

Structure and dynamics of a model glass: influence of long-range forces

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2000 J. Phys.: Condens. Matter 12 8777

(<http://iopscience.iop.org/0953-8984/12/41/303>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.221

The article was downloaded on 16/05/2010 at 06:52

Please note that [terms and conditions apply](#).

Structure and dynamics of a model glass: influence of long-range forces

P Jund, M Ravivomanantsoa and R Jullien

Laboratoire des Verres, Université Montpellier 2, Place E Bataillon, Case 069,
34095 Montpellier, France

Received 2 August 2000

Abstract. We vary the amplitude of the long-range Coulomb forces within a classical potential describing a model silica glass and study the consequences on the structure and dynamics of the glass, via molecular dynamics simulations. This model allows us to follow the variation of specific features such as the first sharp diffraction peak and the boson peak in a system going continuously from a fragile (no Coulomb forces) to a strong (with Coulomb forces) glass. In particular we show that the characteristic features of a strong glass (existence of medium-range order, bell-shaped ring size distribution, sharp boson peak) appear as soon as tetrahedral units are formed.

1. Introduction

The connection between the structure and the dynamics of a given system is of particular interest in glasses since the structural entities at the origin of some specific vibrational features like the boson peak (BP) are not yet well identified. For instance in silica, the archetype of network-forming glasses, the existence of the BP has been connected alternatively to the presence of SiO_4 tetrahedra [1], ‘domains’ [2] or voids [3]. In molecular dynamics (MD) simulations the most important ingredient is the force field used to mimic the interparticle interactions: the aim is to reproduce as closely as possible the experimental vibrational data and then, by looking at the atomic positions, to give an interpretation in terms of structure. In that sense the so-called ‘BKS’ potential [4] has been widely used to describe silica and the results obtained on the structure [5, 6], the dynamical [7] and the thermal properties [8] compare well with experiments. This pairwise classical potential is the combination of a short-range term and the long-range Coulomb interaction (CI) which is obviously the most important ingredient of the force field [9]. One remarkable property of this potential is that CI forces alone are sufficient to reproduce the tetrahedral covalent bonding network of the silica atoms without the addition of extra terms such as angular terms. Our idea in this paper is to vary the *amplitude* of the CI (this is not strictly equivalent to varying the range) in order to study the variation of the structure and the dynamics of what can be seen as a toy silica glass. With this procedure we can study the properties of a system going from a strong network glass (the silica glass described by the usual BKS potential) to a fragile two-component soft-sphere glass when the CI is turned off. The question we would like to address is: how do the structure and the dynamics change along this path? The aim is to study the connection between structural features like the first sharp diffraction peak (FSDP) or the existence of a tetrahedral network and the BP, this connection being the topic of contradictory interpretations in the literature [3, 10, 11].

2. Simulations

We performed molecular dynamics simulations for microcanonical systems containing 216 silicon and 432 oxygen atoms confined in a cubic box of edge length $L = 21.48 \text{ \AA}$, which corresponds to a mass density of $\approx 2.18 \text{ g cm}^{-3}$ very close to the experimental value of amorphous silica (2.2 g cm^{-3}). Periodic boundary conditions were used to limit surface effects. The particles interact via the BKS potential whose standard functional form is, for two particles i and j (which can be either Si or O),

$$U(r_{ij}) = \frac{q_i q_j e^2}{r_{ij}} + A_{ij} \exp(-B_{ij} r_{ij}) - \frac{C_{ij}}{r_{ij}^6} \quad (1)$$

where r_{ij} is the interparticle distance, e the charge of an electron and the parameters A_{ij} , B_{ij} and C_{ij} are fixed as follows: $A_{\text{SiO}} = 18\,003.7572$ and $A_{\text{OO}} = 1388.773 \text{ eV}$; $B_{\text{SiO}} = 4.873\,18$ and $B_{\text{OO}} = 2.76 \text{ \AA}^{-1}$; $C_{\text{SiO}} = 133.5381$ and $C_{\text{OO}} = 175.0 \text{ eV \AA}^6$. The partial charges used to compute the standard CI are given by $q_{\text{Si}} = 2.4$ and $q_{\text{O}} = -1.2$. This original form contains an unphysical divergence at very short distances which we have corrected by adding a short-range repulsive term ($\sim 1/r_{ij}^{40}$).

