Mémoire d'Habilitation à Diriger des Recherches

Spécialité Physique

Structural order in disordered systems: from glasses to supercritical solutions. Contributions from atomistic simulations

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Université Pierre et Marie Curie (UPMC) Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC)

Soutenance prévue le 16 septembre 2016 devant le jury composé de :

Noël JakseexaminateurEdouard KierlikexaminateurWalter KobrapporteurPaul F. McMillanexaminateurNormand MousseaurapporteurJean-Yves Ratyrapporteur

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Curriculum Vitae

Guillaume FERLAT Né à Tassin-la-demi-lune (France), le 16 juin 1976, 40 ans En union libre, un enfant (né en 2014)

Adresse professionnelle

Institut de Minéralogie, Physique des Matériaux et Cosmochimie UMR 7590 CNRS - UPMC Campus Jussieu, Couloir 23/24 - 4^{ème} étage - Bureau 423 Case courrier 115, 75252 Paris Cedex 05 Tel.: 01 44 27 98 22, Fax: 01 44 27 37 85 Email : guillaume.ferlat@impmc.upmc.fr

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Formation

1999-2002	Thèse de doctorat de l'Université Claude Bernard Lyon-I, spécialité physique.
	Thèse effectuée au Département de Physique des Matériaux (devenu Institut Lumière
	Matière) sous la direction du Pr. Alfonso San Miguel, soutenue le $16/12/2002$.
	Contributions expérimentales et numériques à l'étude de la structure de liquides en conditions
	de haute température et hautes pressions.
1998-1999	Diplôme d'études approfondies Matière Condensée, surfaces et interfaces
	Ecole doctorale Matériaux de Lyon (UCBL-ENS-ECL-INSA), mention bien (rang: 2 ^{ème}).
	Stage de DEA effectué au DPM (UCBL) et à l'ISM (Univ. Bordeaux) sous la direction des
	Pr. A. San Miguel et Ph. A. Bopp.
	Etude MD-XAS de solutions aqueuses supercritiques.
1997-1998	Licence et Maîtrise de Physique. Université Claude Bernard Lyon-I.

Experiences professionnelles de recherche

Depuis 2003	Maître de conférences à l'Université P. et M. Curie, Paris VI, section CNU 28
	Laboratoire: Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie
	(IMPMC) - UMR 7590
2010-2012	Délégation CNRS (deux fois un an à mi-temps)
2003	Contrat Post-doctoral, Cambridge University, Department of Earth Sciences,
	Cambridge, Royaume-Uni.
	Travail effectué sous la direction des Pr. E. Artacho et M. Dove. Financement: NERC
	Modélisation ab initio d'interfaces eau-minéraux par une méthode d'ordre $\mathcal{O}(N)$.

Experiences professionnelles d'enseignement

Depuis 2003	Maître de conférences à l'Université P. et M. Curie, Paris VI, section CNU 28
	UFR: Physique fondamentale et appliquée (925).
	Enseignement (192 heures annuelles) dispensé à l'UPMC (L3, M1, M2), l'ENS Cachan (L3,
	parcours PHYTEM) et au CHU Pitié-Salpêtrière (PCEM-PAES).
	Responsable de l'UE Cohésion de la matière (L3, LP358) depuis 2011
	Co-responsable de l'UE Etats de la matière (L3, LP350) depuis 2010
	Co-responsable de l'UE Physique numérique et modélisation (M1, 4P020) depuis 2015
<u>1999-2002</u>	Moniteur de l'enseignement supérieur à l'Université Claude Bernard, Lyon-I
	Travaux dirigés et travaux pratiques (niveaux L1 et L2) dans les filières Sciences de la matière
	et Sciences de la vie.

Activités de recherche et collaborations

Mots-clés: structure, propriétés vibrationnelles et électroniques, systèmes désordonnés (liquides, verres, fluides supercritiques), conditions de haute température et haute pression.

Techniques expérimentales et numériques: calculs ab initio, simulations de dynamique moléculaire empirique et *ab initio*, spectroscopie d'absorption de rayons X, diffusion de neutrons.

Collaborations internes au laboratoire (IMPMC):

- Georges Calas, Laurent Cormier, Laurence Galoisy, Gerald Lelong

- Etienne Balan, Marc Blanchard, Delphine Cabaret, Michele Casula, Maria Hellgren, Michele Lazzeri, Francesco Mauri, Fabio Pietrucci, Marco Saitta

Collaborations internes à l'UPMC:

- Matthieu Micoulaut (LPTMC), Mathieu Salanne (PHENIX), Ari P. Seitsonen (ENS), Rodolphe Vuilleumier (ENS)

Collaborations nationales:

- Thibault Charpentier (CEA, Saclay), François-Xavier Coudert (Chimie-ParisTech, Paris), Jean-Marc Delaye (CEA, Marcoule), Jean-Louis Hazeman (IN, Grenoble), Gleb Pokrovski (GET, Toulouse), Denis Testemale (IN, Grenoble)

Collaborations internationales:

- Phil Salmon, Anita Zeidler (Bath, Royaume-Uni)
- Oliver Alderman, Chris Benmore (Argonne, Etats-Unis)
- Akira Takada (Asahi Glass Co. Ltd, Japon)
- Grant Henderson (Toronto, Canada)
- Martin Dove, Kostya Trachenko (Londres, Royaume-Uni)
- Emilio Artacho (Cambridge, Royaume-Uni)

Contrats de recherche

- ANR Programme Blanc, Projet SOUMET (Rôle du soufre pour le devenir des métaux d'intérêt économique dans les fluides géologiques). Coordinateur: Gleb Pokrovski. Période: 01/10/2011-01/06/2016.

- DIM OxyMORE - Matériaux oxydes, Projet BOROSIMOD (Modélisation de la structure des verres de borosilicates). Coordinateur: Thibault Charpentier. Période: 01/10/2012-01/04/2014.

- ANR Jeune Chercheur, Projet CrIMin (Cristallochimie des minéraux ferrifères et implications dans le cycle géochimique des polluants métalliques). Porteur: Marc Blanchard. Période: 01/10/2011-01/10/2014.

- Programme Emergence - UPMC, Projet Solvatation supercritique de métaux précieux. **Porteur:** Guillaume Ferlat. Financement de la thèse de Romain Jonchière. Période: 01/10/2010-01/10/2013.

- ANR Programme Blanc, Projet GCWEB (low phonon-energy Glass Ceramics with tunable and ultra Wide absorption and Emission Bands for highly efficient frequency conversion). Coordinateur: Xianghua Zhang. Période: 01/01/2011-01/01/2014.

- ANR Programme Matériaux Fonctionnels et Procédés Innovants, Projet *POSTRE (Modélisation des propriétés optiques et structurales des verres fondus et fibrés dans une optique environnementale).* Coordinateur: Georges Calas. Période: 01/01/2009-01/01/2013.

- ANR Jeune Chercheur, Projet Nucleo-Vitro (Mechanisms of nucleation in nanocomposite glass-ceramics). Porteur: Laurent Cormier. Période: 01/01/2007-01/01/2009.

- ANR Jeune Chercheur, Projet SPIRSE (Spectroscopie infrarouge pour les sciences de l'environnement: mesures et modélisations). Porteur: Etienne Balan. Période: 01/01/2006-01/01/2009.

Fonctions d'intérêt collectif, responsabilités administratives

- Membre du panel d'experts FAP-2 (liquides et matériaux désordonnés) de la source de neutrons du Royaume-Uni (ISIS) depuis 2013 et jusqu'en 2017

- Membre nommé du conseil d'unité (IMPMC) depuis janvier 2014

- Membre élu du Conseil Scientifique de l'UFR 925 de l'UPMC de 2009 à 2013

- Membre du vivier d'experts de la commission de spécialistes de la section 28 à l'UPMC de 2009 à 2012

- Membre du comité de sélection MCF 28 pour l'UPMC en 2016

Organisation d'ateliers, colloques et conférences (4)

- Co-organisateur d'un atelier international CECAM Atomistic Simulations in Earth Sciences, 17-19 juin 2015, Paris, France

- Co-organisateur de l'atelier national SiMaDes-IV (Simulations de la Matière Désordonnée), 28-29 janvier 2011, Paris, France

- Co-organisateur d'un mini-colloque *eau, mélanges et solutions aqueuses* aux Journées de la Matière Condensée (JMC12), 23-27 août 2010, Troyes, France

- Co-organisateur du XI^{ème} congrès international *Non-Crystalline Materials* (NCM11), 28 juin-2 juillet 2010, Paris, France

Autres tâches d'animation au sein de la communauté scientifique

- Participation en tant qu'examinateur à des jurys de thèse (3): Sébastien Leroux (11/07/2008), Aurélie Ortiz (11/07/2014), Wilfredo Ibarra Hernández (4/09/2015)

- *Referee* pour Physical Review Letters, Physical Review B, Journal of Physics: Condensed Matter, Journal of Physical Chemistry B, Journal of Chemical Physics, Solid State Communications, Journal of Non-Crystalline Solids, Chemical Geology, Geochimica Cosmochimica Acta

- Membre des GDR Modélisation des matériaux et Verres

Publications (30)

Revues internationales à comité de lecture, hors actes de congrès (19)

- A19. Sulfur radical species form gold deposits on Earth
 G. S. Pokrovski, M. A. Kokh, D. Guillaume, A. Y. Borisova, P. Gisquet, J.-L. Hazemann,
 E. Lahera, W. Del Net, O. Proux, D. Testemale, V. Haigis, R. Jonchiere, A. P. Seitsonen,
 G. Ferlat, R. Vuilleumier, A. M. Saitta, M. C. Boiron, and J. Dubessy
 Proc. Natl. Acad. Sci. USA (PNAS), 112, 13484-13489 (2015). DOI : 10.1073/pnas.1506378112
- A18. Dispersion effects in SiO₂ polymorphs: An ab initio study Henri Hay, Guillaume Ferlat, Michele Casula, Ari Paavo Seitsonen, and Francesco Mauri Physical Review B, 92, 144111 (2015). DOI : 10.1103/PhysRevB.92.144111
- A17. Liquid B₂O₃ up to 1700 K: x-ray diffraction and boroxol ring dissolution
 O. L. Alderman, G. Ferlat, A. Baroni, M. Salanne, M. Micoulaut, C. J. Benmore, A. Lin,
 A. Tamalonis, and J. K. R. Weber
 Journal of Physics: Condensed Matter, 17, 455104 (2015). DOI : 10.1088/0953-8984/27/45/455104
- A16. Density-driven structural transformations in B₂O₃ glass
 Anita Zeidler, Kamil Wezka, Dean A. J. Whittaker, Philip S. Salmon, Axelle Baroni, Stefan Klotz, Henry E. Fischer, Martin C. Wilding, Craig L. Bull, Matthew G. Tucker, Mathieu Salanne, Guillaume Ferlat, and Matthieu Micoulaut
 Physical Review B, 90, 024206 (2014). DOI : 10.1103/PhysRevB.90.024206
- A15. Equilibrium fractionation of H and O isotopes in water from path integral molecular dynamics C. Pinilla, M. Blanchard, E. Balan, G. Ferlat, R. Vuilleumier, and F. Mauri Geochimica et Cosmochimica Acta, 135, 203-216 (2014). DOI : 10.1016/j.gca.2014.03.027
- A14. Silver in geological fluids from in situ XAS and first-principles molecular dynamics
 Gleb S. Pokrovski, Jacques Roux, Guillaume Ferlat, Romain Jonchiere, Ari P. Seitsonen,
 Rodolphe Vuilleumier, and Jean-Louis Hazemann
 Geochimica et Cosmochimica Acta, 106, 501-523 (2013). DOI : 10.1016/j.gca.2012.12.012
- A13. Hidden polymorphs drive vitrification in B₂O₃
 Guillaume Ferlat, Ari Paavo Seitsonen, Michele Lazzeri, and Francesco Mauri Nature Materials, 11, 925-929 (2012). DOI : 10.1038/nmat3416

- A12. Evidence for fivefold-coordinated Ge atoms in amorphous GeO₂ under pressure using IXS G. Lelong, L. Cormier, G. Ferlat, V. Giordano, G. S. Henderson, A. Shukla, and G. Calas Physical Review B, 85, 134202 (2012). DOI : 10.1103/PhysRevB.85.134202
- A11. Van der Waals effects in ab initio water at ambient and supercritical conditions R. Jonchiere, A. P. Seitsonen, G. Ferlat, A. M. Saitta, and R. Vuilleumier Journal of Chemical Physics, 135, 154503 (2011). DOI: 10.1063/1.3651474
- A10. First-principles calculations of structural changes in B₂O₃ glass under Pressure K. Trachenko, V. V. Brazhkin, G. Ferlat, M. T. Dove, and Emilio Artacho Physical Review B, 78, 172102 (2008). DOI : 10.1103/PhysRevB.78172102
- A9. Boroxol Rings in Liquid and Vitreous B₂O₃ from First Principles
 Guillaume Ferlat, Thibault Charpentier, Ari Paavo Seitsonen, Akira Takada, Michele Lazzeri, Laurent Cormier, Georges Calas, and Francesco Mauri
 Physical Review Letters, 101, 065504 (2008). DOI : 10.1103/PhysRevLett.101.065504
- A8. Nature of the Structural Transformations in B₂O₃ Glass under High Pressure
 V. V. Brazhkin, Y. Katayama, K. Trachenko, O. B. Tsiok, A. G. Lyapin, E. Artacho, M. Dove,
 G. Ferlat, Y. Inamura, and H. Saitoh
 Physical Review Letters, 101, 035702 (2008). DOI : 10.1103/PhysRevLett.101.035702
- A7. Amorphous-amorphous transformation at high pressure in gallo-germanosilicate tetrahedral network glasses
 L. Cormier, G. Ferlat, J.-P. Itié, L. Galoisy, G. Calas, and G. Aquilanti
 Physical Review B, 76, 134204 (2007). DOI : 10.1103/PhysRevB.76.134204
- A6. Evidence for symmetric cationic sites in zirconium-bearing oxide glasses G. Ferlat, L. Cormier, M. H. Thibault, L. Galoisy, G. Calas, J. M. Delaye, and D. Ghaleb Physical Review B, 73, 214207 (2006). DOI : 10.1103/PhysRevB.73.214207
- A5. Remote determination of sample temperature by neutron resonance spectroscopy H. J. Stone, M. G. Tucker, Y. Le Godec, F. M. Méducin, E. R. Cope, S. A. Hayward, G. P. J. Ferlat, W. G. Marshall, S. Manolopoulos, S. A. T. Redfern, and M. Dove Nuclear Instruments & Methods in Physics Research Section A, 547, 601-616 (2005). DOI : 10.1016/j.nima.2005.03.140
- A4. Semiconductor-metal transitions in liquid In_{100-x}Se_x alloys: A concentration-induced transition G. Ferlat, A. San Miguel, H. Xu, A. Aouizerat, X. Blase, J. Zuniga, and V. Munoz-Sanjose Physical Review B, 69, 155202 (2004). DOI: 10.1103/PhysRevB.69.155202
- A3. Ab initio studies of structural and electronic properties of solid indium selenide under pressure G. Ferlat, H. Xu, V. Timoshevskii, and X. Blase Physical Review B, 66, 085210 (2002). DOI: 10.1103/PhysRevB.66.085210
- A2. Structure in liquid Hg-Rb alloys: An x-ray absorption study
 A. San Miguel, G. Ferlat, J.-F. Jal, A. Mizuno, T. Itami, and M. Borowski Physical Review B, 65, 144203 (2002). DOI: 10.1103/PhysRevB.65.144203
- A1. Hydration of the bromine ion in a supercritical 1:1 aqueous electrolyte
 G. Ferlat, A. San Miguel, J.-F. Jal, J.-C. Soetens, P. A. Bopp, I. Daniel, S. Guillot, J.-L. Hazemann, and R. Argoud
 Physical Review B, 63, 134202 (2001). DOI : 10.1103/PhysRevB.63.134202

Actes de congrès, revues internationales à comité de lecture (9)

- B9. First principles simulations of liquid and vitreous B₂S₃
 G. Ferlat, and M. Micoulaut Physics and Chemistry of Glasses, 50, 284-288 (2009). On-line access
- B8. Liquid structure of Rb-Hg alloys studied by neutron diffraction A. Mizuno, T. Itami, G. Ferlat, A. San Miguel, and J.-F. Jal Journal of Non-Crystalline Solids, 353, 3022-3026 (2007). DOI : 10.1016/j.jnoncrysol.2007.05.033

- B7. Ab initio calculations on borate systems
 G. Ferlat, L. Cormier, F. Mauri, E. Balan, G. Calas, T. Charpentier, and E. Anglada Physics and Chemistry of Glasses, 47, 441-444 (2006). On-line access
- B6. Two exchange-correlation functionals compared for first-principles liquid water M. V. Fernandez-Serra, G. Ferlat, and E. Artacho Molecular Simulations, 31, 361-366 (2005). DOI: 10.1080/08927020500066726
- B5. Combining EXAFS with numerical simulations for disordered systems
 G. Ferlat, J.-C. Soetens, A. San Miguel, and P. A. Bopp Journal of Physics: Condensed Matter, 17, S145-S157 (2005). DOI : 10.1088/0953-8984/17/5/015
- B4. High pressure-high temperature phase diagram of InSe
 G. Ferlat, D. Martinez-Garcia, A. San Miguel, A. Aouizerat, and V. Munoz-Sanjose
 High Pressure Research, 24, 111-116 (2004). DOI : 10.1080/0895790310001635756
- B3. The quest for ion pairing in supercritical aqueous electrolytes
 G. Ferlat, A. San Miguel, J.-F. Jal, J.-C. Soetens, P. A. Bopp, J.-L. Hazemann, D. Testemale, and I. Daniel
 Journal of Molecular Liquids, 101, 127-136 (2002). DOI: 10.1016/S0167-73220200087-9
- B2. Local structure in liquid Hg-Rb alloys studied by EXAFS
 A. Mizuno, T. Itami, A. San Miguel, G. Ferlat, J.-F. Jal, and M. Borowski
 Journal of Non-Crystalline Solids, 321-314, 74-79 (2002). DOI : 10.1016/S0022-30930201652-6
- B1. Structural disorder in supercritical aqueous ionic solutions as seen by MD-EXAFS
 G. Ferlat, A. San Miguel, J.-C. Soetens, and P. A. Bopp
 High Pressure Research, 22, 399-401 (2002). DOI : 10.1080/08957950212820

Autres publications (2)

- C2. Resolving the enigma of gold deposit formation using x-ray absorption spectroscopy Highlights of the ESRF 2015, 94-95 (2015). On-line access
- C1. The Structure of Liquid Hg-alkali Alloys Highlights of the ESRF 2001, 80-81 (2001). On-line access

Chapitres de livre (2)

- L2. Atomistic simulations of boron oxide glasses in Computer Simulations of Glasses: Methodologies and Applications Eds. Alastair Cormark, and Jincheng Du Wiley (2017) En préparation.
- L1. Chapter 14 Rings in network glasses: the B₂O₃ case in Molecular Dynamics Simulations of Disordered Materials Eds. Carlo Massobrio, Jincheng Du, Marco Bernasconi, and Philip S. Salmon Springer (2015) 367-414. ISBN 978-3-319-15674-3 DOI : 10.1007/978-3-319-15675-0_14

Conférences invitées (15)

Conférences, colloques et ateliers internationaux (14)

- 114. Hidden polymorphism in B₂O₃ revealed by ab initio searches.
 International Workshop iPolymorph Novel Routes to Inorganic Polymorphs.
 Donostia (Espagne), 22-24 juin 2016.
- 113. Numerical exploration of the B₂O₃ phase-diagram: challenges and progresses. 2nd International Workshop on Challenges in the Atomic Scale Modelling of Glasses. Wuhan (Chine), 22-24 juin 2015.

- 112. Understanding the glass and liquid properties from the underlying polymorphism in borates systems. Materials Research Society Fall Meeting. Boston (Etats-Unis), 30 novembre-5 décembre 2014.
- MD-XAS studies of supercritical fluids.
 EMLG-JMLG annual meeting group. Lille (France), 9-13 septembre 2013.
- 110. Anomalies in glassy B₂O₃ unveiled from topological predictions of crystalline polymorphs. 10th Pacific Rim Conference on Ceramic and Glass Technology. San Diego (Etats-Unis), 2-7 juin 2013.
- Polymorphism and the glass transition in borates: the relevance of small rings. 1st International Workshop on Challenges in the Atomic Scale Modelling of Glasses. Strasbourg (France), 4-6 juin 2012.
- Hidden polymorphism in B₂O₃: the glass transition and the crystallisation anomaly explained.
 7th International Conference on Borate Glasses, Crystals, and Melts. Halifax (Canada), 21-25 août 2011.
- 17. Rings in liquid and vitreous B₂S₃ from first-principles.
 Vth International Conference on Amorphous and Nanostructured Chalcogenides.
 Bucarest (Roumanie), 26 juin-1^{er} juillet 2011.
- 16. Structure determination of liquids and glasses beyond the pair correlation function. International Conference on Advances on Condensed and Nano Materials. Chandigarh (Inde), 23-26 février 2011.
- First-principles simulations of glasses.
 Glass and Optical Materials Division Annual Meeting. Corning (Etats-Unis), 16-20 mai 2010.
- X-ray absorption in aqueous solutions (Lecture).
 CECAM Workshop Aqueous solvation of ions. Zürich (Suisse), 22-24 février 2010.
- Can we probe rings in glasses with XAS? XIVth International Conference on X-ray Absorption Fine Structure. Camerino (Italie), 26-31 juillet 2009.
- Structural and electronic properties of InSe liquids: a combined XRD, EXAFS and AIMD study. Joint CECAM - ESRF Workshop - Polymorphism in liquid and amorphous matter. Grenoble (France), 7-9 juillet 2004.
- EXAFS close to the critical point: strengths and limitations. ESRF Workshop - The structure and dynamics of the liquid and glassy states: X-ray and complementary methods. Grenoble (France), 22-23 mai 2000.

Conférences, colloques et ateliers nationaux (1)

N1. Spectroscopie d'absorption X appliquée aux systèmes désordonnés: méthodes numériques d'analyse (combinaison MD-XAS). Journées thématiques du GDR Verres - Modélisation des verres: de la structure aux propriétés. Marcoule (France), 9-13 mai 2011.

