Diffusive motion and structural correlations in condensed disordered systems

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Abstract. A model of condensed disordered systems, based on theories of random spatial and temporal processes for local atomic structures, is used to derive analytic expressions for the contribution of the diffusive atomic motion to the van Hove time correlation function $G_D(r, t)$ and its spectral representations. The spatial random process determines the static atomic correlations in space whereas the temporal diffusion process contributes to the central (Rayleigh) peak of the dynamic scattering function $S_D(k, \omega)$. The relaxation time of the intermediate scattering function $F_D(k, t)$ exhibits the known phenomenon of slowing down in the neighbourhood of the first peak of $S(k)$, but in the limit of small k it remains finite, contrary to the infinite slowing down of heat dissipation predicted by linearized hydrodynamics.

1. Introduction

The collective modes predicted by linearized hydrodynamics have served as a useful reference state and guide in modelling the shape of the dynamic scattering function (structure factor) $S(k, \omega)$ of liquids as a function of frequency ω up to the region of large wavevectors k (wavelengths of the order of interatomic distances), even when no distinct side peaks or shoulders typical of sound modes could be observed [1–3]. In the notation of de Schepper and co-workers [1,3] the intermediate scattering function has the following form:

$$F(k, t) = A_h(k) \exp[-z_h(k)t] + 2A_s(k) \exp[-z_s(k)t] \cos[\omega_s(k)t] \tag{1}$$

where $A_h(k)$ and $A_s(k)$ are the weights of a heat mode and of two sound modes, respectively, and $z_h(k)$ and $z_s(k)$ are the decay rates of a heat mode and of two sound modes, respectively. In the limit of small k, one has according to linearized hydrodynamics

$$z_h(k) = D_T k^2 \qquad z_s(k) = \Gamma k^2 \qquad \omega_s(k) = c_s k \tag{2}$$

where D_T is the thermal diffusivity, Γ the sound attenuation coefficient and c_s the velocity of sound. Nevertheless, even for large k-values, equation (1) can still be fitted well to empirical scattering or computer simulation data, using now $A_j(k)$, $z_j(k)$, $j \equiv h, s$, and ω_s as adjustable parameters for each k separately. The collection of such parameters thus constitutes their empirical k-dependence.

However, in linear hydrodynamics the collective modes are related only to the ordered motion of the atoms in the liquid. The dissipative processes considered are

concerned only with transformation of internal energy into heat by large-scale density fluctuations and ignore the diffusive motion of the atoms which is responsible for the time evolution of the microscopic spatial correlations between pairs of atoms. This is manifest not only in the large-k range but also in the limit of small k where the width of the central (Rayleigh) peak of $S(k, \omega)$, which according to (2) must shrink to zero, evidently remains finite [4].

In the following we offer an alternative approach to the modelling of the pair correlation $G(r, t)$ and its spectral representations $F(k, t)$ and $S(k, \omega)$, which uses as a reference state the static correlations and provides a direct connection to their time evolution. This is done by applying the structural diffusion model (SDM), based on the concept of random spatial and temporal processes and their simplest formulation in terms of diffusion-type processes in 'structure space', evolving both in space and in time. At present we restrict the modelling to the central (Rayleigh) peak contribution to $S(k, \omega)$, leaving the treatment of the acoustic modes (Brillouin peaks) to a separate publication.

In section 2 we present the model in some detail and examine its implications for the computation of static and dynamic correlation functions. In section 3 we derive an analytic expression for $F(k, t)$, which is a functional of the characteristics of the static structure and of a temporal diffusion parameter. We illustrate the usefulness of our approach by explicit computations for an amorphous metal (supercooled liquid Al). The relaxation time of $F(k, t)$, computed in section 4, exhibits the well known slowing down [5] when k is close to the main peak of the static structure factor $S(k)$. (A remnant of this behaviour is also observed for the second peak.) For $k \to 0$ the relaxation time remains finite. We give a brief summary and discussion of further implications of our model.