In order to vary the strength of the CI (which is calculated using the Ewald summation method) we simply multiply the partial charges by a parameter λ which is fixed at the beginning of each simulation:

$$q_i \longrightarrow \lambda q_i. \quad (2)$$

A simulation starts from a liquid configuration at 7000 K which is equilibrated during 50 000 time steps (35 ps). This system is then cooled to zero temperature at a quench rate of $2.3 \times 10^{14} \text{ K s}^{-1}$ which is obtained by removing the corresponding amount of energy from the total energy of the system at each iteration. The aim here is not to obtain fine details of the structure of real silica, which explains the use of a rather fast quenching rate compared to the rates that can nowadays be achieved. In any case computer quenches are still far away from those used in experiments. The quenched glass samples are finally relaxed in the microcanonical ensemble during 100 000 time steps (70 ps) after which the temperature has reached $\approx 2 \text{ K}$. We then average the structural information over the last 20 000 time steps to avoid transient configurations and we diagonalize the dynamical matrix corresponding to the final configuration to obtain the vibrational density of states.

This procedure has been repeated for eleven values of λ going from $\lambda = 0.1$ to $\lambda = 1.1$. The ideal ' $\lambda = 0$ ' system would consist of a soft-sphere-like arrangement for the oxygen atoms (similar to the systems we have studied earlier [12]) together with a random arrangement of the silicon atoms in the interstices of the oxygen structure. Because of the weak attractive O–O interaction present in the short-range part of the BKS potential, a small Coulomb interaction is necessary in order to stabilize this system: we found that a value of λ around 0.065 is sufficient which explains why we started our investigation at $\lambda = 0.1$. For this lowest λ -value we have checked on the radial pair distribution functions as well as on other structural characteristics that the structure was indeed very close to the ideal arrangement described above. On the other hand, strong values of λ lead to an artificial local densification of the samples which are non-homogeneous (holes start to form in the structure): for this reason the maximum value of λ is limited to 1.1. Of course the standard BKS results are recovered for $\lambda = 1$.

3. Results and discussion

In order to examine the 'quality' of the tetrahedral network we first study the tetrahedral O–Si–O angle θ which should be ideally equal to 109.47° in a perfect tetrahedron as well as

the Si–O–Si angle ϕ which measures the relative position and orientation of two neighbouring SiO_4 tetrahedra. To numerically determine the bond angle O–Si–O (Si–O–Si), we determine for each Si (O) atom the two nearest O (Si) atoms and we calculate the angle between the two corresponding segments Si–O (O–Si), the result being averaged over all the Si (O) atoms. The variation of θ and ϕ as a function of λ is plotted in figure 1. For $\lambda \leq 0.5$ it is obvious that the SiO_4 tetrahedra are not formed and that the network is not connected: the system remains analogous to a soft-sphere glass up to a threshold value of about 0.6. This can also be seen in the inset of figure 1 where the Si coordination number is plotted versus λ . This quantity has been calculated by the integration of the Si–O radial pair distribution functions up to a cut-off distance of 2.3 Å which corresponds to the first minimum for all the values of λ . This coordination number is greater than 5.5 for $\lambda = 0.1$ and is close to 4 for $\lambda \approx 0.6$ –0.7. Nevertheless for $\lambda \geq 0.5$ θ , the tetrahedral angle, θ , is almost constant and close to the angle in a perfect tetrahedron (indicated by the hollow arrow) while the angle ϕ , between the tetrahedra, is continuously increasing with λ . This indicates that the CI has a direct influence on the medium-range order and once the tetrahedra (the building blocks) are created, they form a connected network whose characteristics depend on the strength of the CI. In agreement with a previous study [6] the mean Si–O–Si angle is close to 150° for $\lambda = 1.0$ (standard BKS description) slightly larger than the experimental value of ϕ (144° [13] indicated by the filled arrow). The calculated value closest to 144° corresponds to $\lambda = 0.7$ but this value is not sufficient to recover other structural features of vitreous silica as we will see below; therefore this is not an argument to modify the standard BKS charges.