Autres communications (42)

Outre les conférences invitées précédentes, mes communications se répartissent de la façon suivante:

- 11 communications orales dans des conférences et ateliers internationaux
- 9 communications orales dans des conférences et ateliers nationaux
- 14 communications par poster dans des conférences et ateliers internationaux
- 8 séminaires dans des laboratoires français

Encadrements

Stage Licence	Encadrement du stage de licence L3 de Yann Varin (ENS Cachan, parcours PHYTEM) intitulé : <i>"Etude de l'ordre microscopique dans des géomatériaux désordonnés"</i> . Durée : 5 semaines (mai-juin 2008).
Thèse	 Thèse de Romain Jonchière intitulée :
(PhD)	"Solvatation supercritique de métaux précieux : apports de la simulation moléculaire". Co-encadrement (50 %) partagé avec Rodolphe Vuilleumier (40 %) et Marco Saitta (10 %). Financement : UPMC, contrat EMERGENCES. Thèse démarrée le 01/10/2010, soutenue le 17/06/2013. Directeur de thèse : Pr. Marco Saitta (saitta@impmc.upmc.fr) Publications : PNAS (2015), GCA (2013), JCP (2011) [références A19, A14, A11 de ma liste de publications. Deux autres articles sont en préparation]. Statut actuel de Romain Jonchière : Ingénieur Chercheur au service R&D de EDF.
Thèse	 Thèse d'Axelle Baroni intitulée :
(PhD)	"Etude structurale de B ₂ O ₃ à l'aide de dynamique moléculaire incluant des potentiels polarisables", Co-encadrement (40 %) partagé avec Mathieu Salanne (40 %) et Matthieu Micoulaut (20 %). Financement : Labex MATISSE. Thèse démarrée le 01/10/2012, soutenue le 10/09/2015. Directeur de thèse : Pr. Matthieu Micoulaut (mmi@lptl.jussieu.fr) Publications : JPCM (2015), PRB (2014) [références A17, A16 de ma liste de publications. Un autre article est en préparation]. Statut actuel d'Axelle Baroni : Post-doctorante au CEA Marcoule.
Thèse (PhD)	Thèse d'Henri Hay intitulée : "Etudes ab-initio du polymorphisme dans les oxydes de silice (SiO_2) et de bore (B_2O_3) ", Co-encadrement (50 %) réalisé avec Michele Casula (50 %). Financement : Ecole doctorale 397. Thèse démarrée le 01/10/2013, date prévue de soutenance: $30/09/2016$. <u>Directeur de thèse</u> : Pr. Delphine Cabaret (cabaret@impmc.upmc.fr) <u>Publications</u> : PRB (2015) [référence A18 de ma liste de publications. Deux autres articles sont en préparation].
Stage Post- doctoral	 Stage post-doctoral de Volker Haigis intitulé : "Solvatation supercritique du soufre et calculs de solubilité" Co-encadrement (40 %) partagé avec Rodolphe Vuilleumier (50 %) et Marco Saitta (10 %). Financements : ANR SOUMET et Labex MATISSE. Durée des contrats : 2 fois 1 an, du 01/11/2013 au 01/11/2015. Responsable : Pr. Rodolphe Vuilleumier (rodolphe.vuilleumier@ens.fr) Publications : PNAS (2015) [références A19 de ma liste de publications. Un autre article est en préparation]. Statut actuel de Volker Haigis : Ingénieur Chercheur à Saint-Gobain Recherche.
Stage	 Stage post-doctoral de Silvio Pipolo intitulé :
Post-	"Métadynamique topologique pour l' étude du poly(a)morphisme" Co-encadrement (10 %) partagé avec F. Pietrucci (60 %), M. Saitta (20 %) et M. Salanne (10 %).
doctoral	Financement : Labex MATISSE. Durée du contrat : 18 mois, démarré le 01/07/2015 (fin prévue le 31/12/2016). Responsable : Dr. Fabio Pietrucci (pietrucci@impmc.upmc.fr) Publications : Un article est en préparation.

Encadrements ponctuels (M2, thèses, post-docs) :

Formation à la spectroscopie d'absorption X (EXAFS) et au code Gnxas :

1. Marie-Hélène Thibault, stage de M2, encadrants principaux : L. Galoisy et G. Calas, publication commune: PRB (2006) [Ref. A6 de ma liste de publications]

- 2. Olivier Dargaud, thèse, encadrant principal : L. Cormier
- 3. Aymeric Dugué, thèse, encadrant principal : L. Cormier

Formation à la dynamique moléculaire :

4. Simon Delattre, thèse, encadrant principal : E. Balan

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Chapter 1

General introduction

This dissertation provides an overview of my scientific activity for the last 13 years (2003-2016), i.e. since I became an assistant professor at UPMC. I started my PhD thesis (1999-2002, Université Claude Bernard Lyon I) as an experimentalist (under the direction of Alfonso San Miguel), using mainly the x-ray absorption (XAS) spectroscopy¹ to investigate the local structure of various types of liquids under high-temperature and -pressure conditions [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11]. From the very beginning however, as I was working on supercritical aqueous solutions, the need for theoretical models to support the data analysis became very clear. Indeed, we quickly realised that we were facing (a severe case of) the inverse problem: the limited amount of structural information contained in the experimental signal renders the solution non unique. This is how I came to introduce molecular dynamics (MD) simulations in my works as a mean to constrain the XAS data analysis. I have been introduced first to classical MD by Jean-Christophe Soetens and Philippe A. Bopp (University of Bordeaux) and later to first-principles MD (FPMD) by Hong Xu and Xavier Blase. MD were used to produce robust (since energetically-constrained) structural models from which theoretical XAS spectra could be derived and compared to experiments [2]. In return, the experiments could in some cases help to refine the MD model [4, 8]. The combined MD-XAS methodology [10] has then been applied systematically to my subsequent investigations of liquids.

During my post-doctoral position (2003, University of Cambridge), I deepened my experience in FPMD, with a special focus on $\mathcal{O}(N)$ methods and water simulations [12] while still keeping a remote connection with experiments (ND) [13].

Then, I was recruted in 2003 as *Maître de conférences* at UPMC, the position I am still currently holding. From then, I incorporated structural studies of glasses as my main research topic in the *glass* group at IMPMC. I brang my expertise of XAS and/or MD simulations to elucidate the local structure of specific elements from simple oxides (such as B_2O_3 or GeO_2) to chemically complex glasses (e.g. borosilicates, gallo-germanosilicates) [14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26]. Studies of water and aqueous solutions were re-introduced in my research activities from 2010, through local and external collaborations and thanks to significant financial supports (1 PhD and 3 post-doc contracts) [27, 28, 29, 30, 31, 32, 33].

The common line behind all these studies (from the PhD up to now) is, first, to find *order in disorder* (in liquids and glasses), second, to confront as much as possible the simulations with various experimental probes (either to test the models or to assess the information content and sensitivity of the experiments). Beyond my initial field of expertise (XAS), calculations of several others spectroscopic tools (such as Raman and nuclear magnetic resonance) have been progressively incorporated thanks to many collaborations. A future direction is the use of *enhanced sampling* methods (such as metadynamics).

¹and to a much lesser extent, neutron diffraction (ND)

For the sake of concision, the choice is made for this manuscript to focus with some details on one *story*, that of B_2O_3 , rather than covering all topics. The B_2O_3 case (chapter 2) illustrates not only the type of methodology that I use but also well the problematic of finding *order in disorder* and its unexpected ramifications. The corresponding chapter is to a large extent a shortened and slightly modified version of the book chapter I recently wrote [25] with an updated part (section 2.5) and an additional part (section 2.7) from on-going works. Finally, projects (connected to this topic) for the next years are proposed in the last chapter.

Because the studies related to water and aqueous solutions will not be discussed further in this manuscript, I recap very briefly some of the most salient results obtained. The overall project is to obtain microscopic models of ions solvation in fluids and conditions relevant to Earth-Sciences: in particular, in supercritical conditions, the drastic decrease of the water dielectric constant can give rise to unusual ion associations. In pure water, using both FPMD and classical MD, we have explored the effects of dispersion forces on the fluid structure and dynamics, from ambient to supercritical conditions [27]. This allowed i) to assess the performances of recent schemes to incorporate these terms within DFT ii) to assess the range of these forces (and their counter-intuitive effects in supercritical conditions) iii) to evidence the crucial role played by the 5th oxygen neighbour. Then, the hydration of precious metals such as Ag^+ and Au^+ in water were investigated (using FPMD and XAS + solubility measurements) [28, 29, 31, 32]. In the case of Ag⁺, our FPMD-XAS study allowed to evidence the clusters preferentially formed under various conditions and to decipher between two thermodynamic models of solubility which were coexisting in the literature (and whose predictions were varying by almost two orders of magnitude when extrapolated at high temperature) [29]. In the case of Au^+ , the formation of stable complexes with the radical species S_3^- (rather than the commonly believed sulfide species) has been confirmed and showed to play a key role for the efficient transport of gold [31]. This latter communication had a large impact, largely covered in the media². Similar studies are on-going for other ions and more complex solutions (such as water- CO_2 mixtures) [33].

I would like to thank the many collaborators which I had the chance to work with and learn from, in particular Francesco Mauri, Thibault Charpentier, Ari P. Seitsonen, Michele Casula, Rodolphe Vuilleumier, Mathieu Salanne, Matthieu Micoulaut. For reasons related to the other side of my position (teaching assistant), I would also like to express gratitude and much consideration to Philippe Depondt, Delphine Cabaret and Guillaume Radtke.

²Including scientific (*Pour la Science*) as well as general media (*The Huffington Post*), from local newspapers (e.g. 20 minutes) to national radio (*France Inter, journal de 8h du 14/10/2015*) and television (*France 2, émission Télématin du 21/12/2015*) broadcasts ...

Chapter 2

Structural transformations in liquid, glassy and crystalline phases of B_2O_3

Related articles: [15, 17, 18, 19, 20, 22, 23, 24, 25]

This chapter is devoted to the structural transformations in boron trioxide (B_2O_3), which together with SiO₂ and P₂O₅ is an archetypal network-forming system [34] and also the end member of the large family of borate glasses [35]. Because of the open and low-coordinated network it forms at ambient condition, B_2O_3 is prone to structural transformations, driven either by high-temperature or high-pressure. However, we start first with an extensive discussion of the ambient glass structure.

The presence of 3-fold rings in the glassy phase, $v-B_2O_3$, is perhaps the most well-documented case of intermediate-range order [36]. However, quantitative estimates have been controversial for many decades, especially since the apparition of the first MD simulations of this system. We have contributed to reconcile experiments and simulations and we have hopefully settled this issue. However, the obtention of a good numerical model of $v-B_2O_3$ using conventional (i.e. quench from the melt) techniques is still extremely challenging. We thus use the B_2O_3 example as a (possibly exacerbated) illustration of the challenges to be faced when simulating the medium-range order of a glass. I will show how a strategy was devised to assess the rings content. Then, I will show that the specific rings found in $v-B_2O_3$ have direct implications for our understanding of the crystalline and liquid phases, not only of B_2O_3 but also of parent systems such as B_2S_3 .

2.1 Boroxol rings in liquid and vitreous B₂O₃: a review of the literature

In pure boron trioxide, the basic building unit is the planar BO₃ triangle [37] (see Fig. 2.1). The first proposed structural model of v-B₂O₃ is that of a continuous random network of such cornerlinked triangles [34]. This view was however questioned, as soon as 1953 [38], by the observation of an extremely sharp peak at 808 cm⁻¹ in the Raman spectrum (see Fig. 2.14 page 33), which was attributed to the presence of planar 3-fold rings (B₃O₆) of triangles, called boroxols (Fig. 2.1). This mode was indeed later unambiguously assigned to the in-phase breathing of oxygens inside the rings, in particular thanks to elegant measurements in isotopically substituted glasses [39]. The sharpness of the peak, which is different from the broad features usually observed for glasses, is a consequence of the strongly localised character of this mode [40]. Unfortunately, the quantitative determination of the proportion of atoms involved in these rings is not trivially derived from the peak area since it would require an accurate knowledge of the Raman cross-section for the mode under consideration;



Figure 2.1: Left: The BO₃ triangle (indicated here BO_{3/2}). Right: The B₃O₆ boroxol ring (indicated here B₃O_{9/2}). Both units are self-similar: the replacement of all triangles by boroxol units in a given 2D- or 3D-structure, increases the number of atoms by a factor of 3, the surface by 2^2 and the volume by 2^3 ; the density is thus lowered from the initial one by a factor $\frac{3}{4}$ in 2D or $\frac{3}{8}$ in 3D.

these calculations have become available from *first-principles* only recently [41, 19]. In any case, the existence of these rings in the glass is, at least at this point, very disturbing since there are no such rings in any of the two known crystals of B_2O_3 : the closest polymorph, B_2O_3 -I, is made of independent BO_3 triangles. I will come back to this point in section 2.4.

Other experimental evidences for boroxols typically come from NMR and nuclear quadrupolar resonance experiments. These techniques do evidence the presence of two populations in both ¹⁷O and ¹¹B spectra [42, 43, 44, 45, 46, 47, 48, 49] which were assigned to atoms *inside* and *outside* the rings. These assignments were supported by the comparison of the spectra with borate crystals of known structure [50] as well as by molecular orbitals calculations on cluster models [51, 52, 53]. Quantitative measurements have consistently established that the ratio of the two populations (rings / non-rings) is typically about 1 : 1, i.e. that there are about as many boroxol units as independent BO₃ groups, confirming the model originally proposed by Krogh-Moe [54]. Note that the convention in the literature is to report the proportion of boron atoms involved in boroxols, f. The 1 : 1 model corresponds to f= 75 % (while the corresponding proportion of oxygens in rings, f_O , is 50 %). More precisely, the values derived from NMR range from f = 65 to 85 %. Hereafter, structures in this range of f will be referred to as *boroxol-rich* models.

Diffraction data analyses have been used by both sides to support [55, 56, 57] or dispute [58, 59, 60] the boroxol-rich model: f values ranging from essentially 0 to 80 % were reported. This should come as no surprise since the 3-body information is largely washed out in these data. However, both camps had seemingly good arguments. It has been claimed that some peaks in the partial distribution functions are narrower in the presence of large amounts of boroxols and thus that they could serve as signatures of the rings [57]. However, Swenson and Börjesson (SB) argued [60] that previous diffraction analyses lack an essential constraint, namely the density: using reverse Monte Carlo (RMC) simulations, they came to the conclusion that it is not possible to produce structural models containing more than 30 % of boroxols that simultaneously reproduce the experimental density and the neutron and x-ray diffraction data [60]. This claim is however overlooking an earlier RMC study by Bionducci et al. [61] which showed that various hand-made models, containing from 0 to 50 % boroxols, gave equivalent and good fits of the diffraction data. In their simulations both the density and the boron coordination were constrained. It was rightly concluded that in the absence of interatomic potentials, it is very improbable that a structural order will spontaneously emerge from a disordered configuration [61]. We will discuss (and refute [19, 62]) the arguments of SB [60] in the section 2.2.

Indeed, the density is a key quantity. Early hand-made *ball-and-stick* models had difficulties producing reasonable models at the correct glass density. The BO_3 -made model of Ref. [63] has a too high density while that of the boroxol-made (and lamellar) model of Ref. [64] is too low. To this extent, SB [60] are right: having a model at the correct density is mandatory before any claim is made regarding the structure. Because of simple steric considerations, a structure made of boroxols will tend to have a much lower density than the corresponding structure made solely of BO_3 units. This has been used by both pros- and opponents of the boroxol model. On one hand, the density of the glass (1.84 g.cm^{-3}) is surprisingly lower (by ~ 40 %) than that of the closest crystal polymorph, B₂O₃-I (2.54 g.cm^{-3}) : this is indicative of a very different structure, compatible with a significative amount of rings in the glass. On the other hand, a structure topologically identical to B₂O₃-I but entirely made of boroxols should have a density reduced by $\frac{3}{8}$ (i.e. 62.5 %), that is even lower than the glass density. This value is derived by simple scaling arguments using the self-similarity between the BO₃ triangle and the B_3O_6 supertriangle (Fig. 2.1), first noted by Bell and Carnevale [64]: the replacement of all BO_3 by B_3O_6 units in a given 3D-structure, everything else being unchanged, increases the volume by a factor 2^3 but the number of atoms only by a factor of 3; the resulting density is thus lowered from the initial one by a factor $\frac{3}{8}$. That is to say, to match the glass density, a structure topologically equivalent to B₂O₃-I would seemingly incorporate a manipum amount of $f \sim 44$ %. We will further explore this question in section 2.4. To conciliate simultaneously a large amount of boroxols and a high enough density, the possibility of interpenetrating networks, as commonly found in borate crystals, has been suggested [54]. For instance, the structure of caesium enneaborate has two interlocking twin networks from which a very good hand-made model of $v-B_2O_3$ can be made, as first pointed out by Krogh-Moe [54] and further used by Takada [65, 66] and others [67, 19]. I will show however in section 2.4 that the interpenetrating networks hypothesis is not a necessary condition, i.e. that single networks of boroxols can match the glass density.

Given its anomalous intensity, there has been suspicion [36, 68, 69] that the Raman peak at 808 cm⁻¹ is strongly affected by matrix-element enhancement effects since the corresponding peak in inelastic neutron scattering (INS) data, closer to the bare vibrational density of states, is much smaller. However, more recent analyses of high-resolution INS spectra [70, 71] and the comparison of these data with those obtained from borate crystals for which f is known, fully support the view that f > 67 % [71]. Teter claimed that the intensity of the the Raman peak at 808 cm⁻¹ corresponds to f = 10.7 %, using a normalisation to the corresponding intensities from sodium metaborate solutions with known proportions of metaborate rings [72]. However, this claim, which is at variance with the rest of the Raman literature, is likely erroneous because of some of the assumptions made. In particular, this value is derived assuming that the Raman scattering matrix enhancement for the metaborate ring peak at 745 cm⁻¹ in aqueous solutions is the same than that of the boroxol ring at 808 cm⁻¹ in v-B₂O₃. This is very unlikely given the different nature of the rings (the metaborate involving four-fold coordinated boron atoms) and given the different dielectric constant of the materials (since water is a polar molecule, its polarisation will reduce the electric field acting on the ring). A direct assessment of the Raman peak sensitivity to f will be provided in section 2.2.

The very same peak (808 cm^{-1}) has been used by various authors to monitor the amount of rings in pressure- or temperature-induced transformations [73, 74, 75, 76, 77, 78, 79, 80, 81]. This has been done by assuming that the peak area (after appropriate normalisation) is proportional to the number of oxygen atoms in boroxols¹. Note that these measurements do not provide absolute values of f but relative ones (to that used for the absolute scaling). However, when cross-checking was possible, very good agreement with values derived from NMR [82, 79] was obtained [80].

The temperature dependence of the Raman peak (808 cm^{-1}) has been measured [73, 74, 75] from 77

¹Being related to a vibration of the oxygen atoms in the rings, the peak area is proportional to f_O , which is directly related to f, the number of boron atoms in the rings, by $f = 1.5f_O$.



Figure 2.2: Temperature dependence of the number of boron atoms in boroxol rings, f, as obtained from the Raman peak at 808 cm⁻¹. The solid lines represent graphical interpolations of experimental data from various authors [73, 74, 75] using different normalisation procedures. The experimental data of Walrafen et al. [73, 74] were modelled by these authors with the function $ln\{\frac{f(T)}{A-f(T)}\} = B/T + C$ where A, B, C are constants (A is the value of f at T_g). The values of $\{A, B, C\}$ are $\{0.644, 3237.66, -2.58893\}$ in Ref. [73] and $\{0.7882, 2490.5, -2.3734\}$ in Ref. [74]. The data from Hassan et al., which were digitised from Fig. 9 of Ref. [75] originally provide f_{at} , the number of atoms in boroxol rings and are represented here as f, using the relationship $f = \frac{7.5}{6}f_{at}$. The vertical arrows indicate the glass transition (T_g) and melting (T_m) temperatures.

up to 1867 K, i.e. from the glass to the liquid state (see Fig. 2.2). The rings concentration is essentially constant from room temperature up to the glass transition. Then at T_g (~ 470 - 540 K), boroxols start to open, and above T_g the number of rings steeply decreases [75]. Using a simple two-state model, the Raman measurements have been used to derive an energy for the (temperature-induced) boroxol-BO₃ transformation: Walrafen et al. reported values of about 6. \pm 1 kcal/(mol boroxol) [73, 74].

The change with temperature of various properties like density [83, 84, 85], heat capacity [86], viscosity [85, 87, 88, 89, 90, 79] and surface tension [91] have also been claimed to be consistent with a marked structural change taking place between room temperature and 1300 K [54]. In other words, boroxol rings essentially form in the temperature range 500-1300 K as the liquid is cooled. In this range, the viscosity increases by typically 12 orders of magnitude, as shown in Fig. 2.3. This is an important aspect to keep in mind as we now briefly review molecular simulations of B_2O_3 .

Although a broad consensus (in favour of boroxol-rich models) could be reached from the experimental side in the early eighties [54, 56], a resurgence of criticisms appeared at that time (up to recently) with the emergence of atomistic simulations. Indeed, unbiased MD or MC simulations have systematically failed so far to produce boroxol-rich configurations (from liquid quenches) while simultaneously fulfilling some basic experimental constrains (density, proportion of coordination defects).

Molecular dynamics (MD) simulations of $v-B_2O_3$ using empirical 2-body potentials were pioneered by Soules [92, 93, 94] and Amini et al. [95], followed later by others [96, 68, 97, 98]. In all cases, a random network of BO₃ triangles without any boroxols was obtained. The authors thus challenged the boroxol model though the simulations were at the most confronted either to neutron diffraction only [95] or to limited x-ray diffraction results [98]. At least in one case were the limitations in the simulations clearly pointed out [93], namely the short simulation times (10 ps) and the absence of directional or covalency forces in the interatomic potentials.



Figure 2.3: Temperature dependence of the viscosity in B_2O_3 . The line, taken from Ref. [87] is a graphical interpolation of actual data points [85]. Note that there exist several other sets of experimental data [85, 87, 88, 89, 90, 79], for which absolute values can differ by up to an order of magnitude; the trends are however identical to the one illustrated here.

Incorporation of 3-particle interactions in the MD simulations were then considered [99, 100, 101, 102, 65, 103, 104, 105, 106, 107] by various groups with however varying degrees of success. In most cases, these interactions were modelled in the form of a B-O-B and/or O-B-O bond bend term. In some cases, 4-particle interactions in the form of a torsion angle were also added [103, 108, 109]. The proportion of boroxols obtained in these works vary from 0 to 53 % (with however some structural flaws in all cases). Higher amounts were obtained when using biased sampling [110] or *tweaked* initial configurations [66].