2. Structural and temporal diffusion

The SDM was originally devised for static correlations. It is based on associating the spatial atomic configurations with a reference ordered structure, specified by a lattice L. It is assumed that the local atomic configuration, i.e. the relative position of small groups of neighbouring atoms, can always be well approximated by a suitable domain in the ordered structure L. Furthermore, spatial disorder is introduced as a random relative displacement of the locally observed lattice structures at different points in space [6]. The random process is taken to be a spatially (radially) evolving diffusion process in 'structure space'. The resulting expression for the radial distribution function $g(r)$ has the form of a theta-type infinite series:

$$\rho g(r) \equiv G(r) = \sum_{\nu} G_{\nu}(r) \tag{3}$$

where

$$G_{\nu}(r) = \rho C_{\nu} \exp(-W b_{\nu}^{2})[\sin(b_{\nu} r)]/b_{\nu} r. \tag{3'}$$

Here (3) is a sum over all points (shells) of the reciprocal lattice $L^{*} = \{b_{\nu}\}$ in 'structure space', ρ is the density and C_{ν} is a 'unit-cell structure factor' given by $C_{\nu} = C(b_{\nu})$, where

$$C(k) = \left| \frac{1}{n_{\nu}} \sum_{\sigma} \exp(i k \cdot a_{\sigma}) \right|^{2} \tag{4}$$

with the sum in (4) extending over the n_v points in the unit cell. $W = W(r) > 0$ serves as a 'width function' which is a measure of the decay of coherence between local structures at two localities separated by a distance r. By the SDM it follows that $W(r)$ is a monotonic increasing function of r satisfying

$$W(r) \simeq Dr \qquad r \to \infty \qquad W'(r) \to 0 \qquad r \to 0 \tag{5}$$

with D a characteristic coefficient of the 'structural diffusion' process.

An alternative representation of $G(r)$ obtained by applying the Poisson sum formula to (3) exhibits the role of W as a dispersion function. In this representation, $G(r)$ is given as a sum over all points of the direct lattice $L = \{a_\mu\}$ in structure space:

$$G(r) = \sum_\mu G_\mu(r) \tag{6}$$

where, in the case of a simple lattice in three-dimensional space, when $C_\nu = 1$, we have

$$G_\mu(r) = [1/(4\pi W)^{3/2}]\langle \exp(-|a_\mu - r|^2/4W)\rangle_o \tag{6'}$$

with the o-subscripted angular brackets denoting an average over all orientations of the position vector r or, alternatively, over all orientations of the lattice L. Thus (6) presents $G(r)$ as a sum of nearly Gaussian-shaped functions each centred at some $r \simeq a_\mu$ and having approximately a dispersion $W = W(a_\mu)$. The two representations (3) and (6) stress different aspects of the function $G(r)$. Series (6), which converges rapidly for small r, exhibits mainly the spatial arrangement of neighbouring atoms, whereas (3), which converges rapidly for large r, exhibits the extent of spatial coherence between local structures at medium and large separation.

The SDM has been shown to be a useful tool for modelling static pair correlations of liquids and amorphous solids (see references in [7]). However, as we wish to extend the model to dynamic correlations, it has been suggested previously [8] that van Hove's time correlation function $G(r, t)$, which is an extension of $G(r)$ to $t > 0$, can be obtained by adding a temporal diffusion to the structural diffusion process. On the assumption that the two processes are independent, this amounts to replacing $W(r)$ by

$$W = W(r, t) = W_1(r) + W_0(t) \simeq Dr + D_0 t \qquad r, t \to \infty \tag{7}$$

in (3') and (6'). Here D_0 has the dimensions of a diffusion coefficient of a usual time-evolving diffusion process while $D_0/D = c_0$ has the dimensions of a velocity. Either D_0 or c_0 can serve as an additional independent parameter required in modelling the time correlation function. Clearly, the resulting correlation function, which we denote by $G_D(r, t)$, can represent only a diffusive and not an ordered motion of the atoms.

Applying (7) to (3') and (3), we have immediately

$$G_D(r, t) = \sum_\nu f_\nu(t) G_\nu(r) \tag{8}$$

where

$$f_\nu(t) = \exp[-W_0(t)b_\nu^2]. \tag{8'}$$

Since $f_\nu(0) = 1$ for all ν, we have $G_D(r,0) = G(r)$. Adopting the asymptotic form

$$W_0(t) = D_0 t \tag{9}$$

as valid for all $t > 0$, equation (8) enables an explicit evaluation of $G_D(r,t)$ to be made from available data on the static structure.

