Eur. Phys. J. E **12**, 195–204 (2003)
DOI 10.1140/epje/i2003-10070-2

THE EUROPEAN PHYSICAL JOURNAL E

Eur. Phys. J. E 12, s01 (2003) 001
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-001-9

Received January 2003
Published online 5 November 2003

De-mixing dynamics of a binary liquid system in a controlled-pore glass

A neutron spin-echo spectroscopy and small-angle neutron scattering study

T. Hellweg, S. Schemmel, G. Rother, A. Brûlet, H. Eckerlebe, G.H. Findenegg

PACS. 64.60.Cn Order-disorder transformations; statistical mechanics of model systems – 61.12.Ex Neutron scattering (including small-angle scattering) – 64.70.Ja Liquid-liquid transitions

Abstract. The temperature-induced microphase separation of the binary liquid system iso-butyric acid+heavy water (iBA + D_2O) in a mesoporous silica glass (CPG-10-75) of nominal pore width 7.5 nm was investigated by neutron spin-echo spectroscopy (NSE) and small-angle neutron scattering (SANS). Two mixtures of different composition were studied at different scattering angles at temperatures above and below the bulk phase transition temperature. The phase separation in the pore space is found to occur at a lower temperature than the bulk transition and extends over a significant temperature range. The effective diffusion coefficient derived from NSE at low scattering angles is found to decrease by one order of magnitude from 70 °C to 20 °C. This observation is attributed to the growing size of concentration fluctuations having a cut-off at ca. 8 nm, which corresponds to the mean pore size. The dynamics of the concentration fluctuations appears to be strongly influenced by the confinement in the pores, as it differs strongly from the bulk behaviour. These results are consistent with the preliminary results of the SANS study.

Eur. Phys. J. E 12, s01 (2003) 002
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-002-8

Received January 2003
Published online 5 November 2003

Collective dynamics near a phase transition in confined fluids

M. Schoen, F. Porcheron

PACS. 68.55.-a Thin film structure and morphology – 62.10.+s Mechanical properties of liquids – 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 62.25.+g Mechanical properties of nanoscale materials

Abstract. We performed molecular dynamics simulations in the microcanonical ensemble (MEMD) for a "simple" fluid confined between two solid substrates. From the calculation of the intermediate scattering function $F(k_{\|}, t)$

and through the memory function formalism, we extract material (*i.e.* transport and thermodynamics) coefficients in the vicinity of the liquid-gas phase transition. Our results show that approaching the limit of stability (*i.e.* the spinodal), the dynamics of the system changes markedly.

Eur. Phys. J. E 12, s01 (2003) 003
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-003-7

Received January 2003
Published online 5 November 2003

Confined phonons in glasses
A study by nuclear inelastic absorption and Raman scattering

T. Asthalter, M. Bauer, U. van Bürck, I. Sergueev, H. Franz, A.I. Chumakov

PACS. 61.43.Fs Glasses – 61.18.Fs Magnetic resonance techniques; Mössbauer spectroscopy – 63.50.+x Vibrational states in disordered systems

Abstract. We have applied nuclear inelastic absorption (NIA) to the molecular glass former dibutyl phthalate/ferrocene, both in bulk and in nanoporous matrices having pore sizes of 50 and 25 Å. The quantity $g(E)/E^2$, where $g(E)$ is the vibrational density of states (VDOS) of the iron atoms, exhibits a pronounced maximum around 2 meV. Confinement in pores leads to a suppression of the VDOS below 1.5 meV, independent of the pore size. The influence of local interactions at the pore wall was assessed using Raman scattering. Our observations are discussed in the light of experimental and theoretical results on nanoparticles and for the Boson peak.