No boroxols at all were found in the simulations of Verhoef and Den Hartog [100, 101]. Their simulated structures do not compare favourably with either the neutron or x-ray diffraction data. Calculated infra-red spectra were claimed to reproduce the most salient features (although the explicit comparison with experiments was not provided). Raman spectra were calculated using a bond polarisability model and showed a peak at ~ 870 cm⁻¹ arising from the BO₃ breathing mode, which the authors identify with the experimental peak at 808 cm⁻¹, although the calculated peak is a factor 10 too large [100]. Subsequently [102], the authors went as far as to reinterpret the Raman data in isotopically substituted samples [39] despite the poor agreement of their calculations with experiments (not even shown in [102]). One should further note that these potentials give poor results in the crystalline phases, in particular regarding the B-O-B bond angles [65].

In order to improve the agreement with the experimental static structure factor, Bermejo et al. [104, 105] proposed a refinement of the two- and three-body terms initially constructed by Verhoef and Den Hartog [101]. The addition of a four-body term was also considered [108]. However, the obtained data still show some drastic mismatch with the experiments, in particular for values of the scattering vector q below 5 Å⁻¹. The authors reported that a nearly perfect match could be obtained on either the low- or high-q range but never simultaneously on both ranges. With potentials limited to three-body interactions [104, 105], no boroxols were detected while a small amount, f = 3.6 %, was obtained in the simulations involving the four-body term [108]. In our opinion, not only may these potentials suffer from intrinsic limitations due to e.g. their analytical form, but also may there be an even stonger bias in the strategy used for the equilibration. Indeed, the liquid was equilibrated with only twobody interactions down to a temperature as low as 900 K (i.e. quite close to the experimental glass transition temperature, 540 K, and very likely well below the numerical glass transition temperature corresponding to the quenching rate actually used in the simulations) and only afterwards were the higher-order interactions switched on for a limited time (100 ps). Within such a short time, and given the extremely slow dynamics at these temperatures (see Figs. 2.3 and 2.5), the system is unable to re-equilibrate and thus the rings are unlikely to form, even if their presence is favoured by the higher-order interactions.

Still with a potential of 3-body type, the first MD simulation for which the presence of boroxols was reported is actually that by Inoue et al. [99]. The predicted B-O-B bond angles distribution (peaked at 120 °) is in much better agreement with the experimental value (~ 130 °), derived indirectly from x-ray scattering [55] and from NMR [42], than in the previously mentioned MD [93, 95, 68, 101] (~ 150-160 °). The obtained number of boroxols in the glass, f = 23 %, is however too small and the reason was attributed to the too high quenching rate (2.3 10¹⁴ K.s⁻¹).

Later, Takada and co-workers [111, 65, 103] put the emphasis on constructing interatomic potentials from the crystalline phases which are transferable to the vitreous one. The two known polymorphs [112, 113] were used: B₂O₃-I, which is made of corner-shared BO₃ triangle units (i.e. three-coordinated boron atoms, ^[3]B, and two-coordinated oxygens ^[2]O) and B₂O₃-II, which involves BO₄ tetrahedral units (four-coordinated borons, ^[4]B, and a mixing of both two- and three-coordinated oxygens, ^[2]O and ^[3]O). A series of potentials were parametrised using the energy surfaces from Hartree-Fock calculations [65, 103]. In addition to three-body (and in some cases four-body) terms, the introduction of coordinationdependent terms was proposed for the two-body potentials. More specifically, these latter terms depend on the oxygen coordination (^[2]O or ^[3]O) [103]. Regarding the boroxols, significant amounts were obtained, from f = 25 to 53 %, depending mostly on the potential but also on the statistical ensemble (*NPT* or *NVT*) [103]. However, two serious problems arose: using *NPT* simulations, the final glass densities were significantly underestimated (from -10 to -36 %) while using *NVT* simulations at the glass densities led to the formation of unrealistic coordination defects, such as ^[4]B or ^[3]O, in small but sizeable amounts (1-6 %). Thus, the authors pointed out the difficulty to realise simultaneously a high proportion of boroxol rings and the experimental density.

A significant contribution of Takada et al. [65, 66] is the hand-made construction of B₂O₃ crystalline structures with high boroxol contents, obtained from topological modifications of related compounds such as HBO₂-III or Cs₂O-9B₂O₃. The obtained crystals were shown to have structural and vibrational characteristics similar to those of the glass [65]. In the initial report [65], the models densities were still lower than that of the glass. However, additional polymorphs were subsequently generated with the same strategy [66] and among them, one with a density of 1.85 g.cm⁻³ and f=75 %, which are the typical values expected for the glass. The next section will show a detailed testing of this model using *first-principles* calculations. Still a bit later [110], Takada followed a different route to produce a glass model of B₂O₃ by using a hybrid MD/MC simulation scheme: the MC part is used to bias the acceptance of boroxol rings and the obtained structures are then relaxed within MD simulations using the potentials that were constructed in earlier works [65]. A genuinely amorphous structure of 1500 atoms could be obtained with f = 74 % at the glass density. However, this model, although providing a very good match of the experimental structure factor, was found by the present author to be unstable when relaxed within *first-principles* calculations (unpublished work).

Cormack used a coordination-dependent 2-body potential supplemented by three-body terms [107, 114], slightly modified from Takada's potential. A value of $f \sim 15$ % was obtained. A discrepancy with the experimental total radial distribution function in the region around 3.7 Å was noted and seen as an indication of a too small value of boroxol rings in the simulations. The origin was ascribed to finite-size effects (systems of 1010 atoms at the most were used) and possibly to the glass-forming process [107].

A different route to incorporate the many-body, non-additive interactions comes from polarisable models [72, 115, 116, 117, 23]. A first attempt in this direction was made by Teter [72] who used a simple representation of the oxygen polarisation by assigning four auxiliary charges in tetrahedral symmetry to each oxygen ion. The parameters were calibrated from *ab-initio* calculations using the LDA exchange-correlation functional. Within this crude representation, the proportion of boroxols was found to increase from 1 to 12 % as the magnitude of the auxilliary charges was increased from zero. However, it should be noted that the resulting glass does incorporate coordination defects which do not exist in the experimental glass. This is likely a reflection of the flaws of the LDA functional which

uncorrectly predicts the high pressure crystal (B_2O_3 -II) to be more stable than B_2O_3 -I (as visible in Fig. 3 of Ref. [72]). Note that the work of Teter [72] is sometimes quoted to be of *ab-initio* type [69, 67], although this is actually not the case: this is an empirical model whose parameters have been calibrated from *ab-initio* calculations. To the best of our knowledge, this is the only MC study of B_2O_3 (apart from the hybrid MD/MC simulation of Takada [110]).

A more realistic representation of polarisability was then provided by the group of Maranas et al. [115, 116, 117]: this model incorporates induced dipoles arising from charges and from other induced dipoles on oxygen atoms. The polarisation effects of oxygen atoms were found to be important: in particular, boron atoms within boroxol rings were found to have a slightly lower energy than those outside of the rings and this effect originates from the polarisation part of the potential [115]. This is a crucial findings confirmed very recently in our own works using other types of polarisable forcefields [118, 23] (see section 2.7). Regarding the glass preparation, Maranas et al. used an original yet fancy protocol aimed at simulating the formation of the B_2O_3 network from the dehydration of boric acid, H_3BO_3 : forces were imposed so as to act as semipermeable membranes that selectively pass or block individual atomic species, thus creating, according to the authors, a chemical reactor containment vessel [115]. On one hand, this is an interesting procedure in the sense that it gives some control over the network formation in particular through the temperature of dehydration and equilibration. On the other hand, the dehydration of boric oxide is the route usually followed experimentally to obtain the crystalline phase B_2O_3 -I, rather than the glass. In any case, the formation of boroxols was observed and interestingly, the amount of rings was found to depend upon the temperature during the network formation. More specifically, two procedures were used in which after a high temperature run (used for dehydration) and prior to the final cooling, the sample was held at either 2000 K or 1800 K for about 100 ps (i.e. until a network of BO_3 units had formed). The proportion of boroxols varies from about 8 to 33 % depending on whether the sample is quenched from 2000 K or from 1800 K. The authors pointed out that the latter value is consistent with experimental estimates [75] (40 % at 1000 K^2 . I however note that the values claimed are subjected to some ambiguity since some of the boron atoms are not three-coordinated as they should because of the method used in the simulations to form the glassy network [115]: the 8 and 33 % values, obtained when considering the ^[3]B atoms only, become respectively 3.75 and 15~% if taking into account all the boron atoms in the simulated samples. This modest increase may not be statistically significant given the small total number of boron atoms (81). However, the authors further show that as the temperature is decreased below 2000 K, ring structures become energetically favoured (by 1.6% at about 1800 K). In summary, the authors conclude that boroxols form at temperatures less than about 2000 K. Using a higher preparation temperature prevents the formation of rings; as soon as the network is formed, ring formation won't occur even if the system is subsequently cooled into the favourable range, perhaps because of an energy barrier or kinetic limitations for the transformation within the network. They also note that the temperature range over which the glass transition is observed in their simulations, 1500 - 3000 K, is significantly displaced from the corresponding experimental range (500 - 1200 K). This was expected in light of the very short simulation times [115]. I strongly adhere to these conclusions which are fully supported by the *first-principles* simulations detailed in the next section. One can regret however that the performances of the polarisable potentials of Marana et al., regarding e.g. the structure [115] or the dynamics [116], were never assessed by any comparison with experimental data.

The potentials developed recently by Kieffer et al. [67, 119, 120] combine coordination-dependent and charge redistribution features in addition to explicit three-body terms. Both two- and three-body interactions depend on the effective number of nearest neighbours of an atom. A charge transfer term controls the extent of charge polarisation in a covalent bond, as well as the amount of charge transferred between atoms upon rupture or formation of such a bond. Conditional three-body terms,

²The incorrect 32 % value quoted in [115] actually corresponds to f_{at} in [75], thus to f = 40 %.

i.e. which depend on the degree of covalency in atomic interactions, constrain both B-O-B and O-B-O angles. The potential parameters were parametrised so as to match structural and vibrational data for the liquid and crystal phases. The authors used the methodology of Takada to produce an initial glass structure having f = 75 % at the glass density [66]. This structure was equilibrated at 2500 K, under which conditions the boroxols gradually dissolved. Thus, by heat treating the system for various periods of time (up to a nanosecond), liquid structures having f = 75, 63, 50 and 10 % were generated and quenched (at a rate of $2.5 \ 10^{12} \ \text{K.s}^{-1}$). No additional boroxols were generated upon cooling, and here again this was attributed to the fast quenching rates [67]. The resulting densities vary from 1.75 to 1.81 g.cm⁻³ in good agreement with the experimental values. The static structure factors for both the f = 10 and 63 % glasses were shown to reproduce very well the experimental data [67, 121]. Another interesting findings of this study is the possibility to generate a new polymorph, B_2O_3 -0 but the presence of larger rings, which can be either *puffed* or *puckered* were related to the thermomechanical anomalies of B_2O_3 (i.e. the existence of a minimum in the mechanical modulus in the molten state) [67, 121].

Using a potential with three- and four-body terms, Kashchieva et al. [109] intended to explore the effects of cooling rates and of system sizes. They reported results for 10 systems from 100 to 2000 atoms and used, for each of them, two cooling rates differing by 2 orders of magnitude, respectively 3.3 10^{12} and 3.3 10^{10} K.ps⁻¹, between 1300 and 300 K. With the *fastest* cooling rate, a low value $f \sim$ 10-15 % was obtained for all glasses, with no apparent size-dependency. With the *slowest* cooling rate, a maximum value of $f \sim 33$ % was obtained for the 400 atoms system and an almost linear decrease down to $f \sim 17$ % for the larger systems sizes. In my opinion, this latter trend is due to an incomplete relaxation of the larger systems: indeed a strictly equivalent simulation time (800 ps at $1300 \text{ K} + 30\ 000 \text{ ps}$ from 1300 to 300 K) was allowed for each system irrespectively of their sizes, whereas it should be larger for bigger systems. This is supported by the results obtained for the density: with the *fastest* cooling rate, a much too low density (~ 1.64 g.cm⁻³) is obtained with no sizedependency beyond statistical errors whereas with the *slowest* cooling rate, one observes an (almost linear) decrease from reasonable values ($\sim 1.77 \text{ g.cm}^{-3}$) for the smallest systems down to much poorer values ($\sim 1.68 \text{ g.cm}^{-3}$) for the larger systems. Thus, this study is rather an additional illustration of the importance of the sampling given the slow rate of appearance of boroxols at low temperatures: a too fast quench (on a small system) has the same detrimental consequences than has an improper equilibration (of a big sample). In my opinion, finite-size effects per se are likely not a crucial issue at least for the quantity of interest here, f. In their structural and thermomechanical study, Kieffer et al. [67] noted no size-dependency in excess of statistical errors for systems of 640 and 2560 atoms [67].

First-principles molecular dynamics (FPMD) simulations, based on the density functional theory (DFT), were recently applied to B₂O₃ by different groups [41, 19, 17, 18, 122, 123, 124]. The obtained proportion of rings in the glass, quenched from the melt, varies from about 6 [18] to 22 % [19]. The first report, that of Umari and Pasquarello [41], actually revived the controversy [69]. While the configuration obtained from the liquid quench contained only 9 % of boroxols, strong evidences were provided from Raman and ¹¹B NMR analysis that the *true* value should be ~ 75 % (the Raman peak at 808 cm⁻¹ being underestimated and the population ratio being incorrect in the NMR spectra) [41]. However, this extrapolation has been immediately criticised by SB [69]: these authors argued that a) it is difficult to estimate f from calculated Raman spectra b) the Raman peak at 808 cm⁻¹ is actually consistent with f = 11 % (Teter's argument [72]) c) other techniques such as NMR are not directly sensitive to f d) they have shown, using RMC simulations, that it is not possible to produce boroxol-rich models which would simultaneously reproduce the experimental density and the diffraction data. I have already mentioned that the argument d) is actually denied by different works which came either before [61] or after [67, 19, 125] its formulation. Regarding the points a), b) and c), it is a fact that

some underlying assumptions (such as the proportionality of the Raman signal with f) behind the indirect determination [41] were arguable. However, we subsequently provided a boroxol-rich model able to reproduce all the experimental information within a *first-principles* scheme [19]: this work answers all the previous criticisms made by SB [69] and is detailed in the next section.

Finally, Salanne et al. recently devised several types of polarisable models [23, 24] which parameters were calibrated using previous *first-principles* calculations [19]. The performances of these models are described in detail in section 2.7.

Other modelling studies not relying on interatomic potentials include the statistical model of agglomeration of Micoulaut et al. [126, 127]. With a boroxol formation energy of 5.3 ± 0.7 kcal/mol as a fitted parameter, a boroxols proportion of 83 % was predicted.

Thus, although the MD results in the literature are scattered, several preliminary conclusions can already be drawn. The inclusion of many-body interactions is mandatory in order to generate boroxol rings. The origin of the rings' stabilisation is to be found in the oxygen polarisation. However, this does not mean that the potential should explicitly be polarisable since polarisation effects may be accounted implicitly by, e.g. angular three-body terms or by an additional rings stabilisation term.

The incorporation of many-body effects is of course a necessary but not sufficient condition. As important as the *goodness* of the potential, is the glass formation process. This has been stressed in the majority of the studies reviewed above. The problem comes from the fact that in B_2O_3 , the marked structural change accompanying the increase of f as the liquid is cooled is occurring just a few hundreds of Kelvin prior to the glass transition (Fig. 2.2): most of this change occurs in a temperature range where the viscosity is dramatically increasing (Fig. 2.3). Thus, following numerically this change is extremely challenging for atomistic simulations since this requires an increase in the simulation time by several orders of magnitude.

Typically, at 2000 K, the viscosity is of the order of 1 Pa.s, a value comparable to that of oil, and from our own experience (see Fig. 2.5) it requires simulations times of at least 100 ps to escape from the caging regime (and thus to enter in the diffusive regime). Even with a nanosecond timescale, the lowest temperature that can be explored ergodically is ~ 1800 K. At this temperature, f is typically 20 % or less (Fig. 2.2) whereas to get a chance to observe rings proportions greater than 50 % would require an extensive sampling at about 800 K. However, should the simulation time scales proportionally to the viscosity, an increase of at least 3 orders of magnitude would be needed from 1800 to 800 K. Note that this is a minimal estimate, only accounting for the time needed to reach the diffusive regime. Longer simulation times may be needed for a full structural relaxation. Indeed, the rings stabilisation energy being quite small (of the order of 5-10 kcal/mol), the system may stay trapped for long times in high energy configurations before a new basin is found (corresponding here to a network re-organisation to a more boroxol-rich configuration).

The time scale of all the simulations reviewed above is typically a 1 ns or less. With only one exception [109], the quenching rates are in the range 10^{12} - 10^{14} K.ps⁻¹. Such time scales give rise to high fictive temperatures, typically above 1500 K which are thus considerably displaced from the corresponding experimental temperatures. It is therefore no surprises that the values reported for f rarely exceed 30 %, the value expected for a stuctural arrest at 1500 K (Fig. 2.2). In my opinion, the values reported from the various MD studies are better understood when taking account the time spent in the *mildly high* temperature range, i.e. in between the onset of rings formation (≤ 2000 K) and the lowest temperature that could be sampled ergodically within the afforded time (≥ 1500 K) before the structural arrest occurs. This is further supported by reporting the f values obtained from the various MD studies *not* at the final temperature (usually the room temperature) but at the lowest temperature sampled prior to the final quench (thus assuming that the quench is essentially instantaneous). As seen in Fig. 2.4, there is an overall good match between the simulated and experimental values. I stress however that there are cases where such a report is difficult to made and thus subjected to some



Figure 2.4: Values for the proportion of boroxol rings, f, reported from various MD simulations studies [99, 103, 114, 115, 67, 19], indicated by the first author's name. The solid lines represent graphical interpolations of experimental data [73, 74] while the dotted lines are extrapolations of these data to temperatures higher than those actually measured, using the formulas given in [73, 74] (see also the caption of Fig. 2.2). Lozenge symbols indicate values from simulations obtained in the liquid phase which are therefore directly comparable to the experiments. Values shown by stars were initially reported in the glass at 300 K but are represented here at the lowest temperature prior to the final quench (see text).

ambiguities. Further, a proper quantitative comparison with the experiments would require some corrections to be accounted for, in particular for the density mismatch or the residual pressure in the simulated models [128]. I thus intend this comparison to be qualitative. Notwithstanding, Figure 2.4 shows that some force-fields in the literature may be good enough. Contrary to the prevailing belief, some potentials might even tend to *over-estimate* the proportion of boroxols. Now that classical force-fields of quality comparable to *first-principles* ones are available ([23, 118], see section 2.7), I think that the efforts should be put on longer sampling and/or better glass processing. It thus would be very desirable to use methods allowing for accelerated dynamics, such as e.g. metadynamics (using the rings proportion as an order parameter) [129, 130]. A proposal in this direction is presented in section 3.3. Alternatives to the standard *quench-from-the-melt* procedure such as *bond switching* [131] methods could also be of high interest.

2.2 Assessing the proportion of boroxols from *first-principles*

As seen previously, doubts about the boroxol-rich model have been expressed from time to time in the literature, the latest being that of SB [69]. In order to provide clear-cut answers we recently assessed the performances of models with varying amount of boroxol rings, within a *first-principles* scheme [19].

Unless stated otherwise, the calculations³ were carried out using the SIESTA code [134]. The electronic structure is described within a generalized gradient approximation to density functional theory using the PBE functional [135].

³We used norm-conserving pseudopotentials [132] and DZP basis sets. The real-space grid was defined by a 280 Ry cutoff. The basis quality has been extensively tested by comparing the results with those from fully converged plane-wave basis sets (mostly using the CPMD code [133]): the systems used for benchmarking included known borate crystals [15] as well as pure B_2O_3 liquid. The time step in the MD simulations is 1 fs.



Figure 2.5: Mean-squared displacement (MSD) obtained from the *first-principles* MD simulations in liquid B_2O_3 . Left: oxygen and boron MSD at temperatures of 4000 and 2000 K for a density of 1.84 g.cm⁻³ (corresponding to the glass density at 300 K). Right: boron MSD at 2000 K for densities of 1.84 and 1.49 g.cm⁻³. The latter density is that of the liquid at ~ 2000 K.

Before discussing the glass structure, results in the liquid phase are briefly reported. Several conditions of temperatures and densities were explored in the NVT ensemble, using system-sizes of mostly 100 atoms (up to 320 atoms). Let's first consider liquid simulations at the glass density (1.84 g.cm⁻³), as it is quite common in the literature to use NVT simulations at the final target density.

Figure 2.5 shows the mean-squared displacement of the atoms at various conditions. As seen in the left panel, a severe slowing down of the dynamics is occurring as the temperature is lowered from 4000 to 2000 K: whereas it takes about 1 ps to reach the diffusive regime at the higher temperature, a much longer time of the order of 100 ps is needed at 2000 K to escape from the caging regime. The diffusion coefficient, obtained from the slope in the diffusive regime, is reduced by more than 2 orders of magnitude in this temperature range. As a measure of the equilibration time, let's define, following Ref. [136], τ as the time at which $\sqrt{\langle r_O(t)^2 \rangle} = 5.6$ Å, i.e. the average time it requires for an O ion to move twice its diameter of 2.8 Å: τ is ~ 5.8 ps at 4000 K and ~ 650 ps at 2000 K. This sets up a typical time scale for the simulations: ideally one would like to simulate over several τ for a reliable (i.e. ergodic) sampling of the liquid. It is seen here that the value of τ obtained at 2000 K is already quite demanding for *first-principles* MD simulations within present-day's computational resources. Even for a classical force-field, it seems rather challenging, at least in the near future, to sample temperature conditions lower than, say 1500 - 1800 K, given the exponential increase of the viscosity with decreasing temperature (Fig. 2.3).