The corresponding dynamic scattering function $S_D(k,\omega)$ consists of a single central peak which does not include contributions of the elastic motion (hydrodynamic modes) of the fluid. Clearly, this motion exists in all condensed systems independently of any dissipative processes. Its contribution to $G(r,t)$ can be obtained by considering the vibrational motion in a solid and using the SDM assumption of a reference ordered state to extend the results for solids to condensed systems in general. A further extension of the SDM is also required to include a random process for the local ordered motion of the atoms [9]. Details of this treatment will be presented in a separate publication. Here we only note that by linearized hydrodynamics the contribution of the hydrodynamic modes to the central peak of $S(k,\omega)$ is small for liquid metals, where $C_p/C_v \simeq 1$. Thus, for such liquids the main contribution to the central (Rayleigh) peak of $S(k,\omega)$ should come from $S_D(k,\omega)$.

3. Evaluation of static and dynamic scattering functions

The intermediate scattering function is related to $G_D(r,t)$ by

$$F_D(k,t) = \int [G_D(r,t) - \rho] \exp(i\mathbf{k} \cdot \mathbf{r}) \, \mathrm{d}^3 r. \tag{10}$$

Substituting (8) into (10), we obtain the series representation

$$F_D(k,t) = {\sum_\nu}' f_\nu(t) S_\nu(k) \tag{11}$$

where

$$S_\nu(k) = \int G_\nu(r) \exp(i\mathbf{k} \cdot \mathbf{r}) \, \mathrm{d}^3 r \tag{11'}$$

and the primed summation indicates omission of the $\nu = 0$ term. Again, note that $F_D(k,0) = S(k)$. The dynamic scattering function has similarly a series representation

$$S_D(k,\omega) = {\sum_\nu}' \tilde{f}_\nu(\omega) S_\nu(k) \tag{12}$$

where

$$\tilde{f}_\nu(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} f_\nu(t) \exp(-i\omega t) \, \mathrm{d}t. \tag{13}$$

For the purpose of an accurate numerical evaluation of $F_D(k,t)$ as a function of k, (10) can be used provided the contribution from self-correlations, i.e. the contribution from $G(r)$ in the neighbourhood of $r = 0$, is properly taken into account. Since in the numerical integration of (10) we use series (6) (with (6') or its

extension to $t > 0$) to evaluate $G(r,t)$ at small r-values, we see that the dominant contribution in the neighbourhood of $r = 0$ comes from the $\mu = 0$ term of (6):

$$G_0(r) = [1/(4\pi W)^{3/2}] \exp(-r^2/4W).\tag{14}$$

In fact, since for the condensed systems considered we usually find that $D/a \leqslant 0.02$ (where a is the nearest-neighbour distance), it follows that $G_0(r)$ is a sharply peaked, approximately Gaussian function at around $r = 0$ with a width much less than a. Thus, $G_0(r)$ can be viewed as effectively representing a $\delta(r)$ function which is the correct contribution of the self-correlations to $G(r)$. Furthermore, for $t > 0$, where $W_1(r) \ll W_0(t) = D_0 t$ in the neighbourhood of $r = 0$, one can replace $W = W(r,t)$ in the $\mu = 0$ term in (14) by $W_0(t)$ and obtain for $G_0(r,t)$ an exact Gaussian in space. This term will then contribute to the integral in (10) a term $\exp(-k^2 D_0 t)$, which conforms to the correct asymptotic behaviour of $F(k,t)$ at $k \to \infty$ for all $t \geqslant 0$. As an example, figure 1(a) shows $F_D(k,0) = S(k)$ evaluated numerically from (10), using the $g(r)$ of liquid Al obtained from (3) or (6) with optimal parameters ($L \equiv$ a distorted FCC unit cell: $\alpha = \beta = \pi/3$, $\gamma = 67.7° \simeq \frac{5}{13}\pi$; $D/a = 0.008$ for $T = 930$ K) found by Lopez and Silbert [10] when fitting the Monte Carlo simulation data of Smolander [11] to the SDM.
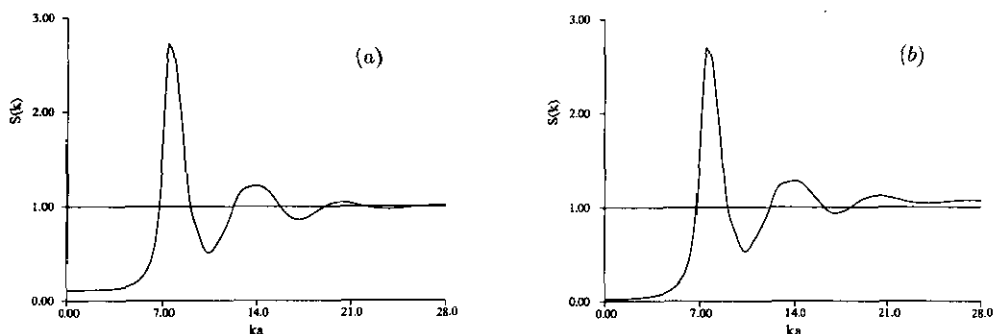