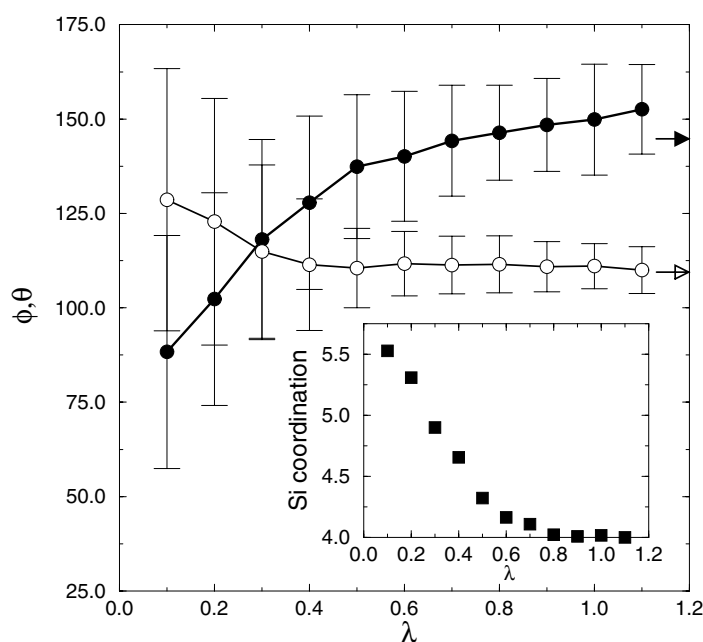


Figure 1. Variation of θ (O–Si–O angle: \circ) and ϕ (Si–O–Si angle: \bullet) as functions of λ . The hollow and filled arrows indicate the perfect tetrahedral value of θ and the experimental value of ϕ respectively. In inset the Si coordination number is shown as a function of λ .

A second way to analyse the connectivity of the network is to monitor the distribution of n -fold rings: an n -fold ring is defined as the shortest closed path of alternating Si–O bonds. Therefore an n -fold ring consists of $2n$ alternating Si–O bonds. The ring distribution as a

function of ring size is plotted in figure 2 for three values of λ : 0.2, 0.5 and 1. For $\lambda = 0.2$ the ring distribution is typical of an open structure with a majority of small rings (the estimated number of large rings should be taken with a pinch of salt since finite-size effects due to the limited length of the simulation box bias the results). For $\lambda = 0.5$ the distribution becomes peaked for rings with a specific size (5 and 6) which extend over distances greater than the inter-atomic distances: molecules are formed in the system. Finally for $\lambda = 1.0$ we find the usual distribution of rings, peaked at sixfold rings and almost symmetric around $n = 6$ [14], typical of the silica network.

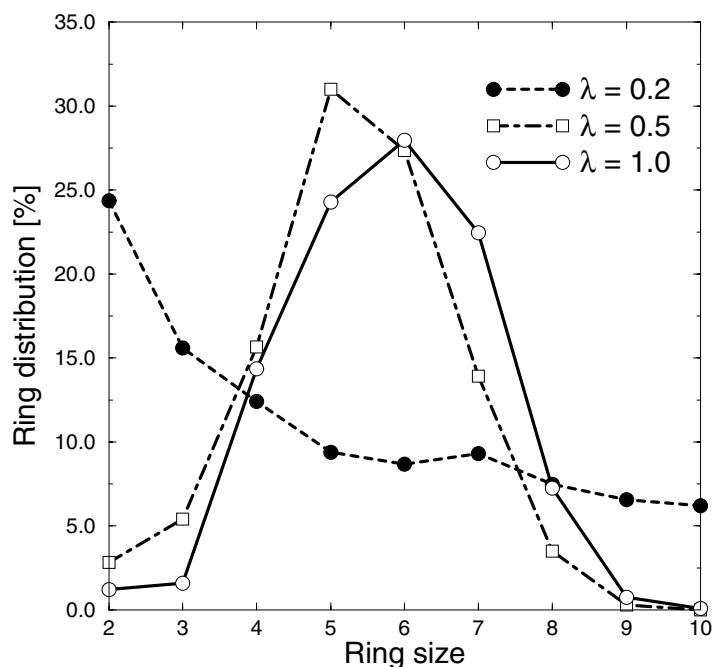


Figure 2. Ring size distributions for $\lambda = 0.2, 0.5$ and 1.