Eur. Phys. J. E 12, s01 (2003) 004
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-004-6

Received January 2003
Published online 5 November 2003

Solid state polymorphism of liquid crystals in confined geometries

C. Fehr, Ph. Dieudonné, J. Primera, T. Woignier, J.-L. Sauvajol, E. Anglaret

PACS. 61.30.Pq Microconfined liquid crystals: droplets, cylinders, randomly confined liquid crystals, polymer dispersed liquid crystals, and porous systems – 61.12.Ld Neutron diffraction – 78.30.-j Infrared and Raman spectra (condensed matter) – 64.60.My Metastable phases

Abstract. Solid polymorphism of 4-alkyl-4′-cyanobiphenyl (nCB) was studied so far as a function of thermal history. In this paper we show that metastable solid phases of 4-octyl-4′-cyanobiphenyl (8CB) are also formed when the mesogens are confined in porous silica matrices and we study their structure by neutron diffraction and by Raman spectroscopy. Three metastable solid states are identified: one crystalline phase $\mathbf{K}'$, two frozen-in smectic-like phases $\mathbf{K}_s$ and $\mathbf{K}'_s$. We discuss the relation between the structure of the metastable solid phases and that of the mesomorph phases.

Eur. Phys. J. E 12, s01 (2003) 005
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-005-5

Received January 2003
Published online 5 November 2003

Nematic ordering of suspension of charged anisotropic colloids detected by multinuclear quadrupolar spectra and ^{1}H PGSE-NMR measurements

P. Porion, M. Al-Mukhtar, A.-M. Faugère, S. Meyer, A. Delville

PACS. 82.70.Dd Colloids – 76.60.-k Nuclear magnetic resonance and relaxation

Abstract. The structure of aqueous dispersion of charged anisotropic nano-composites (synthetic Laponite clays) has been studied by NMR and numerical simulations based on a multi-scale statistical analysis have been used to interpret the mobility of the confined water molecule diffusing within dense Laponite aqueous dispersions (29–52% w/w) prepared by uniaxial compression. Firstly, the lineshape detected by NMR quadrupolar spectroscopy of the counterions (^{23}Na or ^{7}Li) exhibits a large residual splitting $\Delta\nu$ which is the fingerprint of the macroscopic nematic ordering of the anisotropic particles. Secondly, these results are also confirmed by the anisotropy of the self-diffusion tensor of the water molecule measured by ^{1}H Pulsed Gradient Spin Echo NMR. This self-diffusion anisotropy increases with the suspension density. Thirdly, the multi-scale statistical analysis of the water mobility bridges the gap between the time-scale (ps) accessible by Molecular Dynamics simulations and the time-scale (μs) accessible by Brownian Dynamics, leading to macroscopic behaviour comparable with PGSE-NMR data measurements.

Eur. Phys. J. E 12, s01 (2003) 006
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-006-4

Received January 2003
Published online 5 November 2003

Structure and properties of confined sodium nitrite

A. Naberezhnov, A. Fokin, Yu. Kumzerov, A. Sotnikov, S. Vakhrushev, B. Dorner

PACS. 77.84.Lf Dielectric, piezoelectric, ferroelectric, and antiferroelectric materials – 61.43.Gt Powder, porous materials – 61.12.Ld Neutron diffraction

Abstract. The temperature evolution of the structure of $NaNO_2$ nanocomposite ferroelectric material in a porous glass with 7 nm pores was studied by neutron diffraction in temperature region from room temperature up to the melting, *i.e.* in the ferro- and paraelectric phases. It is demonstrated that in the ferroelectric phase the structure is consistent with the structure of the bulk, but above the ferroelectric phase transition (and up to $\approx$ 513 K) a volume premelted state is formed, manifesting itself in a growth of amplitudes of ion thermal vibrations, a steep increase of elementary cell volume and "softening" of lattice. For the first time the temperature dependence of order parameter η for confined sodium nitrite is determined. η (T) follows a power law with $T_C = 425.6 \pm 2.1$ K and $\beta = 0.31 \pm 0.04$, which is essentially different from that for bulk $NaNO_2$. Our obtained data are in a good agreement with the results of earlier dielectric and neutron diffraction measurements.