Figure 1. $S(k)$ calculated from (a) equation (10) and (b) equations (11) and (16).

4. Time dependence of $F_D(k,t)$

Using (10) to evaluate $F_D(k,t)$ as a function of t, we have observed a persistent unphysical behaviour violating the condition $|F_D(k,t)| < S(k)$ for short time intervals, in particular in the small-k range where $S(k) \ll 1$. We attribute this to an unresolved sensitivity to errors in the numerical integration. Consequently we have sought to devise a function $W(r) = W_1(r)$ which enables an analytic evaluation of (11′) to be made. We made use of a form previously introduced by Egelstaff and Schofield [12] and Schofield [13], namely

$$W(r) = D\left(\sqrt{r^2 + r_0^2} - r_0\right).\tag{15}$$

Substituting (15) into (3′) and applying to (11′), we obtain

$$S_\nu(k) = 2\pi r_0^2 D b_\nu \exp(D r_0 b_\nu^2)(1/k)[K_1(X_-)/X_- - K_1(X_+)/X_+]\tag{16}$$

where $K_1(X)$ is a modified Bessel function of the second kind and

$$X_{\pm} = X(\pm k) = r_0\sqrt{(Db_\nu^2)^2 + (b_\nu \pm k)^2}. \tag{17}$$

The resulting $S(k)$, obtained by substituting (16) into (11), with $t = 0$, is represented in figure 1(b). Comparing with figure 1(a), we see that the analytic expression (11) obtained gives an accurate representation of $F_D(k,t)$ for $k \geqslant 0$ up to and including the first peaks of $S(k)$ and that only for $ka \geqslant 15$ does it show significant deviation from the correct asymptotic form. Possibly the deviation is due to the slower convergence of the series for larger k but it might also arise from an inconsistency of non-integrability of $G(r)$ at around $r = 0$, due to the r^{-3} divergence of $G_0(r)$ produced when (15) is substituted into (14). This divergence can be eliminated by adding a small correction $\epsilon \ll Dr_0$ to $W_1(r)$, i.e. making the replacement $W_1 \to W_1 + \epsilon$. This amounts to replacing the exponent in (16) by $(Dr_0 - \epsilon)b_\nu^2$, which almost eliminates the deviation from the correct asymptotic behaviour, observed in figure 1(b), within the range $ka \leqslant 30$. Necessarily a suitable choice of ϵ depends on D and r_0.

Returning to the t-dependence of $F_D(k,t)$, we look for a unified time scaling over a large range of k-values. Two different definitions of a characteristic relaxation time have been considered: (1) an average lifetime given by

$$\tau = \tau(k) = \left(\int_0^\infty t F_D(k,t)\,\mathrm{d}t\right) \Big/ \left(\int_0^\infty F_D(k,t)\,\mathrm{d}t\right) \tag{18}$$

and (2) a reciprocal initial rate of decay given by

$$\tau_0 = \tau_0(k) = -([\mathrm{d}\{\log[F_D(k,t)]\}/\mathrm{d}t]|_{t=0})^{-1}. \tag{19}$$

Writing (11) in the form $F_D(k,t) = \sum_\nu S_\nu \exp(-\lambda_\nu t)$, $\lambda_\nu = D_0 b_\nu^2$, we have

$$\tau = \sum_\nu \frac{S_\nu}{\lambda_\nu^2} \Big/ \sum_\nu \frac{S_\nu}{\lambda_\nu} = \frac{1}{D_0} \sum_\nu \frac{S_\nu}{b_\nu^4} \Big/ \sum_\nu \frac{S_\nu}{b_\nu^2}$$

$$\tau_0 = \sum_\nu S_\nu \Big/ \sum_\nu \lambda_\nu S_\nu = \frac{1}{D_0} \sum_\nu S_\nu \Big/ \sum_\nu b_\nu^2 S_\nu. \tag{20}$$

