best fit of eqn (8) to the experimental loss data of Clemett and Davies[4] (see fig. 2). The optimum value of β_ω is now 27.5 in reduced units.

RESULTS AND DISCUSSION

Microwave and far infrared data for liquid 2-chloro-2-nitropropane have been collected by Clemmett and Davies[4] and by Davies.[5] The least mean squares fit of eqn (8) and (10) to the loss and power absorption is shown in fig. 1 and 2. The return to high frequency spectral transparency is too slow compared with that of the experimental absorption, the asymptotic high frequency fall off being as ω^{-2}. The optimised value of β_1 is 27.5 units. Alternatively the $\varepsilon''(\omega)$ data may be least mean squares fitted and the loss curve evaluated. The result is of poor quality, and this time an optimised β_1 of 11.7 in reduced units is needed for best fit. Naturally the values of β_1 estimated from both methods ought to be the same for internal consistency. The representation of high frequency motions by a rough sphere roto-translation is therefore not satisfactory, and presumably would not be so for the description of neutron scattering from molecules which are both translating and rotating. The ratio $C_l(Q,t)/C_1^{(\mathrm{unc.})}(Q,t)$ from eqn (5) is a very sensitive function of the roughness parameter λ and β_ω, much too much so to be realistic (table 1). To summarise: (1) In the $Q \to O$ limit, eqn (5) reduces to that for *J*-diffusion. This fails to match the characteristic frequency shift between gas and liquid of the far-infrared power absorption peak frequency. (2) A full treatment of rotation/translation with Langevin equations (representing the diffusion limit) reveals that an exponential decay as used by Berne and Montgomery is no longer possible for any type

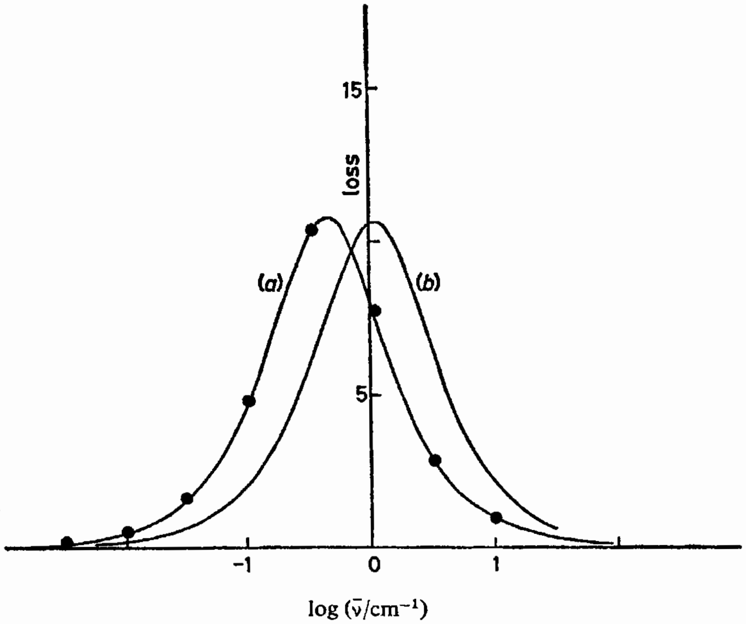

FIG. 2.—Some points taken at regular intervals along the experimental loss curve [4] of liquid 2-chloro-2-nitropropane. (—) (*a*) Least mean square best fit of eqn (8) to these points. This curve extrapolated into the far-infrared is the one labelled (*b*) in fig. (1). (—) (*b*) Curve (*a*) of fig. 1 converted into loss and extrapolated into the microwave frequency region. The experimental loss data are poorly reproduced.

TABLE 1.—RATIO (x) OF MIXED [$C_1(Q, t)$] TO UNMIXED [$C_0($, $Qt)(C_1(O, t)$] AUTOCORRELATION FUNCTIONS FOR THE ROUGH SPHERE FLUID [EQN (5)]. $\kappa = 0.4$

$t^* = 50.0^a$	λ^b	$\beta_\omega{}^c$	x
	0.1	50.0	4.5
	0.1	20.0	42.0
	0.1	10.0	3000.0
	0.5	50.0	1.8
	0.5	20.0	4.5
	0.5	5.0	6000.0
	1.0	50.0	1.2
	1.0	20.0	1.6
	1.0	5.0	5.2

[a] t^* = reduced time units. [b] λ = roughness parameter. [c] κ = mass distribution parameter.

of autocorrelation function associated with the observable power spectra. (3) In the so-called decoupled limit ($Q \rightarrow O$) the orientational autocorrelation functions P_l should still be calculated using both rotational and translational equations such as the Mori-generalised Langevin formalism.

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