In any case, the instantaneous evolution of the boroxols proportion, f, along a liquid simulation of 300 ps at 2000 K (and at the glass density, 1.84 g.cm⁻³) is shown Figure 2.6. Significant fluctuations are observed between 0 and 30 %, the average being $\langle f \rangle \sim 9$ %. Several quenches to 300 K were branched from the simulation at 2000 K, using quenching rates in the range 10^{13} - 10^{14} K.ps⁻¹. The value of f in the glassy samples shows dependency upon the starting liquid configuration; however no (or marginal) change with temperature was observed (beyond that expected from the liquid trajectory, Fig. 2.6). This reflects that the system is unable during the quench to escape from the liquid initial *inherent structure*. In the following, one of the obtained glassy samples, containing f = 22.5 %, is used for a more detailed study: it is herefater referred as the boroxol-poor (BP) model.

A final note about the liquid is made regarding the statistical ensemble. Experimentally the density of B_2O_3 increases from ~ 1.5 to 1.84 g.cm^{-3} as the temperature is decreased from 2000 to 300 K and this variation should be accounted for during the numerical quench. Thus in principle the *NPT* ensemble



Figure 2.6: Instantaneous evolution of the boroxols proportion f, in the liquid at 2000 K and $\rho = 1.84$ g.cm⁻³. The density is that of the ambient glass.

in which the system's volume adapts itself to the target temperature and pressure should be favoured. However, given the small systems sizes affordable within FPMD simulations, the pressure is hardly well estimated and in practice this results in poorly driven volumes. Thus, FPMD simulations are commonly realised in the *NVT* ensemble all along the quench using the glass density. However, this induces a bias since the liquid prior to the quench is then simulated at a too high density, resulting in a net residual pressure which, in B₂O₃, is of the order of 1 GPa⁴. Now it should be reminded that high pressure conditions are unfavourable to the presence of boroxols (see later Fig. 2.33) [77, 138, 78, 80, 81, 23]. To check the magnitude of this bias, simulations at 2000 K at the corresponding liquid density (~ 1.5 g.cm⁻³) were carried out. The average proportion of boroxols < f > increases from ~ 9 % at the glass density to ~ 22 % at the liquid density (see Fig. 2.24 in section 2.5). This variation is slightly above the error bars ($\pm 7 \%$, as defined by the root mean square of the distributions of f): this shows the importance of being at the *correct* equilibrium density (or at zero-pressure conditions) [128].

Note that the dynamics are even more sluggish at the *actual* liquid density (Fig. 2.5, right panel): the relaxation time τ previously defined is estimated to be ~ 2300 ps. In other words the viscosity decreases with increasing density: this behaviour, albeit *anomalous* is well known in silica and water and has been recently discovered in B₂O₃ [139, 123, 124, 79].

In summary, the results obtained from the FPMD simulations in the liquid phase essentially confirm the findings from others authors which were summarised in the previous section. At this point, it is rather clear that glassy structures obtained from conventional numerical quench are doomed to underestimate f given the affordable simulation times. We thus sought for a glassy model produced by an alternative method [66] which has both f = 75 % and the correct glass density. This model was originally constructed by Takada et al. [66] from topological modifications of the Cs₂O – 9B₂O₃ crystal structure so as to remove the ceasium atoms and delete/create some bonds, this low-alkali compound being the closest known analogue to the v-B₂O₃ structure. It has been used in other MD studies [66, 140, 67, 23] using empirical force-fields and subjected in our work [19] to *first-principles* MD simulations at 300 K on systems containing 80 and 320 atoms (for durations of 20 ps). No size-effects were observed and the obtained structures are hereafter referred as the boroxol-rich (BR) model.

⁴Another source of errors in DFT-based calculations comes from the exchange-correlation functional used (which is an approximation of the unknown exact one). Gradient-generalised approximation (GGA) based functionals, such as PBE [135] used here, tend to overestimate the equilibrium volume and thus lead to positive residual pressures in simulations at the experimental density. This problem is significantly reduced in some recently proposed functionals by the incorporation of van der Waals contributions. However, no systematic nor significant variation of $\langle f \rangle$ (beyond the statistical error bars, \pm 7 %) were observed in the liquid phase using the PBE-D2 [137] functional.



Figure 2.7: Boron-boron, boron-oxygen and oxygen-oxygen partial radial distribution functions obtained at 300 K for the boroxol-poor (BP, f=22 %) and boroxol-rich (BR, f=75 %) models. Interatomic distances more pronounced in the BR model are highlighted.

Figure 2.7 shows the partial radial distribution functions obtained for the BP and BR glassy models. Note that the B-O and O-O first peaks (at $r_{BO} \sim 1.37$ and $r_{OO} \sim 2.37$ Å, respectively) are almost identical in both models. The main differences lie in the shape and the position of the B-B first peak, which is sharper and shifted to shorter distances, by about 0.1 Å, in the case of the boroxol-rich model. Other less marked differences include more prominent peaks in the BR case, at ~ 2.75 Å in the B-O partial and at ~ 4.1 Å in the O-O partial. These differences reflect the greater coplanarity of the BO₃ triangles in the BR model. The former peak arises from oxygen second neighbours (of boron atoms) within a same ring (at a position $\sim 2 \cdot r_{BO}$) [57]. However, as mentioned by SB [60], the peak at \sim 3.6 Å in the B-O partial is only slightly different for BR and BP models and thus is a poor signature of the boroxol rings proportion contrary to previous claims [57].

The O-B-O and B-O-B bond angular distributions are shown in Figure 2.8. The former one is a single symmetric peak centered at $\sim 120^{\circ}$ and is essentially similar for both models, albeit slightly narrower in the BR case. The B-O-B distribution, which is related to the connection between the BO₃ units, shows a much wider spread from ~ 110 to 170 ° and differs for each model. In the BR model, a sharp peak at $\sim 120^{\circ}$ and a shoulder-like contribution from $\sim 130^{\circ}$ are visible. The former contribution arises from triplets within the boroxol rings while the shoulder corresponds to oxygens bridging different units. In comparison, the BP model shows a redistribution from the 120 to the 130 ° region as a result of the smaller amount of rings.

To gain deeper insights, a structural analysis was carried out according to the different atomic sites. There are two possible sites for boron atoms: *inside* or *outside* a boroxol ring. For oxygens, up to 4 different sites, labelled A, B, C, D in Ref.[45] can be defined (see Fig. 2.9). The results, which are similar in both BP and BR models, are summarised schematically in Fig. 2.9. A non-ring BO₃ unit has three slightly nonequivalent B – O bonds of average length ~ 1.37 Å and three O – B – O angles of $\sim 120^{\circ}$. A boroxol unit has 6 larger *internal* B – O bonds (~ 1.38 Å) and 3 shorter *external* bonds (~ 1.36 Å). B – O – B angles *internal* to the rings equal $\sim 120^{\circ}$ while these angles for oxygens which



Figure 2.8: O-B-O and B-O-B bond angular distributions obtained at 300 K for the boroxol-poor (f=22%) and boroxol-rich (f=75%) models.

Figure 2.9: A schematic 2D representation of the different atomic sites encountered in the simulations of v-B₂O₃. The structural values reported are those obtained with the PBE functional. Boron atoms are shown as small (gray) balls while oxygens are big (red) balls. Up to 4 different types of oxygen environments (A, B, C, D) can be identified.



are bridging different units (B, C, D) tend to be much larger, ~ 133 °. Although the absolute values of the reported angles and interatomic distances slightly vary with the exchange-correlation functional used in the simulations, the mentioned trends were found to be independent of this choice.

The static structure factor is an obvious first basic test of the models. It is computed here for both models from the density fluctuations in Fourier space and compared to available neutron diffraction data in Fig. 2.10. As can be seen, both models reproduce very well the experimental data in the whole q range available, including the so-called first-sharp diffraction peak (FSDP) at ~ 1.6 Å⁻¹. A very slight overstructuration and a frequency misfit are visible at high q for both models which result from the well-known tendencies of GGA functionals such as the one used here (PBE) to overestimate the bond lengths (by typically 0.01 Å). However, given the absence of free-parameters in the simulations, the agreement is quite good. From this sole comparison, no superiority of either model can be evidenced, confirming that the total structure factor is not a good probe of f, as already mentioned in other works [67, 41]. The same conclusions hold when considering the x-ray structure factors (not shown).

This is in contrast with the results of SB [60]: boroxol-rich models generated from RMC simulations were shown to give a slightly but significantly less good agreement than boroxol poor models as a result of some structural artifacts in the former ones. These artifacts, mainly visible as an unrealistic peak



Figure 2.10: Static neutron structure factors calculated for the boroxol-poor (f = 22 %) and boroxol-rich (f = 75 %) models compared to the experimental data [57].

at $\sim 50^{\circ}$ in the O-B-O and dihedral angle distributions, were due to significant distortions of the rings from planarity in boroxol-rich models. According to SB [60], these distortions were the result of the imposed constraints in the model generation procedure to simultaneously reproduce the diffraction data and the glass density. We stress however that none of these artifacts were observed in our BR model (while it was produced at the correct glass density). Thus, these artifacts are certainly not specific of BR models but instead were due to the method used in Ref. [60].

In any case, our work clearly invalidated the claim that it is not possible to simultaneously reproduce the diffraction data and the density for high values of f [60, 69]. This has been further confirmed in a recent investigation by Soper [62, 125], using the empirical potential structure refinement (EPSR) method, a variant of RMC which makes use of potentials in the fitting procedure. The work of Soper [62, 125] complements ours by providing larger models (2000 atoms), which were not made from any underlying crystalline network. The desired amounts of boroxols were introduced ad-hoc and, again, a very good representation of the diffraction data (including simultaneously x-ray and neutron data) could be obtained from a large range (f = 5 to 80 %) of structural models [62, 125]. Although still not perfect, the agreement with experiments was even better than those shown in Fig. 2.10 since EPSR (as RMC) is by construction designed to provide the best possible fits, thus removing the systematic discrepancies due to incorrect interatomic distances as typically obtained in a fixed forcefield simulation. However, the main point here is that a similar level of agreement could be obtained for any type of model, precluding the possibility to distinguish them from diffraction information alone.

Unfortunately, in the case of B_2O_3 only the (neutron and x-ray) total structure factors have been measured and no partials are available. We provide however in Fig. 2.11 a comparison of the neutron weighted Faber-Ziman partials obtained from our models. It is seen that the differences are very tiny and essentially limited to a small frequency shift in the B-B partial. Clearly, a quantitative assessment of f is unlikely to be made from these measurements.

NMR has been extensively used in borates (see [141] for a review) and has played a key role for assessing the existence and proportions of different sites in both crystals and glasses [142, 143, 82, 144].



Figure 2.11: Static neutron partial structure factors calculated for the boroxol-poor (f = 22 %) and boroxol-rich (f = 75 %): O-O, B-O, B-B. The total signals are also shown (bottom right panel).

In v-B₂O₃ in particular, the NMR various techniques (among which ^[11]B MAS, ^[11]B DAS and ^[17]O DOR) have been essential tools for the quantitative determination of the proportion of atomic sites in boroxol rings [42, 44, 45, 46, 47, 50, 19, 145, 146, 147]. Because of their locally different environments, the B and O atoms which are constituents of the rings and those which comprise the non-ring units give rise to different contributions [51, 52, 148] which are, in most cases, readily observable experimentally.

We therefore tested our BP and BR models by computing ^[11]B DAS and ^[17]O MAS spectra⁵, shown in Fig. 2.12. For both ^[11]B DAS and ^[17]O MAS spectra, it is clear that the BR model provides a significantly better representation of the experimental data [44, 45] than the BP one. This is most evident in the ^[11]B DAS comparison and this better agreement is not fortuitous, as revealed by a closer inspection of the contributions from nuclei inside or outside the boroxol rings. These contributions give rise to significantly different NMR signatures as a result of the NMR sensitivity to the O-B-O and B-O-B angles. While the O-B-O angle distribution is essentially the same for in- and out-of rings sites, the B-O-B one differs: average values of ~ 120 and ~ 130 degrees were obtained respectively as shown before, Fig. 2.9. Thus, the NMR observables provide stringent tests of the models' bond angle distributions and an indirect but quantitative way to access the value of f. Although this sensitivity had been exploited before, the present comparison provides the first direct confirmation of the adequacy of boroxol-rich models and they confirm the earlier claims made from the indirect analysis of Umari and Pasquarello [41].

One could also think of using local spectroscopies such as the X-ray absorption spectroscopy (XAS)

⁵The NMR chemical shifts and electric field gradients were calculated within the Gauge Included Projector Augmented Wave formalism as in [149] using the PARATEC code. DAS and MAS NMR spectra of the central transition $(-\frac{1}{2} \leftrightarrow \frac{1}{2})$ were simulated taking into account both the quadrupolar and chemical shift interactions as described in [150] and including spinning sidebands.



Figure 2.12: Top panel: ^[11]B DAS (isotropic projection) NMR spectra obtained for the boroxol-poor (f=22 %) and boroxol-rich (f= 75 %) models compared to the experimental spectrum [44]. Contributions from nuclei inside or outside the boroxol rings are shown as dashed lines. A Gaussian broadening of 100 Hz is applied.

Bottom panel: ^[17]O MAS NMR spectra obtained for the boroxol-poor (f=22 %) and boroxol-rich (f=75 %)models compared to the experimental spectrum [45]. Contributions from nuclei inside or outside the boroxol rings are shown as dashed lines. A Gaussian broadening of 100 Hz is applied.

or the Inelastic X-ray Spectroscopy (IXS). These techniques are sensitive to the very local environment of the excited atom and, close to the absorption edge, to the electronic structure. We carried out calculations at both the boron and oxygen K-edges using the XSPECTRA module of the QUANTUM ESPRESSO package [151]. As in germanates [152], we found that the spectra showed signatures related to the triplet angles involving the absorbing atom: small differences between the BP and BR models were obtained at the O K-edge, as a result of the differing B-O-B angles distributions while essentially no differences were obtained at the B K-edge, as a result of the similar O-B-O angles distribution. In any case, the differences were found to be much smaller than the experimental resolution of presently available data [153, 154].

We now turn to the vibrational properties. The phonons were computed at the Γ point only from the finite-displacement method using the CPMD program [133]. The obtained vibrational density of states, v-DOS, for both models are shown Fig. 2.13. Despite the relatively poor statistics due to the limited number of atoms, several differences are apparent. In particular, the BR model shows a much marked contribution at ~ 800 cm⁻¹ as could be anticipated. The analysis of the modes from our calculations reveals that the contributions at this energy result solely from the breathing mode of the oxygens inside the boroxol rings, as already well established by previous works [39, 41]. Other noticeable differences are visible in the regions 100-200, 400-500, 650-800, 1100-1300 cm⁻¹.

The infra-red and Raman intensities were calculated as in [156] using the PWSCF code, part of

Figure 2.13: Vibrational density of states obtained for the boroxol-poor (f=22 %) and boroxol-rich (f=75 %) models.



the QUANTUM ESPRESSO package [151]. The Raman spectra obtained for the BP and BR models, Fig. 2.14 are drastically different, in particular regarding the intensity of the peak at ~ 800 cm⁻¹. The area under this peak is found to be proportional to f, validating a posteriori the hypothesis made in [41] (note that it is f_O which is actually probed and $f_O = \frac{2}{3}f$). Thus, while it is true that the marked enhancement of this peak as compared to the other modes is due to a scattering-matrix enhancement effect (as seen from comparing Figs. 2.13 and 2.14), it is also true that it can be reliably used as a measure of f: there are no significant non-linear effects in the range f = 22.75 %. The area of this peak is dramatically underestimated in the BP case whereas it matches the experimental one in the BR case within the error bar associated to this comparison (9 %, thus $f_O = 50 \pm 9$ % and $f = 75 \pm 15$ %). Note that the superiority of the BR model is not limited to this peak but is also apparent in the frequency regions 400-600 and 1200-1300 cm⁻¹. Contributions in the latter region have been attributed to modes involving the connection of the boroxols with the rest of the network [75]. We point out that, to our knowledge there are no models in the literature which agree at this level of accuracy over such a large frequency range.

As compared to Raman, the IR calculations, Fig. 2.15, show a deceptively small variation with the models: both reproduce reasonably well the experimental data, the BR model being however slightly superior in the region 1200-1300 cm⁻¹. This shows that the vibrational modes probed by IR are mostly not sensitive to f and should not be used to assess the model quality, contrary to the claims made in [100, 101, 102]. Note that the present level of agreement with experiments is unprecedented and much superior to that shown in [100, 101, 102].

From the 3N vibrational modes ω_i , it is easy to compute at any temperature the heat capacity at constant volume within the harmonic approximation:

$$C_{v}(T) = \sum_{i}^{3N} k_{b} \left(\frac{\hbar\omega_{i}}{k_{b}T}\right)^{2} \frac{exp(\frac{\hbar\omega_{i}}{k_{b}T})}{(exp(\frac{\hbar\omega_{i}}{k_{b}T}) - 1)},$$
(2.1)

where k_b is the Boltzmann constant. As a benchmark calculation, we show Fig. 2.16 (left panel) the obtained C_v for the B₂O₃-I crystal with the experimental data [157] for the heat capacity at constant pressure, C_p , in the temperature range from 5 to 250 Kelvin. The good agreement between the two curves shows that, in this temperature range, C_p is reasonably approximated by C_v and it validates the scheme used in the calculations. The equivalent comparison between our BP and BR models and the experimental data [86, 158] for the B₂O₃ glass is shown in the right panel of Fig. 2.16. An overall good agreement is obtained between the calculations and the experiment, albeit a slight deviation is visible at high temperature, most probably due to the fact that the harmonic approximation becomes



Figure 2.14: Reduced horizontal-horizontal (HH) Raman spectra calculated for the boroxol-poor (f=22%) and boroxol-rich (f=75%) models (solid lines) compared with the experimental spectrum (dash-dotted lines) [155]. A Gaussian broadening of 10 cm⁻¹ is applied.



Figure 2.15: Infra-red spectra calculated for the boroxol-poor (f = 22 %, left panels) and boroxol-rich (f = 75 %, right panels) models compared with the experimental spectrum [155]. The upper and lower panels show respectively the real and imaginary parts of the dielectric constant.



Figure 2.16: Left panel: heat-capacity of B₂O₃-I calculated (at constant volume) and compared to experimental data (at constant pressure) [157, 86]. Right panel: heat-capacity calculated (at constant volume) for the boroxol-poor (f = 22 %) and boroxol-rich models (f = 75 %) compared to experimental data (at constant pressure) [86, 158].

insufficient. However, the main point here is that the values obtained for the BP and BR models are almost identical. Thus, here again, these data cannot be used to infer anything about the proportion of boroxol rings. This invalidates the claim that the difference between the glass and the crystal heat capacities is due to the existence of boroxol rings in the glass [54, 158].

As a summary of this section, the BR model passes more than reasonably well all the experimental tests while the BP one definitely fails for some of them, most noticeably the Raman and NMR tests. This confrontation has demonstrated straightforwardly which observables are sensitive or not to the presence of boroxol rings in the glassy structure: Raman and NMR are by far the best probes allowing for a quantitative assessment while infra-red, heat-capacity, XAS/IXS and diffraction (NRD or XRD) data are weakly or even not sensitive to f at all. Given the incontrovertible superiority of the BR structure, it seems difficult to maintain that v-B₂O₃ can have anything other than a high content of boroxol rings. In finer details, there are some indications (mostly in the Raman data) that the value used in the BR model (f = 75%) is slightly too large. By using the same strategy (i.e. computations of Raman and NMR spectra) for glassy models with varying amounts of boroxols in the range f=0 to 75 % (those used in Fig. 2.17), we have assessed the *optimal* value to be typically $f = 65 \pm 10$ %.

Already at this stage, this work hopefully puts an end to the boroxols controversy by invalidating the common arguments in favour of BP models: previous claims for BP structures were essentially derived from the models' ability to reproduce IR [100, 101, 102] and/or diffraction data [60, 69], which are shown here to be necessary but however not sufficient conditions. Any proposition of a new model of glassy boron oxide will have to reproduce not only the structure factors but also the Raman and NMR data at a level at least as good as the one obtained for the present BR model.

Regarding the diffraction data, the ambiguities in the structure determination arise from the nature of these data being purely pairwise additive information. However, to avoid these ambiguities, an option is to explore the structure as a function of density or temperature since the derivatives of the structural information depend on many body correlations [62]. As will be shown in section 2.7, subtle rings' signatures can be evidenced from high quality sets of neutron [23] or x-ray diffraction data [24] acquired at different conditions, allowing for a qualitative (but still hardly quantitative) follow-up of the rings' presence.

So if experiments and simulations are now reconciled about the fact that the boroxol content in $v-B_2O_3$ is quite high, the reason why it is so remains at this point a genuinely open question that we shall now address in the next sections.



Figure 2.17: Energy for configurations of varying boroxol amount at 0 K and $\rho = 1.84$ g.cm⁻³. The energy reference is the energy obtained for the B₂O₃-I crystal.

2.3 Rings and energy

Thanks to the simulations, attempts to correlate the energy of the system with the the amounts of boroxol rings can be pursued [159]. Structural models with varying amounts of boroxol rings, from f = 0 to 75%, were obtained by gradually melting the BR model, i.e. by increasing the temperature at constant density, a strategy previously employed in Refs. [67, 119, 120]. From these trajectories, instantaneous configurations were picked randomly and their internal positions relaxed at 0 Kelvin at the (fixed) glass density, providing glassy-like models, also known as inherent structures [160]. The obtained total energies are plotted versus the amount of boroxol rings in Fig. 2.17. Within statistical scattering, a monotonic decrease of the total energy with increasing f is observed. Using a linear fit of the data, a slope of $-6.6 \pm 1 \text{ kcal/(mol B}_2O_3)$ was initially found (from structures relaxed using a DZP basis set and the PBE functional) [19], revised to $-5.6 \pm 1 \text{ kcal/(mol B}_2O_3)$ using PW basis sets. A possibly more accurate value of $-4.7 \pm 1 \text{ kcal/(mol B}_2O_3)$ is obtained using the dispersion corrected PBE-D2 [137] functional.

We report on the same Figure the energy of a hypothetical crystalline polymorph, B_2O_3 -0 whose density is close to that of the glass (1.81 g.cm⁻³) at ambient conditions [67]: interestingly it falls well on our data at f = 0.