Eur. Phys. J. E 12, s01 (2003) 007
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-007-3

Received January 2003
Published online 5 November 2003

Molecular mobility of confined phases in model mesoporous (MCM-41) and microporous ($AlPO_4$-5 zeolite) host materials

J.P. Coulomb, N. Floquet, C. Martin, R. Kahn

PACS. 68.35.Rh Phase transitions and critical phenomena – 68.43.Jk Diffusion of adsorbates, kinetics of coarsening and aggregation

Abstract. The considered host materials are well suited to confine quasi-(1d) molecular phases, seeing that their porosities are composed of parallel unconnected cylindrical pores. For such a simple geometry, confinement effects can be simply described by a single parameter, the pore diameter ϕ. Our study concerns medium and ultra confinement ranges (40 Å $\geq \phi \geq$ 7.3 Å). The primary effect of such confinements is the decrease of the molecular interactions within the confined phase. As a consequence, we have observed strong triple point depressure ΔT_{3t} effects for hydrogen and water confined phases in MCM-41 samples. In the limit case of (1d) phase (the neopentane/$AlPO_4$-5 system) it seems that a molecular mobility is observed even at very low temperature $T = 5$ K. The secondary confinement effect is an increase of the interactions between the host inner surface and the confined molecular assembly induced by the pore diameter decreasing. Such host material influence gives rise, for medium range confinement to the physisorption of a curved solid film on the inner surface before the capillary phase condensation (hydrogen/MCM-41 (24 Å)) and for ultra confinement to the solidification of the confined phase when the molecular species are commensurate with the inner surface sites (methane/$AlPO_4$-5).

Eur. Phys. J. E 12, s01 (2003) 008
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-008-2

Received January 2003
Published online 5 November 2003

Gas adsorption in mcm-41 porous silicas dynamic measurements using sans

S. Kallus, A. Hahn, J.D.F. Ramsay

PACS. 61.43.Gt Powders, porous materials – 61.12.Ex Neutron scattering (including small-angle scattering)

Abstract. The isothermal gas adsorption of two hexane isomers (*n*-hexane and cyclohexane) in the mesopores of MCM-41 silica have been investigated by small-angle neutron scattering (SANS). This has been achieved by performing SANS measurements under contrast matching conditions for the silica matrix and condensed hydrocarbon confined in the mesopores. Insight into the kinetics of adsorption have been derived from changes in the intensity of the (100) diffraction peak associated with the ordered hexagonal mesoporous structure of the MCM-41 silica.

Eur. Phys. J. E 12, s01 (2003) 009
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-009-1

Received January 2003
Published online 5 November 2003

Gas diffusion in zeolite beds: PFG NMR evidence for different tortuosity factors in the Knudsen and bulk regimes

S. Vasenkov, O. Geir, J. Kärger

PACS. 47.55.Mh Flows through porous media – 81.05.Rm Porous materials; granular materials

Abstract. Self-diffusion of ethane in beds of zeolite NaX is studied using Pulsed Field Gradient (PFG) NMR.

The ethane diffusivities were measured for displacements, which are orders of magnitude larger than the size of individual crystals. These diffusivities were compared with those, calculated using simple gas kinetic theory. The results of the comparison indicate that for the same bed of NaX crystals the apparent tortuosity factor in the Knudsen regime (*i.e.* when molecule-solid collisions dominate) is significantly larger than that in the bulk regime (*i.e.* when molecule-molecule collisions dominate). This finding is attributed to the more pronounced geometrical trapping by the pore structure of the zeolite bed in the Knudsen than in the bulk regime.

Eur. Phys. J. E 12, s01 (2003) 010
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-010-8

Received January 2003
Published online 5 November 2003

Inversion and suppression of an oxygen bulk phase transition in confined geometry

R. Ackermann, M. Enderle

PACS. 75.75.+a Magnetic properties of nanostructures – 61.43.Gt Powders, porous materials

Abstract. By means of susceptibility experiments on oxygen confined to the pores of a Gelsil substrate we investigated the bulk $\gamma - \beta$ transition. At low fillings, the transformation is completely suppressed. At higher but still incomplete filling we observe a partial transformation from γ to β on cooling and a subsequent inverted transition on heating, *i.e.* the transformation of γ-phase material into the β-phase upon heating. At 100% filling this inversion disappears. We discuss our results on the basis of geometric considerations.