We have found $\tau(k)$ preferable as a scaling parameter for the t-dependence of $F_D(k,t)$ and have used it in a common plot of this function for several different k-values in figure 2. Both $\tau(k)$ and $\tau_0(k)$ (figure 3) exhibit two characteristic features of the relaxation time of $F_D(k,t)$: it remains finite for small k and it has a maximum in the neighbourhood of the first peak of $S(k)(ka \simeq 7.3)$, the latter being in conformity with the phenomenon of de Gennes narrowing in $S(k,\omega)$.

In the foregoing calculations, all distances are given in units of a (the nearest-neighbour distance), and time intervals are given in units of a^2/D_0. D_0 is the characteristic parameter of a random process describing the slow diffusive change in the relative position of a group of neighbouring atoms. There is no doubt that D_0 is related in some way to the diffusive process of a single particle but it cannot be identified with the single-particle diffusion coefficient. The value of D_0 can be found directly from empirical $S(k,\omega)$ data when $S(k,\omega) \simeq S_D(k,\omega)$.
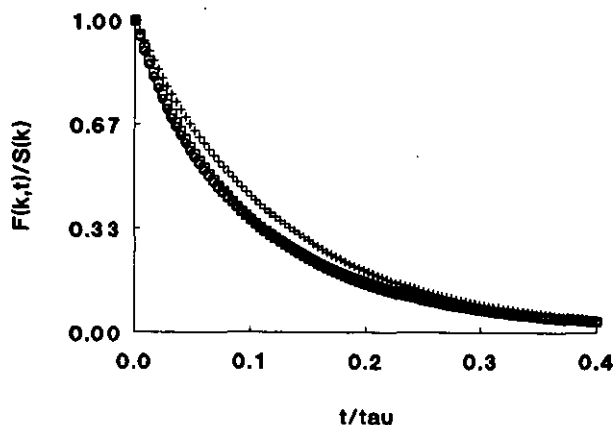
Figure 2. $F_D(k, t)/S(k)$ as a function of $t/\tau(k)$ for ka-values of 0.05 (O), 1 (◊), 7.3 (+) and 10 (×).
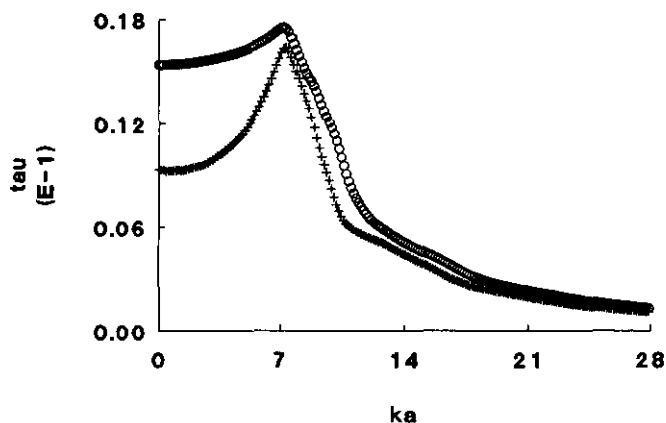

Figure 3. Relaxation times $\tau_0(k)$ (+) and $\tau(k)$ (O) of $F_D(k, t)$, defined by equations (18)–(20).

5. Concluding remarks

The SDM has been designed to answer the following two questions.

(1) How are neighbouring atoms arranged in space?
(2) How does this arrangement vary with position in space and in time?

By relating the local arrangement of atoms to a reference lattice L it is possible to describe the disorder in the system as a kind of mismatch between local arrangements at different localities, and hence to give a formally and computationally compact answer to both questions.

Clearly, an optimal L cannot be strictly unique since disorder introduces an element of randomness into the local arrangement of atoms. Because of this randomness, one can choose for L increasingly complex lattices possessing larger unit cells, together with smaller coefficients D, giving more accurate modelling of given $g(r)$ data. Indeed, in the limit of a large cell having the size of a typical volume used in computer simulations with periodic boundary conditions, putting $D = 0$ we can choose any representative configuration of the atoms as defining the unit cell of L. We denote any such macroscopically complex lattice by L_∞. In practice the usefulness of the SDM lies in finding a relatively simple L which can be visually grasped and yet reproduce with sufficient accuracy the $g(r)$ data. The details of the structure and its statistics are then hidden in the spatial random process, exhibited by $D > 0$.