Thus, at the glass density, boroxol-rich structures are more stable than boroxol-poor ones. This may be understood by the simple steric hindrance argument already mentioned (Fig. 2.1): because of their large volume, boroxol rings are favoured in low-density structures (whereas BO₃-made structures are favoured at higher density, as in B₂O₃-I). Now, the energy decrease with increasing boroxol content, at fixed low-density, is likely a reflection of the situation that occurs as the system is quenched (Fig. 2.2), from the high temperature (boroxol-poor) liquid to the low temperature (boroxol-rich) glass⁶. According to this identification, the slope obtained in Fig. 2.17, $4.7 \pm 1 \text{ kcal/(mol B₂O₃)} = 7 \pm 1.5 \text{ kcal/(mol$ $boroxol)}$ is related to the boroxol stabilisation enthalpy at 0 K for which values of 5.6 ± 1.0 and $6.4 \pm 0.4 \text{ kcal/(mol boroxol)}$ were derived from experimental Raman investigations [74, 73].

The origin of this stabilisation energy remains unclear [159, 35]: it has been proposed that it includes electronic contributions such as π -bonding from p orbitals of atoms within the boroxol rings, i.e. some sort of *aromaticity*. We have attempted to characterise the electronic localisation in our

⁶Although the liquid and glass densities are not identical, it may be a good enough approximation at this point.



Figure 2.18: Schematic illustration of the *crystallisation anomaly*. In B_2O_3 , cooling the liquid at ambient pressure has so far always resulted in a glassy phase of low density, as shown schematically by the path (A). The crystallisation from the melt, path (B), is never observed under ambient pressure: the obtention of B_2O_3 -I requires the melt to be pressurised before being cooled, path (C).

configurations using maximally localised Wannier functions [161]; however no clear differences were observed for atoms inside or outside boroxol rings. Nonetheless, using the very same configurations and a polarisable force-field (section 2.7), we found that the negative slope of Fig. 2.17 could be reproduced only if the oxygen polarisation is turned on [162]. This confirms an electronic character to the boroxol stabilisation energy although it may not necessarily be of aromatic type. Further, we note that this electronic effect may have a topological origin: invoking the steric argument made above, boroxols are progressively incorporated into the liquid to compensate the negative pressure (tensile stress) that would otherwise occur with decreasing temperature at (approximately) constant density.

In any case, the system is eventually quenched in a low-density and low-energy structure. The next section intends to further explore the reason why.

2.4 Boroxol rings in crystals: predictions of new B₂O₃ polymorphs from *first-principles*

Given the trend observed in Fig. 2.17, it seems natural to ask the following questions: i) what would be the energy of a structure entirely made of boroxol rings (f = 100 %)? Could it compete with that of the known crystal, B₂O₃-I? ii) what is the driving force for the energy decrease in Fig. 2.17 and for the fact that the liquid, as it is quenched, follows path (A) in Fig. 2.18 (vitrification in a low-density structure, irrespectively of the quenching rate, even at the lowest experimentally explored) rather than path (B) (crystallisation in the B₂O₃-I polymorph)?

As we shall see, there are strong indications that our knowledge of the B_2O_3 crystalline polymorphism is incomplete and that there are probably yet unknown B_2O_3 crystals to be discovered which would explain the supercooled liquid behaviour and the glass properties.

In contrast to the wide diversity of crystalline structures found in silicates and metal-containing borates, the polymorphism of pure B_2O_3 , is seemingly very poor. Indeed, only two different polymorphs, referred as B_2O_3 -I and B_2O_3 -II, have so far been reported experimentally [112, 113], which are made of BO_3 and BO_4 units respectively (see for instance Figs. 1 and 2 in Ref. [111]). Of particular importance for our discussion, none of these polymorphs contain any boroxol rings at all, whereas these rings can
be found in large amounts (dominating units) in several other crystalline metal-containing borates, such as $YBa_3B_9O_{18}[163]$ or $Cs_2O-9B_2O_3$ [35]. The fact that vitreous B_2O_3 incorporates such regular superstructural units suggests that these might be relevant to form other B_2O_3 crystalline structures.

The lack of *ambient-pressure* polymorphism in B_2O_3 is in stark contrast to the situation observed in most simple oxide systems. By *ambient-pressure* polymorphs, we mean crystals built upon the same structural unit and thus in which the network-forming cations have the same coordination as the ambient glass. In silica for instance, more than 20 polymorphs (quartz, coesite, cristobalite, keatite, moganite, tridymite and pure SiO₂ zeolites such as ferrierite or faujasite) made solely of tetrahedral SiO₄ units have been reported [164]. The fact that B_2O_3 -I is the only known BO₃-based crystal is in itself anomalous as compared to silica: one expects the same kind of topological diversity in both systems as a result of the many various ways to connect the building units.

Also very intriguing are the conditions required to obtain these polymorphs from the melt: crystallisation is observed only if a small pressure is applied (typically above 0.4 and 2.0 GPa for the obtention of B₂O₃-I and B₂O₃-II, respectively), a behaviour known as the *crystallisation anomaly* [165, 166, 167]. Even if the melt is seeded with crystals and maintained for several months at various temperatures below the melting point, no crystal growth is observed at ambient pressure at any imposed cooling rates (within the experimental limits of *patience*: $|dT/dt| > 10^{-5}$ K.s⁻¹) [165, 166, 167]. In other words, cooling the B₂O₃ liquid at ambient pressure has so far always resulted in a glassy phase, v-B₂O₃, of density ($\rho = 1.84$ g.cm⁻³) significantly lower than that of B₂O₃-I (2.55 g.cm⁻³). The fact that pressure is required to crystallise B₂O₃-I from the melt⁷ casts some doubts on whether it is the true ambient polymorph.

The structural and density differences between B_2O_3 -I and v- B_2O_3 have been early recognised [54] and have been a major motivation for the prediction of boroxol-containing crystals [64, 65, 66]. Pioneering the computer synthesis of B_2O_3 polymorphs [65, 66], Takada et al. used *hand-made* modifications of known crystalline structures, HBO₂-III, Cs₂O-9B₂O₃ and B₂O₃-I, to produce pure B₂O₃ structures: by inserting or deleting BO₃ units into the parent compounds (after removal of the unwanted atoms, H or Cs), 7 new crystals of varying amount of boroxol rings were generated [66]. These works showed that it is possible to generate boroxol-rich structures at the glass density, at a time when it was controversial. Other numerical predictions of B₂O₃ polymorphs include the work of Kieffer and Huang [67, 119]. By applying either positive or negative pressure on B₂O₃-I, two polymorphs, referred as B₂O₃-O were generated. The former is a high-coordinated (^[4]B) phase that we shall not consider further since we are interested here in *ambient-pressure* polymorphism. The latter one, B₂O₃-O, is actually a structure of same topology but different symmetry than B₂O₃-I. It has a low density, close to that of the glass, but does not contain any boroxol rings.

We have recently engaged in a more systematic determination of *ambient-pressure* B_2O_3 polymorphs by using topological design principles and *first-principles* calculations [22]. Given that we were only interested in low-energy polymorphs, i.e. those occurring under ambient-like or low-pressure conditions, the search can be considerably simplified by taking advantage of the following considerations: *i*) as a result of its strong and directional bonds, the relevant building block is the BO₃ triangle unit, as in B_2O_3 -I *ii*) being a supertriangle homothetic to the building block (Fig. 2.1), the boroxol ring B_3O_6 can itself play the role of a building block, as in the glass *iii*) since in both units, boron atoms are 3-fold coordinated, an efficient and systematic search can be obtained from the decoration of known 3-connected networks by the relevant units. We thus used all possible 3-connected networks, fully connected in 3D space, with up to six vertices in the unit cell, as obtained from an exhaustive mathematical search, based on graph theory and originally applied to sp^2 -carbon polymorphs [170] (see Fig. 2.19). The lamellar network of (hexagonal) graphite was also added in the database, providing

⁷As an alternative to the high-pressure synthesis, crystalline B_2O_3 -I can also be prepared by the stepwise dehydration of orthoboric acid (H_3BO_3)[168] or by seeding a melt with borophosphate [169].



Figure 2.19: Construction of B_2O_3 polymorphs. Using the self-similarity between a 3-connected vertex (left), the BO₃ triangle (middle) and the B_3O_6 ring (right), new polymorphs can be constructed from the decoration of known 3-connected networks, as illustrated here in the case of a graphene layer. The T0 and T0-*b* polymorphs were obtained by stacking the BO₃- and B₃O₆-decorated layers respectively. The decoration is illustrated here for clarity on 2*D* structures but note that all the other polymorphs of Fig. 2.20 are 3*D* (fully connected) structures. Adapted from Fig. 2 of Ref. [22].

a total of 13 topologically different networks. Vertices of these networks were then decorated by BO₃ triangle units. Among the generated structures, the known B₂O₃-I polymorph was recognised; the 12 remaining novel structures are labelled T0 to T11 in Fig. 2.20. In T8 and T10, 50 % of the boron atoms belong to three-fold rings, i.e. boroxol rings. Further to expand the search and to investigate the role of the boroxol ring as a structural motif, 13 additional structures, indicated by the extension -b, were generated by replacing the BO₃ units by the B₃O₆ ones. In this way, structures which are made of 100 % boroxol units were obtained, taking advantage of the self-similarity between a BO₃ and a B₃O₆ unit (Figs. 2.1 and 2.19). All structures (atomic positions and lattice cell) were then relaxed at 0 K within the DFT framework using the PBE [135] functional, ultrasoft pseudopotentials [171] and the CASTEP plane-wave code [172]⁸. Computation of phonon frequencies ω_i , allowed to check the dynamic stability (absence of negative frequencies) and to obtain the zero-point energy contribution ($E_{vib} = \sum_i \frac{\hbar \omega_i}{2}$), as well as the vibrational free-energy at finite temperature, in the harmonic approximation, as $F_{vib} = k_b T \sum_i ln[2sinh(\frac{\hbar \omega_i}{k_b T})]$. These contributions were found to be small and are thus not considered further⁹.

This resulted in the prediction of 25 new polymorphs containing either 0, 50 or 100 % of boron atoms in boroxol rings. As can be seen in Fig. 2.20, all these crystals have a low-density, that is, lower than B_2O_3 -I and, for most of them, comparable to that of the glass. Some have a very low density (< 1.0 g.cm⁻³), which in silicates would correspond to frawework densities typical of zeolites.

As could be anticipated, most of the crystals based upon boroxol rings (-b) tend to have lower densities than their triangle-based equivalents. The density ratio however largely varies from a topology

⁸As compared to Ref. [22], the calculations were repeated with tighter (more accurate) pseudo-potentials and a larger plane-wave basis-set cutoff of 784 eV. This resulted in some very small differences in the results shown Fig. 2.20.

 $^{{}^{9}\}Delta E_{vib}$ is typically less than 0.6 kcal.mol⁻¹ and thus marginally affects the results shown in Fig. 2.20 (uncorrected from E_{vib}). At the glass transition temperature, the vibrational contribution ΔF_{vib} tends to favour the new crystals over B₂O₃-I by about 1. kcal.mol⁻¹ while leaving the energy degeneracy between the novel polymorphs essentially unchanged.



Figure 2.20: Energy as a function of density for the B_2O_3 polymorphs. The energy reference, E_0 , is that obtained for B_2O_3 -I. The proportion of boron atoms in boroxol rings in the polymorphs are indicated by different symbols. The calculated densities have been rescaled by 1.104, as given by the ratio of the experimental and calculated densities of B_2O_3 -I. The experimental energy for the glass is taken from [86].

to another¹⁰. Many obtained structures, in particular those made of boroxol rings, are very flexible, showing large volume changes upon small pressure variation.

Less trivial but also of great interest is the fact that in many cases the energy is lowered in the triangle-boroxol substitution. The net effect, as seen in Fig. 2.20, is that for densities lower than c.a. 2.0 g.cm⁻³ the lowest-energy crystals are those having a high proportion of boroxol rings. Further, a large number of the predicted crystals tend to be *clustered* in a narrow density and energy range, typically in between 1.5 and 2.0 g.cm⁻³ and -1.5 to 0.5 kcal/mol. This density range typically encompass that in between the high-temperature liquid ($\rho_{liquid}(2000 \ K) \sim 1.5 \ \text{g.cm}^{-3}$) and the ambient glass ($\rho_{glass}(300 \ K) \sim 1.84 \ \text{g.cm}^{-3}$).

We thus argue that these new polymorphs are much more relevant than is B_2O_3 -I for understanding the glass properties and that their energy quasi-degeneracy is responsible for the ease of vitrification: such a situation with many local minima in the energy landscape is expected to prevent the nucleation of a given phase by favouring a disordered structure instead [173]. We also note that for a given topology, several minima were often found (only the lowest energy minimum is shown Fig. 2.20): this further reflects a rugged energy landscape.

As pressure is applied (typically 1 GPa), the energy degeneracy is progressively lifted (not shown here) and the energy difference between B_2O_3 -I and any other polymorph becomes marked [22], rendering the crystallisation of B_2O_3 -I increasingly favourable. This thus provides a scenario to understand the *crystallisation anomaly*, i.e. the fact that pressure is required to crystallise B_2O_3 -I from the melt.

¹⁰If there are no relaxations at all in the triangle-boroxol substitution, that is for exactly homothetical 3*D*-topologies, one expects the density ratio to be $\frac{3}{2^3} = 0.375$. This is close to the value obtained for instance in the T1 to T1-*b* case (0.35). However, the density ratio can be much higher because of structural relaxations, in particular in the directions orthogonal to the boroxol rings plane. For a topology with a strong lamellar character, the triangle-boroxol substitution will double the intra-layers lengths while keeping unchanged the inter-layer distance, resulting in this case in a density ratio of $\frac{3}{2^2} = 0.75$. This is indeed very close to the value obtained in the T0 to T0-*b* case (0.76). There are a few cases for which the density is unchanged (as in the T4 to T4-*b* case); these correspond to initially porous geometries which contain large rings and for which a more efficient packing in the final relaxed structure was achieved by folding the largest rings.



Figure 2.21: Structure factors obtained from MD simulations at finite temperature ($T_g = 540$ K) for some selected polymorphs compared with the experimental data for the glass [57].

Among the lowest energy polytypes and those closest to the glass density, one finds e.g. B_2O_3 -I-b, the boroxol-made equivalent of B_2O_3 -I, T0-b, the boroxol-made equivalent of graphite, T8 and T10 for which f = 50 %. Interestingly, these crystals share greater structural similarities with the glass than does B_2O_3 -I. This is illustrated by the structure factors obtained at finite temperature, Fig. 2.21, in particular in the low-q region, sensitive to the medium-range order. In the T10 structure, shown Fig. 2.22, the dihedral angle distribution between adjacent ring and non-ring units is well in line with the one measured in the glass by two-dimensional NMR[47]. Additional attempts to quantify the geometrical and topological proximities of these new phases with the glass are on-going using recently proposed metrics [174, 175].

These findings, thus, confirm that boroxol rings are essential to stabilise low density structures [19, 176]. As in the previous section, one could ask if this a purely geometrical effect (larger rings are favoured at low density to fill the empty space) or if there is an additional electronic contribution to the formation of these rings. The triangle-to-boroxol substitution used here can help to gain insight on this question. We used a 2D monolayer (topologically equivalent to graphene) to generate triangle- and boroxol-made single sheets, Fig. 2.19. If both structures are unrelaxed (and therefore strictly equivalent topologically), the boroxol-made sheet is favoured by about 11 kcal/mol B_2O_3 : this strongly suggests that there exists an intrinsic electronic origin of that order (c.a. 10 kcal/mol B_2O_3) to the rings stabilisation energy. However, if the internal coordinates are allowed to relax, the gain is reduced to only 1 kcal/mol since there are less degrees of freedom in the boroxol-made sheet than in the triangle-made one. Thus, both electronic and geometric effects compete in the energies shown in Fig. 2.20.

Most of the predicted crystals form cage- or channel-like structures. This could make these interesting materials as guest host, in particular for hydrogen storage [177] or for molecular sieves applications [178]. This nanoporosity may also be reminiscent in the glass structure. Indeed, large specific areas and high hydrogen uptakes were reported both in B_2O_3 fine powders [177] and in amorphous samples [179]. The presence of relatively large voids has also been observed in glassy configurations derived from RMC simulations [180]. Further investigations of these aspects could be all the more promising given the recent discovery that glassy silica is a nanoporous material which can accommodate gases such as He or Ne [181, 182].



Figure 2.22: Views of the T10 polymorph. In this structure, half of the boron atoms are in boroxol rings. Channels-like arrangements, made by larger rings, are clearly visible.

These results reveal a much richer polymorphism in B_2O_3 than expected before. In this sense, the behavior of B_2O_3 appears now much more similar to that from other well-known glassy systems such as silica. The small differences in energy between the polytypes comes from the variability of the B-O-B angle linking the structural units, just as in silica Si-O-Si angles bridging the tetrahedra. In B_2O_3 , the tendency to form 3-fold rings allows for the formation of porous structures. The large angular flexibility of the B-O-B bridges linking the rings gives rise to several energy minima for a given topology. These two aspects, the large number of possible topologies and the many geometrical variations among them, both contribute to a very rugged energy landscape and are likely essential ingredients to the vitrification proneness. This, however, does not exclude that other aspects, either related to the crystal growth kinetics [167] or to the crystals' mechanical unstabilities, might also be at play. An on-going work (Henri Hay's PhD thesis) has indeed showed that most predicted crystals tend to have low mechanical moduli (in all cases lower than those of B_2O_3 -I).

Whether the predicted B_2O_3 crystals can be experimentally synthesised remains an open question. On one hand, most of the structures investigated fall within the energy range of thermodynamically accessible polymorphs (in silica, the highest energy zeolite, ISV, is 3.44 kcal/mol above quartz [164]). On the other hand, kinetics or experimental difficulties may prevent their observation. Part of the difficulty may well lies in the fact that one needs to avoid the glass transition resulting from the polymorphic degeneracy in the energy-density diagram, i.e. one has to find a method which would favour one of the polymorphs over the others. Interestingly, one can find several mentions of low density crystalline structures in the literature [183, 184, 185], although in most cases it was barely noticed and not recognised as a new polymorph discovery (since this was not the priory motivation of these works [184, 185]). Their density varies from 1.8 down to 0.69 $g.cm^{-3}$ and thus these putatively unidentified new polymorphs could correspond to some of our predictions. Note that these were not obtained from a liquid quench but rather from chemical routes such as the dehydration of H_3BO_3 (Ref. [183, 184]) or chemical vapour deposition [185]. Notwithstanding that these could be false results, further experimental studies dedicated to crystal synthesis would be very much indicated. Promising directions may include the various methods used to produce thin films of B₂O₃, such as chemical vapor deposition [185] and its variants [186, 187], magnetron sputtering [188], infrared heating [189] or sol-gel techniques [190] although so far, in most of the cited cases, the obtained structures were either amorphous or nano-objects such as wires. Physical methods able to generate negative pressure conditions (tensile stress) [191] would be highly desirable although technically challenging.



Figure 2.23: Density conditions explored in the liquid at 2000 K. Starting from $\rho = 1.84 \text{ g.cm}^{-3}$ (overpressurised liquid at the glass density), lower densities along path (1) were sampled corresponding to typically ordinary ($\rho = 1.49 \text{ g.cm}^{-3}$) and stretched ($\rho = 1.13 \text{ g.cm}^{-3}$) conditions. The system was then compressed back to the starting density, path (2). Values for the average pressure and proportion of boroxols $\langle f \rangle$ are indicated. The inset shows the evolution of $\langle f \rangle$ along these paths.

2.5 Back to the liquid: transformations under tensile stress

In summary of the previous section, the polymorphs prediction allows to unravel some of the seemingly anomalous properties of B_2O_3 . As the liquid is quenched, it vitrifies in a low density glass (path (A) of Fig. 2.18) because of the many underlying crystals in this region of the phase diagram. It acquires some of their structural characteristics, such as a high proportion of boroxol rings. The formation of these rings compensates the negative pressure that would otherwise exists in the glass at low temperature. As already stated, the structural transformation occurring from the high-temperature liquid to the lowtemperature glass (Fig. 2.2) is extremely challenging to follow numerically because of the exponentially growing viscosity. It has actually remained so far impossible to reproduce this transition (and it is likely to remain so for a long time) with brute-force methods (standard MD or MC techniques) given the affordable computational resources. However, given that low density conditions favour the formation of large rings, it is tempting to follow a different route in the phase diagram, schematically indicated as (1) in Fig. 2.23, i.e. going to negative pressure at constant temperature in the liquid. To do so, we produced simulations in the NVT ensemble starting from the liquid at the glass density (T = 2000 K, $\rho_{\rm glass} = 1.84 \text{ g.cm}^{-3}$) and slowly increase the volume of the simulation box (at a constant rate over a ~ 20 ps timescale) until a density of $\rho = 0.9 \text{ g.cm}^{-3}$ was achieved. Then simulations (of at least 300 ps and up to 900 ps) were branched at different densities (path (1) in Fig. 2.23), which include the liquid at the experimental density ($\rho_{\text{liq}} = 1.49 \text{ g.cm}^{-3}$) and a much smaller one ($\rho_{\text{low}} = 1.13 \text{ g.cm}^{-3}$). The reverse process was also carried out, i.e. compressing the liquid from ρ_{low} to ρ_{glass} , with long simulations sampling intermediate densities ($\rho = 1.29$ and 1.72 g.cm⁻³), along path (2) in Fig. 2.23.

The instantaneous evolution of the boroxols proportion f, at fixed density, monitored along the trajectories branched from path (1) are shown Fig. 2.24. For the lowest density (1.13 g.cm⁻³), a clear step-like increase is observed as time is running. Interestingly, corresponding jumps in the instantaneous pressure were observed: initially at ~ -1.1 GPa at the beginning of the trajectory, the final pressure is reduced to ~ -0.5 GPa. This reflects a correlation between the internal pressure and the boroxols proportion. The final value ($f \sim 52$ %) is quite high given the relatively high temperature (2000 K).



Figure 2.25: Boron-boron and boron-oxygen partial radial distribution functions obtained at 2000 K for the slightly pressurised ($\rho = 1.84 \text{ g.cm}^{-3}$), ordinary ($\rho = 1.49 \text{ g.cm}^{-3}$) and stretched ($\rho = 1.13 \text{ g.cm}^{-3}$) liquids. The dashed line is a guide to the eye, highlighting an anomalous behaviour (contraction of the B-B first peak) as the liquid is stretched. The arrow indicates the appearance of a boroxol rings' signature at ~ 2.75 Å (also visible in Fig. 2.7).

The liquid obtained in these conditions is very viscous: trajectories longer than 300 ps were required before the diffusive regime begins to kick in and the previously defined¹¹ equilibration time τ is estimated as ~ 2.5 ns.