A complementary way of analysing the structure is to compute the static structure factor $S(q)$ as a function of λ . We used the standard way of calculating $S(q)$ [15] and focused our attention on a common feature in glasses: the first sharp diffraction peak. This pre-peak is related to medium-range structures in the glass and its origin has been the subject of vigorous debate over a number of years. In figure 3 we represent the amplitude of the FSDP as a function of λ and in the inset we show the shape of $S(q)$ for $\lambda = 0.2, 0.5$ and 1 in the vicinity of the FSDP, together with the experimental curve [16]. With decreasing values of λ the amplitude of the FSDP decreases and one can say that for $\lambda \leq 0.4$ this feature does not exist any longer in $S(q)$. Indeed the residual value of the amplitude for small values of λ is not significant and is an artifact of the Fourier transform as can be seen in the inset. Together with the results shown in figure 1, this indicates that the FSDP appears when the tetrahedra (*already formed*) arrange themselves into a connected network.

All this structural information shows that below a certain amplitude of the Coulomb interactions the structure of our toy silica glass has lost all the medium- or extended-range features and is similar to a soft-sphere glass. From this study it appears that the transition value of λ between a fragile and a network glass is around 0.5. Of course the only proper

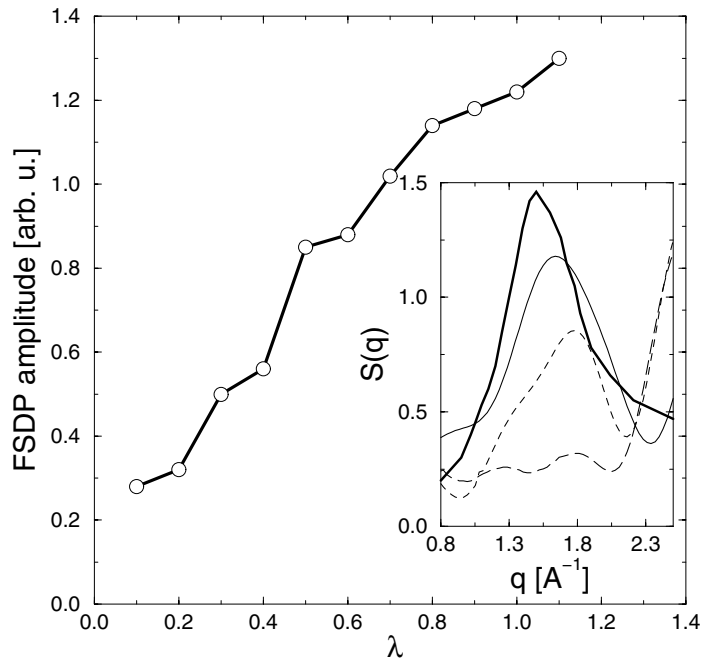


Figure 3. First sharp diffraction peak amplitude as a function of λ . In inset the structure factor $S(q)$ is shown in the vicinity of the FSDP for $\lambda = 0.2$ (long-dashed line), $\lambda = 0.5$ (dashed line), $\lambda = 1.0$ (thin solid line) and compared to the experimental $S(q)$ (bold solid line) for SiO_2 .

way to describe the covalent bonding network of silica atoms would be to use quantum mechanical calculations and therefore no precise physical meaning should be attached to this threshold value $\lambda = 0.5$. This value is linked to the specific form of the BKS potential which does not contain three-body terms and in which the Coulomb interactions are sufficient to build the SiO_4 tetrahedra. Nevertheless the good quality of this ‘simple’ potential has been demonstrated in a recent study which has shown that SiO_2 glass samples generated with the BKS potential are good starting configurations for *ab initio* quantum mechanical molecular dynamics calculations [15]. One interesting consequence of our results is that one should be cautious when screened Coulomb interactions are used to simulate real silica glasses. Indeed screened interactions are in a sense similar to ‘weak’ interactions like the ones we have simulated here with the small values of λ and wrongly treat the summation in reciprocal space which is carried out using the Ewald summation method. We show here that the screening should not be too strong in order to simulate a realistic silica glass.