One could compare the SDM with the recently developed reverse Monte Carlo (RMC) method of generating optimal macroscopic configurations (L_∞) of atoms fitting given experimental structural data [14, 15]. In a way the SDM can be viewed as an economical version of the RMC, replacing the modelling of $g(r)$ (or any other structural data) by $3N$ parameters—the position coordinates of a large number N of atoms, by a small number of parameters, of the order of $3n + 1$ (counting the parameter D as well), where n is the number of atoms in a unit cell of a relatively simple L.

To conclude, the SDM provides a modelling by analytic functions which are computationally convenient and can produce practical results for both the static and the time-dependent pair distributions as well as their spectral representations. As far as static atomic distributions are concerned, the model is expressed in sufficiently general terms to be amenable to systematic improvements. Moreover, new available models of ordered structures, such as incommensurate [16] or aperiodic [17] crystals and quasi-crystalline glasses [18], whose structure is derived from lattices in $m > 3$-dimensional space, or the notion of twinning planes at the unit-cell level [19], which gives a unified characterization of whole families of metallic and metal–metalloid glasses over a continuous range of variable concentrations [20], have provided us with a greatly enriched selection of possible, relatively simple local structures.

As far as the time evolution of such structures is concerned, the model is consistent with the view that a condensed system imposes strong constraints on possible trajectories of individual atoms and forces groups of neighbouring atoms to move collectively with only a slow diffusive change in their relative position [21], passing through a succession of local structures realized in an equilibrium configuration of atoms.

References

[1]   de Schepper J M, Verkerk P, van Well A A and de Graaf L A 1983 *Phys. Rev. Lett.* **50** 974
[2]   McGreevy R L and Mitchell E W J 1985 *Phys. Rev. Lett.* **55** 398
[3]   Cohen E G D and de Schepper I M 1990 *Nuovo Cimento* D **12** 521, and references therein
[4]   See, e.g., Berne B J and Pecora R 1976 *Dynamic Light Scattering* (New York: Wiley)
[5]   Hansen J P and McDonald I R 1986 *Theory of Simple Liquids* (New York: Academic)
[6]   Baer S 1977 *Physica* A **87** 569; 1978 *Physica* A **91** 603; 1979 *Chem. Phys.* **39** 159
[7]   Baer S 1990 *J. Phys.: Condens. Matter* **2** 9675
[8]   Baer S 1978 *Physica* A **94** 139
[9]   Baer S 1982 *J. Phys. C: Solid State Phys.* **15** 3683
[10]   Lopez J M and Silbert M 1989 *Solid State Commun.* **66** 585
[11]   Smolander K J 1985 *Phys. Scr.* **31** 427
[12]   Egelstaff P A and Schofield P 1962 *Nucl. Sci. Eng.* **12** 260
[13]   Schofield P 1962 *Fluctuation, Relaxation and Resonance in Magnetic Systems* ed D ter Haar (Edinburgh: Oliver & Boyd) p 207
[14]   McGreevy R L and Pusztai L 1988 *Mol. Simul.* **1** 359
[15]   McGreevy R L, Howe M A, Keen D A and Clausen K N 1990 *Neutron Scattering Data Analysis (Inst. Phys. Conf. Ser. 107)* (Bristol: Institute of Physics) p 165
[16]   Janner A and Janssen T 1980 *Acta Crystallogr.* A **36** 399, 408
       Janssen T 1986 *Acta Crystallogr.* A **42** 261
[17]   Nelson R D and Halperin B I 1985 *Science* **229** 233
[18]   Stephens P W and Goldman A I 1986 *Phys. Rev. Lett.* **56** 1168
[19]   Hyde B G, Andersson S, Bakker M, Plug C M and O'Keeffe M 1979 *Prog. Solid State Chem.* **12** 273
[20]   Dubois J M, Gaskell P H and Le Caër G 1985 *Proc. R. Soc.* A **402** 323
[21]   Murthy C S and Singer K 1987 *J. Phys. Chem.* **91** 21