Even at the lowest density, the liquid is still fully polymeric (99.9 % of boron are three-fold coordinated by oxygens as in the ordinary, i.e. zero-pressure liquid). Its structure is fully disordered, as evidenced by the usual structural markers (radial distribution functions, structure factors, angular distributions). The inspection of the radial distribution functions (Fig. 2.25) shows the appearance of the boroxol rings' structural signatures already mentioned in the glass study (section 2.2 and Fig. 2.7). More interesting, the boron-boron partial reveals an anomalous trend: the first peak contracts as the density is decreased (while the subsequent peaks expand, as expected). This *locally negative* compressibility could be the marker of thermodynamic anomalies occurring in this regime and possibly indicative of a *liquid-liquid* transition. More works are needed however to confirm this point.

Not surprisingly, the reverse behaviour is observed for trajectories branched along the reverse path (2): as the density is increased and as the simulation time runs, the boroxols proportion tends to decrease from an initially too high value (reminiscent of the starting density, $\rho_{\text{low}} = 1.13 \text{ g.cm}^{-3}$).

¹¹average time required for an oxygen to move twice its diameter (section 2.2).



Figure 2.26: Schematic temperature-density phase diagram of B_2O_3 . As the liquid is cooled and approaches the glass transition, path (A), it undergoes a structural transition from a BO₃- to a boroxol-dominated network. A similar structural transition can be induced by stretching the liquid, path (1). Along both paths, boroxols rings form to compensate the internal negative pressure.

The final f values obtained for all the sampled densities along both paths are shown in the inset of Fig. 2.23. A sort of *hysteresis* curve is obtained as a result of the limited sampling. Therefore, the set of values obtained along path (1) (expansion from $\rho = 1.84 \text{ g.cm}^{-3}$) likely represents a lower bound (as the starting conditions correspond to a pressurised liquid and are therefore unfavourable to the formation of boroxols) while the values obtained along path (2) correspond to an upper bound.

These findings provide useful insights and open interesting questions. A methodology is provided to enhance the content of rings in the liquid. The structural evolution obtained as the liquid is stretched at constant temperature (Fig. 2.23) resembles that observed experimentally as the liquid-glass transition is approached (Fig. 2.2): along both paths, the boroxols rings develop so as to compensate the internal negative pressure. These findings are illustrated Fig. 2.26. From a methodological point of view, the first transformation (stretching the liquid at fixed temperature) is easier to follow with MD than the second one (glass transition) since the ergodicity is better preserved. In addition, by quenching both the temperature and the volume from the structure obtained at ρ_{low} , it has been possible to recover a new boroxol-rich model of glassy B_2O_3 (f = 52 %).

More fundamentally, these findings raises the possibility that B_2O_3 is experiencing a *liquid-liquid* transition along path (1), Fig. 2.26. This transition, in the stretched liquid, is in competition with the liquid-vapor one and possibly with the crystallisation in one of the predicted B_2O_3 polymorphs [22]. We can safely discard that what we observed is the system cavitating¹². Further, no signs of crystallisation were observed, although more work, unfortunately much beyond what is feasible within an *ab-initio* framework [192, 193] would be needed to confirm this point. In any case, it would be interesting to investigate further the thermodynamics and the similarities (structure, porosity) of this phase with the predicted low-density crystals [22]. Its high amount of rings is likely responsible for its high viscosity.

¹²Cavitation happened once in a NPT simulation at large negative pressure and showed marked signatures of the gas phase, such as a strong increase of the diffusion and of the proportion of under-coordinated atoms. Instead the obtained phase at ρ_{low} is very viscous and fully polymeric.

Figure 2.27: Atomic densities of the vitreous and crystalline phases in the B_2S_3 and B_2O_3 systems.

It also likely impacts its surface tension. The two liquid phases would share a common short-range order (that defined by the boron and oxygen coordination) but mostly differ in their medium-range one (as defined in particular by the boroxols proportion). Thus, this transition would somehow resemble the putative and much debated liquid-liquid transition of water [194, 195].

Back to generalities about simulating the structure of the liquid or the glass, a last methodological point should be stressed. In addition to the need for long simulation times, the correlation between the rings structure and the internal pressure raises some warnings. In the NVT ensemble (or any fixed volume ensemble), care should be given that the stress is fully relaxed in the final structures: in the present case, a positive residual pressure (above the target one) will likely reflect an overestimated proportion of boroxols and vice versa. Simulation in a NPT ensemble ensures by definition that the target pressure is reached; however the same kind of caveat applies if the density is unknown: the target pressure might be fulfilled by various structures differing in their rings topology, schematically by a boroxol-rich structure at low density or by a boroxol-poor structure at high density. In this case, the knowledge of either the density or the rings proportion is an essential constraint.

2.6 Rings in a thioborate analog: B_2S_3

A close analog to B_2O_3 is the chalcogenide compound B_2S_3 which thus provides comparative insight concerning the structural chemistry. B_2S_3 is iso-electronic to B_2O_3 and it is well established that the molecular building block in both crystalline and glassy B_2S_3 is the planar BS_3 triangle unit. Interestingly, it is also clear that 3-fold rings, called borosulphols or thioboroxols, which are the equivalent of the boroxol rings in vitreous B_2O_3 are largely present in both the glass [196, 197, 198, 199, 200, 201, 202, 203, 20] and the B_2S_3 -I crystal [204]. A specificity however of the chalcogenide is the existence of 2-fold (edge-sharing) rings. In B_2S_3 -I, the proportions of boron atoms involved in 2- and 3-fold rings are $f_2 = 25$ and $f_3 = 75$ %, respectively. The corresponding values in the glass are less clear.

We have recently undertaken an extensive study of the liquid and glassy B_2S_3 phases using the methodology described previously for B_2O_3 , namely the computation of structure factors, NMR and Raman data from different models, varying by their rings content and obtained by using different thermal histories. Preliminary results can be found in Ref. [20]. As for B_2O_3 , the structure factors from all tested FPMD models reproduced very well the experimental data available [201]. Note however that the structure factor test is sufficient to rule out a chain-like model of 2-fold rings previously obtained from classical MD [205]. This illustrates both the higher degree of realism of the *first-principles* models provided in Ref. [20] and the fact that the reproduction of the total structure factor is a necessary but not sufficient condition. Calculation of the Raman data appeared to be the most instructive test of the models.

It is noteworthy that, unlike the case of B_2O_3 , both 2- and 3-fold rings appeared spontaneously in large amounts in the MD trajectories, without having to *tweak* the models. This can be understood by the comparison of the glass and crystal (atomic) densities for both systems, Fig. 2.27. First, in B_2S_3 the glass density is very similar to that of the known crystal polymorph. Second, the B_2S_3 (atomic) densities are much smaller, typically halves those of B_2O_3 . This is well in line with the findings of the previous sections: low density favours the formation of these rings.

2.7 Development of new interatomic potentials from *first-principles*

In the introductory section (2.1), I made the following points: i) the evaluation of the quality of the existing force-fields (FFs) in the literature is, at least to a certain extent, hindered by the fact that in the case of B_2O_3 , the quenching rate is a crucial issue ii) however, it is also clear that the large majority of the existing FFs are suffering from serious flaws (such as incorrect densities, presence of unrealistic coordination defects) which exceed those expected from quenching issues: this is proved by the fact that these flaws do not show up in the *first-principles* simulations (section 2.2 and Refs. [41, 19, 122]) iii) in a very few cases, significant advances towards realistic descriptions were potentially made [65, 115, 67]; however these FFs remained poorly tested against experimental data (in fact, when feasible, the comparison with experiments is disappointing as shown in the present section).

The availability of accurate, transferable and yet computationally cheap FFs is highly desirable. This would allow in particular for a better exploration of the B_2O_3 phase-diagram: in connection with the topics evoked previously, this could help shedding some lights on a) the nature of the structural transformation from the liquid to the glass (Fig. 2.2) b) the link between the glass and the predicted crystalline phases (section 2.4) c) the possible existence of liquid-liquid transitions (section 2.5) as well as other polyamorphic transitions.

I recently engaged through a collaboration with Mathieu Salanne and Matthieu Micoulaut in the construction and validation of new FFs for B_2O_3 derived from *first-principles* (Axelle Baroni's PhD thesis). In this methodology [206], hereafter called PIM (for Polarisation Ion Model), the polarisation interactions resulting from the dipoles and quadrupoles induced on the oxygen atoms are explicitly represented. The potential is best described as the sum of four different components: charge-charge, dispersion, short-range repulsion and polarisation. A variant, hereafter called the Aspherical Ion Model (AIM), was also constructed in which breathing effects are accounted: additional degrees of freedom allow the shapes of the oxygens to respond to their instantaneous coordination environment (the distortions can have spherical, dipolar and quadrupolar-like components). Both polarisation and breathing effects are directly parametrised from *first-principles* electronic structure calculations in a forces- and dipoles-matching approach. For these reference calculations, we used the CPMD code [133] within the framework described before (Born-Oppenheimer approximation, Troullier-Martins pseudopotentials, PBE exchange-correlation functional). I refer to Refs. [206, 207, 208] for more details about the methodology and to Refs. [23, 24, 209] for explicit details of the parametrisation applied to the B₂O₃ case.

Historically, we first constructed a PIM potential using as a sole reference configuration (used to calibrate the potential) the boxorol-poor glassy model previously described (f = 22 %). The obtained potential provided very good (energies and structural) results for both the glass and the crystalline phases predicted in Ref. [22]. However, at about the same time, experimentalists (Phil Salmon's group) got in touch with us as they felt the need for a model to support the analysis of their experimental high-pressure diffraction data obtained in $v-B_2O_3$. This fortunate coincidence allowed us to test our PIM model in a larger range of conditions and to evidence some of its limitations: the pressure-induced ^[3]B to ^[4]B transition is poorly reproduced. This transferability flaw is obviously related to the fact that the reference configuration contains only ^[3]B atoms. We thus constructed an AIM potential of higher potential transferability (thanks to its larger number of parameters), and which parameters were derived from a larger set of reference configurations, involving both ^[3]B to ^[4]B environments (namely the B_2O_3 -I and B_2O_3 -II crystalline phases in addition to the boxorol-poor glassy configuration). In the following, some of the results obtained using these potentials are presented; these will highlight the strengths and weaknesses of each potential. It should be kept in mind that the comparison of the PIM and AIM results should not be understood as a test of the respective methodologies performances (since the configurations used to construct the different potentials are not equivalent) but rather as a test of these two specific potentials.



Figure 2.28: Energies of B_2O_3 polymorphs (relative to that of B_2O_3 -I) at 0 K as obtained from different schemes. Left: DFT calculations [22] using the PBE exchange-correlation functional. Upper right: calculations using the PIM force-field. Lower right: using the AIM force-field. For both the PIM and AIM calculations, the densities were fixed (to those obtained with DFT-PBE) and the dispersion interactions were turned off for a fairer comparison with DFT-PBE (see Ref. [209] for additional comparisons including these contributions).

Figure 2.28 shows a comparison of the energies obtained in the crystalline phases (as predicted in Ref. [22]). Albeit not perfect, there is a good overall agreement for both the PIM and AIM force-fields with the DFT-PBE results. The maximal error is respectively ~ 3 . and ~ 6.5 kcal/mol for PIM and AIM; the averaged absolute error (calculated over all the polymorphs) is ~ 0.9 and ~ 3.1 kcal/mol for PIM and AIM respectively. Thus, for these low-pressure and low-temperature phases (all made of ^[3]B atoms), PIM provides better energetics than AIM.

We now turn to the glassy phase. To avoid issues related to the quenching rate, we used the boroxol-rich model as the initial configuration for MD simulations of typically several ns in the NVT ensemble at 300 K. Small residual pressures (~ 0.2 GPa) were obtained (resulting in small density variations within NPT simulations). Both FFs provided virtually indiscernible structure factors, in very good agreement with both the *first-principles* and the experimental ones (see the bottom curves of Fig. 2.31). Very tiny differences between the FFs are observed on the B-B radial distribution function (not shown, see chapter 6 of Ref. [209]) which however cannot be discriminated by the experiments¹³. Regarding the energetics, the strategy described in section 2.3 was used to derive the boroxol rings stabilisation energy (i.e. computing the energy of several glassy configurations with varying proportion f, Fig. 2.17). Values of -8.1 ± 1 and -4.5 ± 1 kcal/(mol boroxol) were obtained with PIM and AIM, respectively, to be compared with the *first-principles* value -7 ± 1 kcal/(mol boroxol)¹⁴, and the experimentally derived value [73, 74] of $\sim -6. \pm 1$ kcal/(mol boroxol). Thus, there again, a slightly better performance of the PIM potential is evidenced for the energetics of the ambient glass.

 $^{^{13}}$ The partials are unfortunately not available experimentally in the case of B_2O_3 .

 $^{^{14}}$ Using the dispersion corrected PBE-D2 [137] functional.



Figure 2.29: Left: Energies of glassy configurations using the PIM potential with polarisation terms a) included b) not included. Right: Boroxol rings stabilisation energy (as derived from the slope of the graphs on the left, see text) as a function of the oxygen polarisability α_0 . The dotted horizontal line separates positive from negative values of the stabilisation energy. The red star corresponds to the value obtained from the *first-principles* calibration of the PIM model. Similar trends were obtained with the AIM model.

Interestingly, we found that the polarisation contributions are essential to the rings stabilisation energy, as illustrated Fig. 2.29. Indeed, turning off these terms in the potentials would result in positive values for the rings stabilisation energies, i.e. the rings would be unfavoured in the glassy configurations (Fig. 2.29(b)). By artificially varying the oxygen polarisability (α_0 parameter), all others parameters being fixed, models of varying polarisability were created: a clear correlation between the rings stabilisation energy and the polarisability is revealed in this way, Fig. 2.29(c).

2.7.1 Pressure-driven transformations in the glass

We then carried out a high-pressure study of the glass (using NPT followed by NVT simulations) at 300 K. The evolution of the density as a function of the target pressure is shown in Fig. 2.30. Both PIM and AIM models are in very good agreement with the *in-situ* measurements of Brazhkin *et al.* [17] up to their upper values (8 GPa) and even possibly with their extrapolation at higher pressure. The PIM and AIM equations of state depart slightly from each other from about 8 GPa but the uncertainty associated to the experimental extrapolation does not allow to assess the best model. However, the superiority of these models upon previous ones [120, 140] is quite clear. Note that the apparent density under-estimation in the previous *first-principles* calculations [17] is essentially due to the lack of dispersions contributions (as revealed by unpublished tests from the present author).

The structural performances of our models at high pressure are compared in Figures 2.31 and 2.32. The simulated structure factors (top panels of Fig. 2.31) reproduce quite well the experiments until typically ~ 8 GPa but a progressive misfit is however visible at higher pressures. The disagreement is more apparent on the $G_n(r)$ functions (bottom panels) than it is on the $S_n(q)$ functions. It should be stressed however that according to our experimental colleagues some of the discrepancy at high pressure may result from experimental artifacts¹⁵. One can note a better performance of AIM (right panels) as compared to PIM (left panels). These trends are even more clear from the B-O coordination number (Fig. 2.32). In the pressure range shown, PIM does not catch at all the experimental increase of n_{BO} which reflects a progressive ^[3]B to ^[4]B transition whose onset lies at ~ 4-6 GPa (the onset for PIM

¹⁵The experiments were acquired on two different diffractometers: on the D4c beamline of the ILL reactor for pressures up to 8.2 GPa, and on the PEARL beamline of the ISIS spalliation source for pressures above 8.5 GPa. Difficulties with the processing of the latter data set were reported. In particular, the PEARL data are broader than the D4c ones in similar conditions.



Figure 2.30: The density of v-B₂O₃ as a function of pressure (cold compression). The *in situ* experimental data of Brazhkin *et al.* [17] (black \blacktriangle) are compared to MD results (at 300 K) obtained from different schemes using: (i) *first-principles* (DFT-PBE) from Brazhkin *et al.* [17] (broken olive curve with \Box symbols) (ii) the coordination-dependent potential from Takada [140] (broken magenta curve with \triangle symbols), the coordination-dependent potential from Takada [140] (broken green curve with \triangleleft symbols) and the present PIM (blue \circ) and AIM simulations (red \diamond). The experimental data [17] were fitted to a third-order Birch-Murnaghan equation of state (chained black curve) and to a second order polynomial (broken black curve); the average of these fitted values is given by the solid black curve. Older *ex-situ* [17] or indirect (Brillouin [120]) measurements are not considered in the present comparison (see Fig. 1 of Ref. [23] for an extended comparison)

is actually shifted to ~ 15 GPa). This onset is well captured by AIM although an underestimation of n_{BO} at high pressure is still visible (at 17 GPa, the proportion of ^[4]B is typically 40-50 % as compared to ~ 80 % experimentally). However, note here again the manifest superiority of the AIM model upon others FFs available in the literature [120, 140]. It may seem strange that AIM even outperforms *first-principles* MD results [17]. This could result either from a fortuitous cancellation of errors in our AIM simulations or from the shorter simulation time scale used in the *first-principles* work [17]. In the same manner, the apparent n_{BO} underestimation of AIM (as compared to experiments) is not necessarily due to an intrinsic defect of the potential (progressive lack of transferability) but could also be due to an insufficient relaxation time (1 *ns*). This is anticipated given that structural relaxation phenomena over a time scale of several days were reported experimentally [138].

A detailed analysis of the microscopic structure (obtained by AIM) reveals that the BO₄ units are strongly asymmetric (presence of a 4th oxygen neighbour at distances ranging between 1.45 and 1.60 Å from the boron atom). This is in contrast with the regular tetrahedra formed by Si in silica or Ge in germania but this is well mirrored in the high pressure polymorph B₂O₃-II (presence of two B-O bond lengths: 1.37 and 1.51 Å) [113]. Also of interest is the transition state: as compression starts, the boron atom (initially at the barycenter of the BO₃ unit), is pushed away from the plane defined by its 3 oxygen neighbours. This deviation, first shown by DFT-based MD simulations [18] and recently confirmed by *in situ* NMR [210], is well captured by the AIM model. Such a complex structural change can hardly be caught by simpler FFs. Here, the important ingredients of AIM are the oxide ion breathing and deformation effects included in the short-range repulsion term: the 4th oxygen ion is accommodated into the boron 1st-neighbour shell by reducing the oxides effective radii¹⁶.

 $^{^{16}}$ We note however that some potentials are able to catch such effects by effectively fitting all the possible environments (the family of *reactive* force fields [211]).



Figure 2.31: Neutron total structure factor $S_n(q)$ (upper panels) and total pair-distribution function $G_n(r)$ (lower panels) obtained at different pressure. The experimental data (black curves) are compared to those obtained from the PIM (blue curves) and AIM (red curves) models on the left and right panels, respectively. The $G_n(r)$ functions are obtained by Fourier transforming the $S_n(q)$ functions following the same procedure for each data sets (data processing by A. Zeidler and P. S. Salmon). The experiments were carried out using the D4c (up to 8.2 GPa) and PEARL (13.0-17.5 GPa) diffractometers[23]. The high-pressure data sets have been shifted vertically for clarity of presentation.

Both models show a reduction of the boroxol rings proportion with pressure (see Fig. 2.33) until their disappearance at about 9 GPa for AIM (~ 15 GPa for PIM), in reasonable agreement with the uncertain experimental knowledge (~ 11-14 GPa [77, 78]). The corresponding density, $\rho \sim 2.7$ g.cm⁻³ for AIM (~ 3.0 g.cm⁻³ for PIM) is typically slightly above that of B₂O₃-I (2.55 g.cm⁻³). Further, extrapolating the experimental n_{BO} values, it is seen that a BO₄-made glass is obtained for pressures above 20 GPa, i.e. for densities above 3.2 g.cm⁻³ which correspond typically to that of B₂O₃-II. So, this high pressure study, together with the results from previous sections (2.2 and 2.4) shows that both the boroxol-to-BO₃ and BO₃-to-BO₄ transitions in the glassy phases occur for density ranges which are roughly comparable (albeit slightly higher) to those of the underlying crystalline phases¹⁷.

Finally, Fig. 2.34 shows that the pressure-induced dissolution of the boroxols has a slight but visible *signature* on the $g_{BO}(r)$ (left panel) which is consistent with the differences observed between the boroxol-rich and boroxol-poor glasses studied at ambient pressure (right panel). These differences (in the distance range 2.7-3.1 Å) are discernible in the total $G_N(r)$ functions (Fig. 2.31) although they are very weak (and even more subtle to pinpoint on the $S_N(q)$ since they are spread across q-space).

 $^{^{17}}$ Taking the Ti-*b*, B₂O₃-I and B₂O₃-II polymorphs as representatives of boroxol-, BO₃- and BO₄-made structures, respectively.



Figure 2.32: The pressure dependence at room temperature of the B-O coordination number as obtained from the PIM (\circ) and AIM (\diamond) models, compared to experimental and simulated data from various groups. The experiments include the neutron diffraction works of Zeidler *et al.* [23] [using the D4c diffractometer at ILL (\bullet), or PEARL diffractometer at ISIS (\star)], the x-ray diffraction work of Brazhkin *et al.* [17] (\blacktriangle), and the inelastic x-ray scattering work of Lee *et al.* [153] (\blacklozenge). The simulated results include those using *first-principles* (DFT with the PBE functional) MD simulations from Brazhkin *et al.* [17] (\Box), the coordination-dependent potential from Huang *et al.* [120] (\triangleleft), and the coordination-dependent potential from Takada [140] (\triangle).

As a conclusion, diffraction data are not totally free from boroxols' signatures but these require highresolution in r-space and are best emphasised with a systematic and differential analysis. Even in this case, we believe that the assessment from diffraction experiments can only be at best qualitative.