In parallel with the study of the structure we have calculated the vibrational spectrum as a function of λ . During the diagonalization of the dynamical matrix we did not calculate the eigenvectors (for computer time reasons) but used the eigenvalues (always positive) to compute the vibrational density. We were of course interested in the boson peak which appears to be a characteristic of glasses even though it can also exist in some crystals [2]. This peak, seen in Raman and inelastic neutron scattering spectra, reflects an enhancement in the density of states compared to the Debye distribution and is located at frequencies around $\nu_B \simeq 1.5$ THz in silica. When varying λ , the energy (and the pressure since we consider a microcanonical ensemble) of our system varies appreciably and this is reflected in the variation of the largest frequency of the whole vibrational spectrum, ν_{\max} , which increases from $\nu_{\max} \approx 20$ THz for

$\lambda = 0.1$ to $\nu_{\max} \approx 40$ THz for $\lambda = 1.0$. As expected, the shape of the spectrum also varies with λ : for λ small we have basically one band since the oxygen and silicon atoms are almost identical whereas for large values of λ we observe a clear separation between an acoustic and an optical band typical of the formation of well defined Si–O bonds. But the boson peak is in all cases clearly present. However due to the λ -dependence of the whole spectrum, it is not legitimate to compare the BPs directly and therefore we have first determined the normalized density of states $g(f)$ using reduced frequencies $f = \nu/\nu_{\max}$. The normalization is such that $\int_0^1 g(f) df = 1$. Then we have used a standard way to extract the BP from the vibrational spectrum which is to plot $g(f)/f^2$ because in the Debye approximation $g(f) \approx f^2$ at low frequency. This curve has then been fitted by a ‘generalized Lorentzian’ [17]:

$$I = I_0 f^n \frac{1}{[f^2 + f_0^2]^m} \quad (3)$$

which has been used to extract the position of the BP and the corresponding height in a straightforward manner. In figure 4 we show the $g(f)/f^2$ data together with the fitting curves for three typical values of λ and in the inset we report the position and the intensity of the BP as a function of λ . As expected, due to the normalization of the $g(f)$ curves, the variations of the position and the intensity have opposite trends. Apart from a first decrease of the intensity between $\lambda = 0.1$ and $\lambda = 0.2$ that we cannot interpret simply (at very small values of λ , there are some artifacts due to the form of the potential as indicated above), one observes a net sharpening of the BP when λ becomes larger than 0.5. This seems to indicate that a strong BP is linked to the existence of tetrahedral units or to the presence of an FSDP and therefore

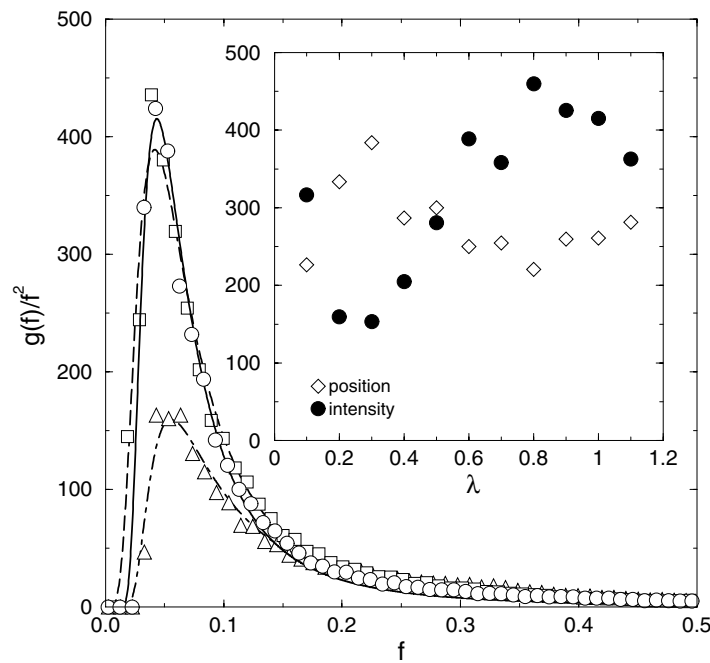


Figure 4. The boson peak represented as a plot of $g(f)/f^2$ versus f , where $g(f)$ is the normalized density of vibrational states and f the ‘reduced frequency’, taken equal to ν/ν_{\max} , where ν_{\max} is the maximum frequency of the spectrum. Δ , \square and \circ correspond to $\lambda = 0.2, 0.6$ and 1.0 respectively. Dot-dashed, dashed and continuous lines are the corresponding fits using formula (3). In the inset the position (\diamond) and the intensity (\bullet) of the boson peak are shown as functions of λ .

supports previous interpretations for the origin of the BP in silica [1]. Moreover the global variation of the BP characteristics with λ confirms the recent experimental observation that the BP increases when going from fragile to strong glasses [18]. Of course these results, based on a comparison between reduced spectra, should be treated with care: in addition to the increase of the bandwidth when increasing λ there is also a deformation of the whole spectrum which is difficult to take into account simply. Finally, if some significance can be given to the apparent decrease of the BP intensity with increasing λ for $\lambda > 0.7$, one could conclude that, once the tetrahedral network is formed, the increase of the medium-range order leads to a decrease of the BP intensity. Of course, such a statement needs to be validated by further investigations.

4. Conclusions

In conclusion, we have performed classical molecular dynamics simulations in a toy silica glass model in which we have changed the intensity of the long-range Coulomb forces. With this procedure it is possible to analyse the structure and the dynamics of a fragile glass (without Coulomb interaction) and a strong glass (with Coulomb interaction) within the same system. We have shown that the formation of a tetrahedral network, the existence of a first sharp diffraction peak in the static structure factor, a characteristic peaked ring size distribution, as well as a relatively sharp boson peak, are correlated with the strength of the Coulomb forces; all these features are absent in the fragile glasses and appear once the Coulomb forces exceed a potential-dependent threshold. Of course our study is limited to a very specific model and other ways of creating locally ordered units could have been explored. Nevertheless it sheds light on what is really happening in a system which can be considered as either a fragile or a strong glass. By tuning one single parameter (which therefore appears to be the predominant ingredient in the simulation of glasses) one is able to connect structural features like the FSDP to vibrational specificities like the boson peak and give answers to questions previously raised by experimental studies.

Acknowledgments

Some of the numerical calculations were done at the computer centre CINES (Centre Informatique National de l'Enseignement Supérieur) in Montpellier.

References

- [1] Buchenau U, Zhou H M, Nucker N, Gilroy K S and Phillips W A 1988 *Phys. Rev. Lett.* **60** 1318
- [2] Kivelson D and Tarjus G 1999 *Physics of Glasses: Structure and Dynamics (AIP Conf. Proc. 489)* ed P Jund and R Jullien (New York: AIP) p 90
- [3] Elliott S R 1992 *Europhys. Lett.* **19** 201
- [4] van Beest B W H, Kramer G J and van Santen R A 1990 *Phys. Rev. Lett.* **64** 1955
- [5] Vollmayr K, Kob W and Binder K 1996 *Phys. Rev. B* **54** 11 808
- [6] Jund P and Jullien R 1999 *Phil. Mag. A* **79** 223
- [7] Taraskin S N and Elliott S R 1997 *Phys. Rev. B* **39** 37
- [8] Jund P and Jullien R 1999 *Phys. Rev. B* **59** 13 707
- [9] Erikson R L and Hostetler C J 1987 *Geochim. Cosmochim. Acta* **51** 1209 and references therein
- [10] Novikov V N and Sokolov A P 1991 *Solid State Commun.* **77** 243
Sokolov A P, Kisliuk A, Soltwisch M and Quitmann D 1992 *Phys. Rev. Lett.* **69** 1540
- [11] Borjesson L, Hassan A K, Swenson J, Torell L M and Fontana A 1993 *Phys. Rev. Lett.* **70** 1275
Levelut C, Gaires N, Terki F, Cohen-Solal G, Pelous J and Vacher R 1995 *Phys. Rev. B* **51** 8606
- [12] Jund P, Caprion D and Jullien R 1998 *Phil. Mag. B* **77** 313 and references therein
- [13] Neuefeind J and Liss K D 1996 *Ber. Bunsenges. Phys. Chem.* **100** 1341

- [14] Rino J P, Ebbsjo I, Kalia R K, Nakano A and Vashishta P 1993 *Phys. Rev. B* **47** 3053
- [15] Benoit M, Ispas S, Jund P and Jullien R. 2000 *Eur. Phys. J. B* **13** 631
- [16] Susman S, Volin K J, Price D L, Grimsditch M, Rino J P, Kalia R K, Vashishta P, Gwanmesia G, Wang Y and Liebermann R C 1991 *Phys. Rev. B* **43** 1194
- [17] Terki F, Levelut C, Prat J L, Boissier M and Pelous J 1997 *J. Phys.: Condens. Matter* **9** 3955
- [18] Sokolov A P, Calemczuk R, Salce B, Kisliuk A, Quitmann D and Duval E 1999 *Phys. Rev. Lett.* **78** 2405
Sokolov A P 1999 *J. Phys.: Condens. Matter* **11** A213