2.7.2 Temperature-driven transformations in the liquid

Following the publication of the high-pressure work [23], another experimental group (Oliver Alderman, Chris Benmore from APS, Argonne, USA) which had measured high energy x-ray diffraction data of glassy and molten B_2O_3 up to 1710 K, contacted us so as to get microscopic models from the simulations. Thus, much in the same spirit than the high-pressure study, a series of simulations were carried out at different temperatures to assist the XRD analysis and to evidence the structural changes from the boroxol-dominated glass to the BO₃-dominated liquid. For the sake of concision, the results from this study [24, 209] will be only briefly evoked here. We restricted the study to the PIM potential for two reasons: first, PIM had shown previously (Fig. 2.28) better results than AIM in purely ^[3]B phases (no ^[4]B are expected along the liquid-glass transition), second, the AIM potential suffers from numerical instabilities (*polarisation catastrophes*) at high temperatures (which we did not attempt to cure yet). Using long NPT simulations (several 100s of ns), the liquid was studied from 2000 K down to the lowest temperature, 1200 K, which allowed reaching the diffusive regime. Simulations at lower temperatures (300-900 K) were realised by heating the boroxol-rich glass described in the previous sections. Along the trajectories were monitored the density and the proportion of boroxol



Figure 2.33: Evolution as a function of the density of the boroxol rings' proportion f obtained with the PIM and AIM models.

rings: for both quantities, large fluctuations and long temporal periods separating abrupt changes were observed, possibly reminiscent of a phase-flipping behaviour. However, as the temperature was decreased, a tendency to underestimate the experimental data (Fig. 2.2) was noticed. Whether this is due to an intrinsic defect of PIM or to an improper sampling remains uncertain (longer tests would be needed). In any case, we decided to generate a new potential, hereafter called PIM^{*}, by increasing the oxygen polarisability (α_0 parameter) so as to favour the rings formation (Fig. 2.29(c)). A slight (8 %) increase above the initial value (that determined from *first-principles*) allowed to reproduce nicely and simultaneously the thermal dependence of the density, the proportion of boroxol rings and the x-ray diffraction data [24].

Here again, thanks to the differential analysis (x-ray structure factor as a function of temperature), it has been possible to evidence regions in the (x-ray) total radial distribution function slightly sensitive to the amount of boroxol rings: these include, in addition to the weak shoulder at ~ 2.8 Å arising from B-O correlations already evidenced in the previous work [23], a more visible peak at ~ 4.2 Å which arises from O-O correlations (Fig. 2.7). However here again, although qualitative, these signatures can hardly be used in a quantitative manner without the support from MD simulations. Nonetheless, from a careful comparison of the residuals between the experiment and various MD models, optimal values of f could be derived as a function of temperature: these values, which are affected by a significant error bar (typically 20 %) cannot pretend to supersede those previously derived from Raman [73] but provide an independent confirmation of the temperature-assisted dissolution of the rings.

As a final word in the liquid state, the atomic diffusion constants have been investigated at various temperatures and pressures. The obtained values [209] are in good agreement with experiments [79] and evidence a *diffusion anomaly*, i.e. the existence of a maximum in the diffusion at high pressure, as reported first in B_2O_3 by a classical simulation [139] and confirmed more recently by both FPMD [123, 124] and experiments [79].

As a final conclusion on this part, several polarisable potentials (PIM, PIM^{*}, AIM) have been constructed. The tests conducted in the various phases and in the various thermodynamic conditions revealed each force-field' strengths and weaknesses. Although all potentials showed much better performances than those previously available in the literature, some technical difficulties and/or limitations were encountered which require some additional work. It would be desirable to get an AIM-type po-



Figure 2.34: Zoom-in of the B-O partial radial distribution function $g_{BO}(r)$ for an r range [2.8-3.2] Å. Left panel: comparison of the boroxol-rich (f = 75 %) and boroxol-poor (f = 22 %) glassy models at near-ambient pressure. Right panel: evolution of $g_{BO}(r)$ as a function of pressure (as obtained from the compression of the boroxol-rich model). The high-pressure data have been shifted vertically for clarity. All the data presented here were obtained with the AIM potential.

tential working at high temperature. Meanwhile, much longer PIM/PIM^{*} trajectories are needed in the low temperature liquid. In the glass, additional tests could include the computation of vibrational spectra as well as mechanical modulii.

Among the many perspectives already opened by the availability of these potentials, we plan in the close future to investigate in particular i) the effect of the quenching rate on the resulting glass properties, in a similar manner than what has been done for e.g. silica [212, 213] ii) the glass nanoheterogeneities (in particular, are the boroxol rings and the BO₃ units distributed randomly or are there *boroxol-enriched* regions?) iii) the structural transformations in the liquid under tensile stress or as it approaches T_g (section 2.5). However, because even year-long simulations may not prove sufficient for realistic description of the glass/melt near T_g , we are considering using enhanced sampling methods (metadynamics, see section 3.3 in the project).

I also note that even within the standard MD framework, two new methods can be envisaged to generate boroxol-rich glasses (in addition to the older *crystal-tweak* method [66]): i) by using the thermodynamic path described in section 2.5 (rapid simultaneous decrease of the volume and temperature starting from a low-density liquid) ii) by using PIM/AIM-like potentials with an artificially enhanced polarisability. I intend to test the quality of models obtained from both schemes (as well as from long conventional quenches).

Chapter 3

Research project

I here mention different possible directions for the coming years, restraining myself however only to those directly connected to the problematics evoked previously. These tasks are of different nature and difficulties and thus will extend on different time-scales. The first task (3.1) is actually close to completion, those described in sections 3.2,3.3 and 3.4 are at a very early stage while the remaining one (3.5) is purely prospective.

3.1 Energetics of B_2O_3 polymorphs: from DFT up to QMC

The results presented in section 2.4 were obtained at a GGA level using the PBE exchange-correlation (XC) functional [135]. This choice was made initially i) to keep consistency with the liquid and glass studies (sections 2.2) ii) because the literature had shown its adequacy (and greater superiority as compared to LDA) [214, 14] to describe the B₂O₃-I to B₂O₃-II transition. However, in an attempt to explore the results' sensitivity with respect to this choice, we have re-investigated the energetics and structure of the B₂O₃ polymorphs using different functionals, taking advantage of recent propositions to include van der Waals contributions. The investigated proposals include DFT-D2 [137], DFT-TS [215], vdW-rVV10 [216] and vdW-DF2 [217] which correspond to different levels of treatment of dispersion interactions (1st, 2nd and 3rd levels of Fig. 3.1), ranging from simple empirical corrections ($\sim \frac{C_6}{r^6}$) up to non-local dispersion-incorporated functionals¹. The LDA functional [220] has also been included in our survey.

Figure 3.1: In analogy with the Jacob's ladder classification of functionals the *stairway to heaven* is used here to classify and group DFT-based dispersion correction (DC) schemes. At ground level are methods which do not describe the long range asymptotics. Simple C_6 correction schemes sit on the first step, on the second step are approaches that utilise environment dependent C_6 corrections. The long range density functionals sit on step 3 and on step 4 and above are approaches which go beyond pairwise additive determinations of dispersion. Adapted from Fig. 4 of Ref. [221]



¹In the case of the DFT-D2 [137] and DFT-TS [215] schemes, the empirical corrections were added to the PBE exchange-correlation functional, thus providing a consistent comparison of PBE, PBE-D2 and PBE-TS. In the case of vdW-rVV10 [216] and vdW-DF2 [217], the underlying exchange-correlation functionals were rPW86 [218] and C09 [219], respectively, which slightly differ from PBE.



Figure 3.2: Energy-density graphs obtained for the B_2O_3 polymorphs using different XC functionals. In each case the energy reference, E_0 , is that obtained for B_2O_3 -I for the given functional. For all polymorphs, the densities have been rescaled by a factor given by the ratio of the experimental and calculated densities of B_2O_3 -I. The proportion of boron atoms in boroxol rings in the polymorphs are indicated by different symbols with the same legend than in Fig. 2.20. The horizontal dotted line indicates the highest energy (above quartz) among known SiO₂ polymorphs (ISV zeolite: 6.88 kcal/(mol 2SiO₂)) [164]. The experimental energies for the B_2O_3 liquid and glass are taken from Ref. [86].

Both the energies and densities show sizeable variations with the XC functional (Fig. 3.2). The polymorphs' energies vary by up to ~ 10 kcal/(mol B_2O_3) from LDA to PBE. Dispersion-corrected (DC) energies tend to fall in between the LDA and PBE scenarios with however some spread (of about 2-3 kcal/mol) from one scheme (e.g. vdW-DF2) to another (vdW-rVV10). The density of the known polymorph, B_2O_3 -I, which was considerably underestimated with PBE (-9.4 %) and overestimated with LDA (+ 6.3 %) is reasonably predicted within dispersion-corrected schemes (e.g. -0.8 % with vdW-DF2) with however no systematic improvements with the supposedly level of scheme².

Interestingly the densities of the new (predicted) polymorphs obtained with the DC schemes are even closer to the glass density than they were with PBE. The *quasi-degenerate* character of their energies is still well apparent. Thus the main conclusions derived in section 2.4 remain unchanged³. However, within DC schemes the new polymorphs' energies are above that of B_2O_3 -I. Thus, depending on the trusted scenario (PBE, DC-corrected ones, LDA), one gets different answers regarding which polymorph is the *true* groundstate and, at a very qualitative level, on the *likelihood* to synthetise the new polymorphs (as very roughly and tentatively indicated by the horizontal dotted line in Fig. 3.2 which indicates in the case of silica the energy of the highest known polymorph).

To better assess the quality of the DFT results, and in particular to decipher between the various DC-corrected schemes, we felt the need first to test our XC survey on a benchmark system, second to use higher-level theories. Silica (SiO₂) provides a relevant benchmark system since many polymorphs are known, which span a large density range and whose energies are experimentally determined within the so-called chemical accuracy (1 kcal/mol). We thus carried out a thorough investigation of the energies, structure and mechanical properties⁴ of six known SiO₂ polymorphs⁵ using the previously mentioned XC functionals [26]. In this system, LDA is known to severely underestimate the energy (relative to quartz) of high-pressure polymorphs such as stishovite (and thus their corresponding transition pressure) while PBE incorrectly predicts coesite (instead of quartz) as the groundstate polymorph [222]. All DC-corrected schemes significantly improve the energetics, the best overall performances (average error bar of about 1.1-1.3 kcal/(mol SiO₂) being obtained for DFT-D2, DFT-TS and vdW-DF2 [26].

 $^{^{2}}$ The best agreement, -0.2 %, is obtained with PBE-D2 which sits on the first level of Fig. 3.1 while the worst, -4.0 %, is that of PBE-TS, corresponding to the ladder's second level.

 $^{^{3}}$ Except that in the DC scenarii the vitrification would be *entropically* driven by the proxies of low-energy crystals which are however not the lowest-energy ones (as they were in the PBE case).

⁴These include: absolute energies at 0 K, zero-point energies correction, heat capacities, equation of state, bulk modulus, transition pressure, lattice parameters, interatomic distances, bond angles.

⁵These include: faujasite, ferrierite, cristobalite, quartz, coesite and stishovite.

However, only vdw-rVV10 and vdW-DF2 succeed in reproducing the correct energy ordering for all the investigated polymorphs. The densities obtained from the DC schemes were also considerably improved, with an average error bar ranging from 1.0 (vdW-DF2) up to 1.8 % (DFT-D2), as compared to the PBE values (-4.2 %). However these encouraging results are plagued by at least two findings. First, when digging deeper into the details, one realises that the very good results from DC schemes on density actually come out from an error compensation, namely a concomitant overestimation of the Si-O interatomic distances and underestimation of the Si-O-Si bond angles. Second, there is no universal nor uniquely-defined *best* scheme: depending both on the quantity of interest and the considered polymorph, a better reproduction may be obtained by a functional or another, with no systematics with the supposedly level of accuracy. This prevents a strict transferability of the quality survey from silica to B₂O₃. In summary, although DC schemes provide in most cases significant improvements over typical GGA results, they do not entirely cure their flaws. Thus, at the present state, DFT still remains an approximated (albeit generally quite good)⁶ method with a somewhat unpleasant empirical character (in the choice of the XC functional).

We are thus turning now to higher level theories such as Quantum Monte Carlo (QMC) and to this aim, I have initiated a collaboration with Michele Casula (CR, IMPMC), through Henri Hay's PhD. QMC is a many-body method which can reach essentially exact energies [223, 224, 225, 226]. As an initial test, we investigated in silica the quartz and cristobalite cases and showed that subchemical accuracy could be reached [26]. A study of three B_2O_3 polymorphs (including B_2O_3 -I) is currently on-going. Because of the huge CPU cost of such calculations, both the number and the size of the polymorphs that can be studied is very constrained. Thus, we will also carry out calculations using an intermediate level between standard DFT and QMC calculations, the Random Phase Approximation (RPA)[227] thanks to a collaboration with Maria Hellgren (CR, IMPMC). After benchmarking the RPA calculations against those from QMC, RPA could be used to extend the survey. These calculations should allow to conclude which scenario (Fig. 3.2) is the most correct and possibly which polymorph is the groundstate. A possibly interesting by-product of this study is the availability of atomic forces obtained from QMC. These could be used to calibrate new force fields, in particular if the FFs derived in section 2.7 prove to be unsatisfying in the forthcoming studies (see 3.3).

3.2 Assessing the properties and expanding the search of new B_2O_3 polymorphs

Within Henri Hay's PhD thesis and through a collaboration with F.-X. Coudert (ChimieParis), we have recently assess the mechanical properties⁷ of the predicted B_2O_3 polymorphs (obtained in section 2.4). Two noticeable findings could be drawn. First, the new polymorphs tend to have poorer mechanical performances (lower modulii and *stiffness*⁸) than the experimentally known polymorphs (B_2O_3 -I and B_2O_3 -II). This could be a factor explaining why these crystals have not been synthesised yet, as well as an additional ingredient favouring the system's tendency to vitrify. Second, for some crystals, remarkable properties such as large porosity, negative linear compressibility [229] and auxeticy [230, 231] were found, which could justify investing efforts to synthesise them. Thus, it could be interesting to check the robustness of these two findings (in addition to the problematic of determining the structural links between the glass and the underlying polymorphism) from a larger database of predictions.

The structure search previously used (section 2.4) was limited in three aspects: i) the number of

 $^{^{6}}$ I believe that the DFT current precision is more than enough for most glass-related problematics. However, its limits may be reached for some specific and very fine questions such as determining the groundstate crystal in polymorphs made from identical structural units.

⁷Elastic tensor eigenvalues, bulk compressibility, Young and shear modulii as well as Poisson's ratio.

⁸Using as a stiffness measure the lowest eigenvalue of the elastic tensor [228].

nodes per unit cell was restrained to a maximum number of 6 ii) all the nodes were decorated by a single unit type, either the triangle or the boroxol ring iii) with the exception of T0 (and T0-*b*), only fully 3D connected networks were considered, thus omitting lamellar systems (and their corresponding polytypes) as well as interpenetrating networks. The search in principle could be pushed further by extending these limitations (larger cells, decoration with mixed amounts of triangle/boroxol units, unconnected networks).

As a matter of fact, two additional predictions have since been made [232] by constructing 3D structures from boroxol-containing 2D layers found experimentally in complex borate systems⁹ [233, 234]. As more and more sp^2 -carbon polymorphs are discovered [235, 236, 237, 238] (and rediscovered [239] ...), one could also use their networks for decorations: the Sacada project [240] for a database of carbon allotropes has taken an inventory of 256 different nets among which 40 are purely 3-connected ones.

I note with interest the recent experimental synthesis of two new borosulfates [241, 242]. Both compounds are made of (neutral) pure B_2O_3 layers intercalated with sulfate groups. In one of them, the layers are identical to those from our T0-*b* structure (i.e. graphene topology fully decorated with boroxol rings) [241] while in the other one the layers are decorated by a 50-50 % mix of triangles and boroxols [242]. From the experimental side, this opens the interesting perspective to obtain new B_2O_3 polymorphs by de-intercalation of the sulfate groups [241]. Further, our calculations reveal (Fig. 3.2) that the mixed-decoration B_2O_3 compound (here labeled T0-f75)¹⁰ has an energy comparable or even smaller than the fully triangle- or boroxol-decorated compounds (T0 and T0-*b* respectively). This provides a motivation to re-investigate all the topologies used in section 2.4 with mixed decoration.

I also note the existence of the *Predicted Crystallography Open Database* (PCOD)[243] which contains in the case of B_2O_3 more than 800 structure candidates (!). These were obtained from the steric accommodation of predefined units (corner-shared BO₃ triangles) using a Monte Carlo algorithm and the minimisation of a very simple cost function (limited to the verification of ideal interatomic distances), without imposing any energetic constraints, with the GRINSP¹¹ code [244]. It would be interesting to investigate the energies and properties of these putative polymorphs. A two-steps strategy could involve i) first, a pre-screening of the 800+ structures with an empirical force-field such as the PIM one derived previously, so as to get rid of high-energy structures (typically above 15 kcal/mol) ii) followed by finer energy calculations among the survivals using a more accurate scheme (typically within *first-principles* with dispersion corrections). This would very likely complement our own set of predicted polymorphs (section 2.4) although it is not possible to predict to which extent.

In my opinion however, making predictions of new polymorphs is not the first priority at the moment (and until experimental syntheses confirm the existence of a genuinely new B_2O_3 structure). More interesting (but also more challenging) would be to assess the *realisability* of such predictions. Although an important quantity, the energy above the ground state alone is not sufficient to predict which structures will actually be realised (or not). Clearly, energy barriers are an obvious ingredient for kinetic trapping (and thus the observation of metastable states) but more subtle aspects related to the *shape* of the potential energy surface may also be at play, such as e.g. the volume of the configuration space occupied by a given basin, the connectivity between the basins (in particular, whether they are part of *funnel*-like superbasins). In a recent work using random structure searches (of MgO, ZnO and SnO₂ polymorphs) [245], it has been argued that the frequency of occurrence of a given structure offers an (indirect) estimate of the volume of configuration space occupied by this structure (funnel of attraction) and a key quantity in assessing the likelihood for its experimental realisation (when combined with the usual criteria of being a low-energy polymorph). Being simple to implement (notwithstanding however its conceptual and practical limitations), it may be interesting to test this tool in a broader range of systems showing contrasting polymorphic behaviours (e.g. SiO₂ versus Si),

⁹Namely $B_6O_9(en)_2@(H_2en)Cl_2$, $B_6O_9(en)$ and $(H_2en)_2(Hen)_2B_{16}O_{27}$ where en stands for ethylenediamine.

¹⁰Since it corresponds to a proportion of boron atoms in boroxol rings f = 75 %.

¹¹Geometrically Restrained Inorganic Structure Prediction.

and to apply it to the much less known B_2O_3 case. Although a more speculative goal, it could also be worth, from the vast amount of both ordered and disordered configurations generated by random structure searches, to look for possible statistical indicators of a system's tendency to vitrify. However, given that both polymorphism and vitrification involve finite temperature conditions, a more rigorous method to determine the free-energy landscape is described in the next section.

3.3 Revisiting the B₂O₃ phase-diagram using enhanced sampling: from crystal-crystal to liquid-liquid transitions

As compared to other oxides such as silica, the B_2O_3 phase-diagram has been considerably less studied. We have however provided in the previous sections strong indications that it is much richer than previously thought. First, we have predicted a number of yet unknown low-energy crystalline polymorphs (section 2.4). However their respective stability regions in the *p*-T phase-diagram remain to be determined. Further, nothing is known about the paths which connect these polymorphs in the energy landscape. Second, we have also found in the liquid state indications of possible structural transitions. One is occurring between a low-density and a mid-density liquid and is linked to the amount of threefold rings (section 2.5). This transformation bears some similarities with the one occurring along the liquid-glass transition. Beside, at the other extreme (high pressure), the liquid also show structural transformations, this times involving coordination changes (^[3]B \leftrightarrow ^[4]B), which resemble those experimentally observed in the crystalline and glassy phases. In this regime, the existence of a *diffusion anomaly* has been reported experimentally [79] and numerically by different groups [139, 123, 209]. In other systems, such as e.g. silica, germania [246] or water, the diffusion anomaly has been linked, at least in some scenarii, to a possible liquid-liquid transition and/or to the underlying polyamorphism.

I believe that the availability of the force-fields previously constructed (section 2.7) opens new perspectives on the above problematics (by allowing for a more systematic investigation and on larger systems or longer time scales than those achievable within *first-principles* MD). However, it is also clear that given the time-scales involved (in particular at low temperatures), advanced methodologies that allow enhanced sampling such as e.g. *metadynamics* [247] are crucial. However, a general difficulty which has prevented so far a broader and systematic use of metadynamics is the need to find an appropriate set of collective variables (CVs). An additional challenge in our case is the need for a methodology able to discriminate not only between different ordered phases (crystal-crystal transitions) but also between ordered and disordered phases (e.g. liquid-crystal transitions) as well as between different disordered phases (liquid-liquid, liquid-glass or glass-glass transitions).

To overcome these difficulties, we intend to combine a new metric based on so-called *Permutation Invariant Vectors* (PIV) [175] recently developed by Fabio Pietrucci (MdC, IMPMC), with metadynamics based on path collective variables ($PathCV^{12}$) [248]. On one hand, the PIV metric allows to

$$s = \frac{\sum_{j=1}^{J} j \ e^{-\lambda D_j}}{\sum_{j=1}^{J} e^{-\lambda D_j}}$$
(3.1)

$$z = -\frac{1}{\lambda} \ln \sum_{j=1}^{J} e^{-\lambda D_j}$$
(3.2)

¹²Within the *PathCV* scheme one projects the 3N-6 (N is the number of particles) degrees of freedom of the system onto a two dimensional space of CVs, i.e. s and z, defined as follows:

where J reference configurations are given as input, and define a guess path between the initial (j = 1) and final (j = J) structure. The symbol D_j stands for the distance between the actual configuration of the system and the j-th reference configuration. Therefore, to use this generic scheme, one needs to define a set of reference configurations and a metric in configuration space. The simplest form of the PathCV, obtained from eqs. (3.1) and (3.2) with J = 2, only needs the a priori knowledge of the initial and the final state of the transformation, and in such a case, following a transformation pathway, one would start with $s \simeq 1$ and reach the final configuration when $s \simeq 2$.

track the atom-detailed transition pathway of a generic activated process. This metric¹³ is based on a very general formulation obtained from the matrix of all-to-all interatomic distances and invariant upon permutation of identical atoms or molecules [175]. In a recent application to water [249], it has been shown that the PIV metric allows to assign a structural distance between the crystalline and even amorphous phases of water, in a way which is consistent with the available experimental knowledge. This approach is general since it does not exploit any information about the system-specific symmetry or chemical bond topology. This allowed to track the evolution of structural transitions among crystalline and amorphous water ices as well as between the liquid and glassy phases of TeO_2 [249]. On the other hand, path-metadynamics grants statistically precise and reproducible free energy landscapes, albeit within a reach that is limited, to date, by the lack of metrics able to discriminate structures irrespective of permutations of identical atoms (a severe problem in the study of amorphous and liquid phases). The combination of the latter two methodologies (PIV + metadynamics) can thus provide a powerful tool to investigate in a seamless way all the various possible phase transitions for a given system. Within a collaboration involving F. Pietrucci, M. Saitta, M. Salanne and myself, a post-doctoral funding has been obtained to implement and test this methodology in various systems, including B_2O_3 . As a first step, currently carried out by Silvio Pipolo, the methodology is tested on water since this system provides both a challenging case (because of the numerous crystalline and amorphous phases) and a benchmark (since the phase-diagram has been extensively studied experimentally and numerically). The preliminary findings, obtained with the TIP4P force-field [250] in the vicinity of a triple point (ice VI, ice VII and liquid water) are very promising [251]: first, all kind of transitions (between ordered and disordered phases) could be observed, in particular the non-trivial disordered-to-ordered ones; second, it provided insightful information along the explored paths, such as energy barriers, free-energy minima and in some cases regarding the existence and nature of intermediate states. The scheme is currently being implemented in the PLUMED [252] plugin. The next coming step, yet to be done, is the investigation of the much less known B_2O_3 phase-diagram. We expect from this study:

- a topological mapping of the structural proximity between the glass and the different polymorphs and between the polymorphs themselves.
- a full characterisation of the free-energy barriers and low-energy paths between the different polymorphs. This may help suggesting the viable preparation routes connecting the structures explored.
- the construction of the stability regions of each polymorph at finite temperature and pressure.
- the obtention of new order parameters able to address the dynamic mechanisms connecting the liquid and the glass phases as well as the putative liquid-liquid transitions in this system.

More generally and beyond the B_2O_3 case, this methodology, if successful, opens the way to exploring glass formation and its competition with crystallisation. In particular, it could shed light on the earliest stages of nucleation, one of the most challenging and fascinating topic in physics.

$$\mathbf{v} = \left\{ \operatorname{sort} \left[\mathcal{C} \left(\frac{1}{3\sqrt{V}} \left| \mathbf{r}_{\alpha} - \mathbf{r}_{\beta} \right| \right) \right] \right\} \quad \text{and} \quad \alpha > \beta$$
(3.3)

here \mathbf{r}_{α} and \mathbf{r}_{β} are two generic atomic position vectors, the function C monotonically decreases from one to zero as $|\mathbf{r}_{\alpha} - \mathbf{r}_{\beta}|$ increases (*switching function*), V is the volume of the simulation cell and the sorting (sort) operation is performed to introduce permutation invariance. The distance between configurations is then defined as follows:

$$D_j = |\mathbf{v} - \mathbf{v}_j|^2 \tag{3.4}$$

¹³The PIV metric acts as a topological fingerprint of the configuration of the system. It has the advantage of providing a global description of the system's configuration by mapping it into a vector, built-up from inter-atomic distances:

where \mathbf{v} and \mathbf{v}_j are respectively the PIV vectors associated to a generic configuration of the system and the j-th reference configuration. In principle any molecular dynamics trajectory $\{\mathbf{r}_{\alpha}(t)\}\$ may be mapped into the PIV-PathCV two dimensional space $\{s(t), z(t)\}$.



Figure 3.3: Proportion of ^[4]B atoms, x_4 , as a function of the modifier content x for the five alkali borate glass systems. Data obtained from NMR [265]. The black line $(x_4 = x/(1 - x))$ denotes the value of x_4 if all of the added network modifier leads to the formation of BO_4^- tetrahedra, with no nonbridging oxygen atoms. Adapted from Fig. 8 of Ref. [266].

A final word regarding liquid-liquid transitions, a highly controversial topic in one-component systems. From the numerical side, I am well aware of the tough on-going (never ending?) debate about liquid water [253, 254, 255, 193, 256, 192]: deciphering the putative liquid-liquid transition from a liquid-solid one requires high quality sampling and sophisticated methods (enhanced sampling on very large systems and very long simulations), so that no consensus has yet been reached. Yet, I also think that because of its open and low-coordinated network, B_2O_3 offers a very favourable case for such transitions to be evidenced¹⁴. If true, this would possibly provide valuable comparative insights with the more studied tetrahedral systems (such as carbon [259], silicon [260, 261], silica [136] and water).

3.4 Exploring more chemically complex borates: rigidity transitions and the borate anomaly

 B_2O_3 is a glass former *par excellence* and forms binary glasses with a wide range of other oxides. While B_2O_3 in its pure form has not yet found any application, the situation is drastically changed as metal oxides are added. Borates crystals have been proposed for a large number of (confirmed or possible) applications, including non-linear optical devices and solid state batteries. In the vitreous form, borates constitute, after silicates, the second most used oxides in glass products (laboratory glasses, waste matrices, fertilisers, etc). Very recently, borates-based glasses in the form of nanofibers have been under the spotlight [262] as bioactive materials [263] for their startling wound-healing properties [264].

In the following the discussion is focused on alkali borates, $(M_2O)_x$ - $(B_2O_3)_{1-x}$ where M is Li, K, Na, Rb, Cs, which despite a rather simple chemical composition, display a rich chemistry (in terms of structural units, see Figs. 3.4 and 3.5) and complex behaviours (in terms of variation of their properties with composition x, see e.g. Fig. 3.3).

Borates are puzzling materials, in both the vitreous and crystalline states, in that their structures and properties do not reflect those of the corresponding silicates. These unusual behaviours, which have led to many reports of *anomalies* in the literature (see [35, 266] for reviews), are believed to arise from two special features that are unique to borate systems, namely the possibility for boron to adopt (even at ambient conditions) different coordination states, ^[3]B and ^[4]B, and the presence of superstructural units.

¹⁴My argument is based in particular on the extrapolation of findings derived in tetrahedral systems [257, 258].



Figure 3.4: Two-dimensional representations of the five major basic structural units (BSU) found in vitreous and crystalline alkali borates (Key: blue, tetrahedral boron; cyan, trigonal boron; red, bridging oxygen and magenta, nonbridging oxygen). Adapted from Fig. 2 of Ref. [266].



Figure 3.5: Commonly occurring borate superstructural units (SSU) in the vitreous and/or crystalline state (Key as Fig. 3.4). x is the modifier composition if the borate network only includes that particular SSU. With the exception of the diborate group, all of the SSUs are based on planar 3-membered rings. Adapted from Fig. 10 of Ref. [266].

Prominent and most studied is the so-called *borate anomaly*: on adding a network modifier, such as (Na₂O), the properties of borate glasses frequently exhibit extrema at specific values of the networkmodifier composition x whereas those of silicates vary monotonically¹⁵. This is illustrated Figure 3.3 which shows the composition dependence of x_4 , the proportion of 4-fold coordinated boron atoms ^[4]B, as determined from NMR measurements, for all five alkali borate glass systems. In the case of this quantity, the presence of a maximum is explained by a two-steps mechanism: at low concentrations $(x \leq 30 \%)$, all introduced alkali cations convert BØ₃ triangular into BØ₄⁻ tetrahedral units while higher contents of alkali lead to the formation of non-bridging oxygen atoms (NBO)¹⁶. The reason for the preferential formation of BØ₄⁻ units over NBO in the initial stage is however unclear. Furthermore, other quantities such as the glass transition temperature, the viscosity, the thermal expansion coefficient also show an extremum as a function of x but not at the same composition. The common belief is that the understanding of these effects requires structural determinations beyond the basic structural units (BSU), i.e. the knowledge of the proportions of the various superstructural units (SSU) involved in the glass structure. In addition, the nature of the modifying cations must also be considered (for instance for the variation in the density).

¹⁵Some authors define the *borate anomaly* as the fact that the various properties $(x_4, T_g, \text{viscosity, etc})$ do not exhibit extrema at the same value of x.

¹⁶The convention adopted here for the formulae of (super)structural units is taken from Ref. [35]: the symbol \emptyset is reserved solely for those bridging oxygen atoms that are shared between adjacent (super)structural units, while negatively charged nonbridging oxygen atoms that form part of a (super)structural unit are denoted O, as are bridging oxygens situated completely within a superstructural unit. An advantage of this notation is that the number of \emptyset indicates the (super)structural unit connectivity.

Indeed, it is largely recognised that (at least up to $x \sim 33$ %) the structures of vitreous and crystalline borates are totally dominated by superstructural units. Their almost universal occurrence¹⁷ strongly suggests that their formation is not just random but that they must have a very favourable formation energy. At least 14 different types of SSU have been identified [35], a selection of the most commonly occurring being represented in Figure 3.5.

However, most of what is known in the glassy phases is derived from the use of (vibrational and NMR) spectroscopic *fingerprints* taken from crystals of known structures. For glasses of a given composition, several SSUs generally co-exist with sometimes spectroscopic signatures hardly distinguishable from others. As a result, absolute and unambiguous quantifications of the corresponding populations are still lacking: different model distributions have been put forward in the literature¹⁸. In addition, there is even a lack of crystallographic information: for instance in the case of sodium borates, a full crystal structure determination has been performed for only 10 out of the total 24 reported compounds. When determined, in most cases complex crystalline structures (interpenetrating networks including several SSUs, even when a single SSU would yield a network of the correct stochiometry) and unusual stochiometries (e.g. $3\text{Li}_2\text{O} - 11\text{B}_2\text{O}_3$ rather than the previously expected $\text{Li}_2\text{O} - 4\text{B}_2\text{O}_3$) have been reported. These features are supposedly related to difficulties of packing large SSU around the network-modifying cations [268]. The fact that the crystalline compounds frequently involve a number of different SSUs, even at the stochiometric compositions for a single SSU, indicates that this is likely to be even more true for the corresponding glasses.

Finally, I note that borates glasses are currently the subject of a controversy regarding the existence and the nature of rigidity transitions [267, 268] whose resolution requires the assessment of the SSUs' populations as a function of x. In short, Vignarooban et al. [267] have recently reported calorimetric, Raman and electrical conductivity measurements (Fig. 3.6) which, in their interpretation, evidence the presence of stiffness transitions and a so-called *intermediate phase*. The latter concept corresponds to a range of *isostatic compositions* between the floppy and stressed-rigid regions, which have been reported initially in chalcogenide systems [269] and more recently in silicate glasses [270]. According to Vignarooban et al. [267], the rigidity transitions in the case of borates are driven by network dimensionality changes (conversion of planar 2D boroxol rings into 3D structural groupings) in addition to the usual topological constraint changes. From a Raman analysis of specific modes, the type and the proportions of the 3D groups responsible for these transitions have been proposed [267]. However, these conclusions have been fiercely refuted by other authors [268] for which the predicted distributions of SSUs are incompatible with those expected on the basis of the corresponding crystalline phases. These authors further stress that the local dimensionality of the SSUs should not be conflated with that of the network into which these units are inserted and they propose an alternative model for predicting the rigidity of oxides which, in addition to re-defining the relevant degrees of freedom, takes into account the intrinsic rigidity of SSUs [268, 271]. The SSUs distributions used in this latter model are claimed to be consistent with both crystallography and previous thermodynamic modeling. They conclude that the *intermediate phase* is not a phase at all, but merely coincides with the region of maximum network connectivity [268, 271]. Thus, interestingly, what is at stake with this controversy are not only structural details for specific systems but rather two different views of rigidity which have ramifications for our understanding of this theory in glasses. Borates appear as a playground to test these ideas thanks to their structure being dominated by SSUs.

Atomistic simulations are an *a priori* first-choice tool to solve some of the borates' enigmas with however the same caveats than those highlighted in the B_2O_3 case (need of sophisticated force-fields to take into account the various bonding environments as well as the subtle effects giving rise to the SSUs formation energies, long simulations, large systems, slow quenches).

 $^{^{17}\}mathrm{within}$ both an hydrous and hydrous borates

¹⁸See e.g. Fig. 15 in Ref. [266] and Fig. 2 in Ref. [267].

Figure 3.6: Glass transition T_g and non-reversing heat flow ΔH_{nr} as a function of sodium content xin $x \text{Na}_2 \text{O}$ -(100-x)B₂O₃ glasses. Adapted from Fig. 2 of Ref. [267].



With only one recent exception [272, 273, 274], all MD simulations of alkali borates have been using empirical force-fields [68, 97, 96, 275, 276, 277, 278, 279, 280, 281], and even more restricting, most studies [276, 278, 279, 280, 281] have actually used *the same* force-field, as initially derived by Verhoef and den Hartog [276]: this is a Born-Mayer-Huggins type of potential with three-body harmonic interactions for the O-B-O angles, which was fitted to experimental infrared vibrational frequencies. All these MD studies have primarily focused on the borate anomaly (Fig. 3.3): overall, the trends were reasonably reproduced but the quantitative numbers (x_4) were in general sizeably underestimated for reasons (intrinsic deficiency of the potential or too fast quenching rates) which remain unclear¹⁹. In all these studies, the presence of SSUs is rarely discussed [107] and the comparison to experimental structure factors, when available [275, 281], shows poor agreements. The first *ab initio* MD simulations of alkali borates appeared very recently [272, 273, 274] but were limited to the (lithium) melts.

There is thus certainly a need for improved force-fields and/or more extensive studies. Thus, in the continuation of our work on B_2O_3 , I have initiated a collaboration with Mathieu Salanne (PHENIX) and Mathieu Micoulaut (LPTMC) for the study of borates melts and glasses. In a first (on-going) step, we are accumulating FPMD trajectories of lithium and sodium borates at different compositions and different temperatures. In a second step, polarisable force-fields (of AIM type) will be calibrated from the FPMD results²⁰. In a last step, a thorough investigation of these systems as a function of T, p, x will be undertaken using the classical potentials. Beside, I also plan to investigate the crystalline polymorphism (within a *first-principles* framework). The ultimate aim will be to address the following important and yet unanswered questions (some originally formulated in Refs. [35, 266]):

• What is the origin of the SSUs formation energy and what are the formation energies for the commonly occurring SSUs (such as the triborate group included in 28 crystalline structures) in the ambient pressure crystalline phases? Why are some (even simple) SSUs not formed²¹? Insights may be gained from quantum chemistry calculations of the (passivated) groups and of the crystalline structures incorporating these groups. In particular, a strategy could consist in generating topologically equivalent structures made of groups of a given connectivity (e.g. 4-connected groups such as BO_4^- and triborate $B_3O_3O_4^-$) so as to determine their relative stabilisation energies in condensed phases.

¹⁹In only two studies [96, 278] were the x_4 values in good agreement with experiments. However a large internal pressure is reported in one case [96] while the results in the other case [278] were not reproduced by other authors who found underestimated x_4 values using the same potential [276] but larger system sizes and longer quenching rates [281]... In a few studies using simple pair potentials, over-estimated x_4 values were produced [275, 68, 97], possibly as a result of large internal pressures (not reported).

 $^{^{20}}$ As an alternative to the AIM potentials, it could also be interesting to test *reactive*-like force fields [211, 282].

²¹For instance, boroxol groups with one or two NBOs are not formed while that with three NBOs are!

- What are the structures of certain important crystalline phases²² which are key to understanding the glass formation (or the lack of it) together with the structure of the corresponding glasses? Why are some structures observed for some alkali and not for others? These require searches in the polymorphic space, a non-trivial task given the complexity of these systems. As a first step, one could play with chemical substitutions using the database of determined structures (e.g. substituting Cs for Li in the enneaborate compound). More general methods, such as random searches [283] (using the various borate groups as fundamental blocks) or genetic algorithms [284], will also be considered. This task will parallel experimental efforts in the team (G. Lelong) [285]. Although a less immediate perspective, I also note that the metadynamics-based methodology, described previously (section 3.3), could be used for instance to characterise the kinetics and the nature (displacive or reconstructive) of the transitions between low- and high-temperature (or low- and high-pressure) polymorphs: this may help understanding curious behaviours such as the *lithium metaborate anomaly* [35] (in the Li₂O B₂O₃ system, the structure of the rapidly quenched vitreous phase is clearly incompatible with the ambient pressure crystalline polymorph while it shows much greater compatibility with some high-pressure polymorphs).
- In the glassy phases, what are the BSU and SSUs' distributions as a function of x? Can the different models proposed in the literature be deciphered? In particular, is it possible to provide a microscopic understanding for the reported *intermediate phase* [267]?
- What is the spatial distribution of the various SSUs: statistically-random or nanoheterogeneous? This has implications for instance for the cationic conductivity of these glasses.

3.5 Poly(a)morphism in other oxide systems: the P_2O_5 case

Even among network-forming oxides, the conditions which favour crystallisation or vitrification for a given system remain poorly known. For instance, B_2O_3 spontaneously vitrifies as the liquid is cooled while As_2O_3 (and Al_2O_3) very easily crystallises, the P_2O_5 case being somehow intermediate. In addition, the medium-range order [286, 287] in these glasses (As_2O_3 , P_2O_5) and the existence of various amorphous phases [288, 289] remain debated.

I intend to focus in the near future on the P_2O_5 case and this for various reasons. First, the (ambient pressure) polymorphism is rather modest with only three known crystals [290], including an hexagonal form, h-P₂O₅ (I) and two orthorhombic ones, o-P₂O₅ (II) and o[']-P₂O₅ (III)²³. This small number is likely a result of a lack of investigations²⁴ and there may well be other low-energy polymorphs to discover. In the crystalline as well as in the glassy phases, the local unit is a POØ₃ tetrahedron in which there is one (double bonded) non-bridging terminal oxygen (while the other three oxygen atoms are corner-shared) [286]: this renders this system's geometry somehow *intermediate* between that of B₂O₃ (threefold corner-shared BØ₃ triangles) and that of SiO₂ (fourfold corner-shared SiØ₄ tetrahedra). This induces both similarities and specificities worth exploring²⁵. In particular, new P₂O₅ polymorphs could possibly be found from a rather easy adaptation of the decoration method used in the B₂O₃ case (section 2.4), using either trigonal or tetrahedral networks. Of course, other general methods, such as random searches [283] or genetic algorithms [284], could also be considered. The comparative study of the (known and unknown) polymorphism²⁶ in the different oxide systems may help unraveling some correlations with their glass-forming ability.

 $^{^{22} \}rm such$ as $2 N a_2 O - 3 B_2 O_3, \, 3 N a_2 O - 2 B_2 O_3$ and $5 N a_2 O - 2 B_2 O_3$

 $^{^{23}}$ The h-form is a molecular crystal made of P_4O_{10} molecular units while the o- and o'-forms are fully polymeric networks of POO_3 tetrahedra.

 $^{^{24}}P_2O_5$ is hygroscopic and volatile. It is used in its pure form only as a dehumidifier.

 $^{^{25}}$ For instance, anomalous structural behaviours under pressure have been claimed to be related to the presence of the double-bonded terminal oxygen atoms [288].

²⁶e.g. through the numbers of polymorphs separated from the groundstate by a given ΔE energy.

Second, despite a reasonable gamut of experimental data, the information regarding the mediumrange structure of the glass is contradictory. From diffraction data, some authors [291] have inferred the presence of P_4O_{10} molecular units, as found in the h-form (I). Still using diffraction, others [292] have proposed that the o'-form (III) is a better structural model for $v-P_2O_5$, which thus would be made up of corrugated sheets of three-fold rings of tetrahedra. However, some others insisted on some dissimilarities between $o'-P_2O_5$ (III) and $v-P_2O_5$, as inferred from IR and Raman spectra [293]. Finally, noticing that the glass density is intermediate between those of the h- and o-forms (I and II)²⁷, it has been suggested [287] that the glass likely contains longer-range structural similarities to both these forms²⁸. Among the available experimental data, I note that there is yet no XAS data which however could bring interesting information regarding the local atomic environments: in particular from IXS at the O K-edge, it should be possible to decipher the contributions from terminal and bridging oxygens (which correspond to well separated P-O bonds²⁹). This would likely provide unique information regarding the P-Ø-P (and P-O-P) angular distributions and possibly to some other features of the medium-range arrangements. I thus plan to carry out preliminary calculations in the various crystalline phases to investigate the sort of information one could retrieve; this could then impulse the first IXS measurements on this system (in collaboration with Laurent Cormier and Gerald Lelong at IMPMC, and in the line of our previous work on the GeO_2 system [21]).

From the numerical side, atomistic simulations of v-P₂O₅ have remained to date very limited (in number and scope) and have used either no potential at all (RMC) [294] or crude empirical ones [295, 296, 62, 297], resulting in all cases in patent failures to describe even basic features of the local order³⁰. To the best of my knowledge there are yet no *first-principles* MD simulations of the glass despite several numerical investigations of the P₂O₅ crystals [299] or more complex phosphate systems [300]. I thus plan to carry out such MD simulations and following a strategy similar to that devised for B₂O₃ (computation of various diffraction and spectroscopic signals for different glassy models), I hope to assess the glass structure and its possible similarities to the underlying polymorphs.

A natural extension of this work could then include numerical investigations of the high-pressure transformations in the liquid and glassy phases for which the experimental information has become available only recently and is still scanty [288]. In the melt, several anomalous behaviours have been reported, in particular a maximum in the melting curve (around 10 GPa) as well as a viscosity decrease with increasing pressure [288]. Here again, the comparative study of the phase diagrams of SiO₂, B_2O_3 and P_2O_5 should help to gain a broader understanding. From a materials perspective, the characterisation of the phase diagram may help guiding the experiments towards synthesising materials of specific properties: recently, a low-hygroscopic form of P_2O_5 has been obtained by quenching the melt under pressure, thus reducing significantly what has been so far a limiting drawback of P_2O_5 for applications [298]. Still from an applied perspective, borosilicates constitute an important class of bioactive materials [301] while borophosphates have sparked interest as solid state batteries [302]. Thus, both types of materials could constitute interesting directions for future research.

 $^{^{27}}$ Densities of the h- and o-forms are 2.28 and 2.705 g.cm⁻³, respectively while that of the glass is 2.38-2.45 g.cm⁻³. Values taken from [287].

 $^{^{28}}$ I note that this could alternatively be interpreted as an additional indication of experimentally missing polymorphs. 29 Typically, 1.42-1.445 and 1.57-59 Å, respectively [287].

 $^{^{30}}$ In the MD-based studies, the proportion of three-fold corner-linked tetrahedra POØ₃, noted Q³, is drastically underestimated (54 % at most versus 100 % experimentally) and the agreement with the experimental structure factor is mediocre. In the RMC works, the Q³ proportion is better (~ 82 %) but unreasonable spikes or shoulders are observed in some pair distances and in the P-O-P angular distribution. A possible exception is [298] but no details regarding Q³ are given.

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