Eur. Phys. J. E 12, s01 (2003) 011
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-011-7

Received January 2003
Published online 5 November 2003

Methyl group dynamics in a confined glass

A.J. Moreno, J. Colmenero, A. Alegría, C. Alba-Simionesco, G. Dosseh, D. Morineau, B. Frick

PACS. 61.43.-j Disordered solids – 61.12.-q Neutron diffraction and scattering – 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes and nanocrystals

Abstract. We present a neutron scattering investigation on methyl group dynamics in glassy toluene confined in mesoporous silicates of different pore sizes. The experimental results have been analysed in terms of a barrier distribution model, such a distribution following from the structural disorder in the glassy state. Confinement results in a strong decreasing of the average rotational barrier in comparison to the bulk state. We have roughly separated the distribution for the confined state in a bulk-like and a surface-like contribution, corresponding to rotors at a distance from the pore wall respectively larger and smaller than the spatial range of the interactions which contribute to the rotational potential for the methyl groups. We have estimated a distance of 7 Å as a lower limit of the interaction range, beyond the typical nearest-neighbour distance between centers-of-mass (4.7 Å).

Eur. Phys. J. E 12, s01 (2003) 012
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-012-6

Received January 2003
Published online 5 November 2003

Aging and memory effects in a clathrate

M.C. Rheinstädter, A.V. Kityk, H. Rieger, K. Knorr

PACS. 75.50.Lk Spin glasses and other random magnets – 77.22.Gm Dielectric loss and relaxation – 64.70.Pf Glass transitions

Abstract. The out-of-equilibrium low-frequency complex susceptibility of the orientational glass methanol(73%)-β-hydroquinone-clathrate is studied using temperature-stop protocols in aging experiments. Although the material does not have a sharp glass transition aging effects including rejuvenation and memory similar to the effects in spin glasses are found at low temperatures.

Eur. Phys. J. E 12, s01 (2003) 013
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-013-5

Received January 2003
Published online 5 November 2003

Dynamics of water in molecular sieves by dielectric spectroscopy

H. Jansson, J. Swenson

PACS. 77.22.Gm Dielectric loss and relaxation – 77.22.Gm Dielectric loss and relaxation – 61.43.Gt Powders, porous materials

Abstract. We present recent dielectric data on the dynamics of water confined in molecular sieves with pore

sizes 5 and 10 Å. The dielectric measurements in the frequency and temperature ranges 10^{-2}–10^{6} Hz and 120–300 K show three relaxation processes for both samples. In the case of the 10 Å pore the slowest process shows an Arrhenius temperature dependence at low temperatures (< 220 K), while at high temperatures the relaxation appears to follow a more Vogel-Fulcher-Tammann (VFT) like behaviour. The relaxation time for this process is 100 s at about 170 K. The second slowest process is at low temperatures very similar to the main process of (bulk-like) water in a fully hydrated clay, but also this process seems to exhibit some kind of dynamical transition, in this case at $T \approx 185$ K. All the three processes in the 5 Å pore exhibit Arrhenius temperature dependence, and two of them are considerably slower than the main relaxation in the hydrated clay. Thus, dynamics of bulk-like water is only observed in the 10 Å molecular sieves, and most of the water molecules in both 5 and 10 Å pores have considerably slower dielectric relaxation than has been observed for water confined in clay, most likely due to strong interactions with the considerably more hydrophilic inner surfaces of molecular sieves.

Eur. Phys. J. E 12, s01 (2003) 014
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-014-4

Received January 2003
Published online 5 November 2003

A FT-IR absorption analysis of vibrational properties of water encaged in NaA zeolites: evidence of a "structure maker" role of zeolitic surface

V. Crupi, D. Majolino, P. Migliardo, V. Venuti, U. Wanderlingh

PACS. 78.30.-j Infrared and Raman spectra – 78.30.Cp Liquids

Abstract. We performed, in the O-H stretching region, Fourier-Transform Infrared (FT-IR) Absorption measurements for investigating the vibrational dynamics on water confined in NaA zeolite, *vs.* temperature and for different hydration percentages. The spectral substructure of the O-H stretching band is explained postulating the existence of three major components centred at $\sim$ 3290 cm^{-1} (ω_1), $\sim$ 3470 cm^{-1} (ω_2), $\sim$ 3590 cm^{-1} (ω_3), with different dynamical properties traced over the full T-range investigated.

Eur. Phys. J. E 12, s01 (2003) 015
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-015-3

Received January 2003
Published online 5 November 2003

Dynamics of supercooled water in mesoporous silica matrix MCM-48-S

A. Faraone, L. Liu, C.-Y. Mou, P.-C. Shih, C. Brown, J.R.D. Copley, R.M. Dimeo, S.-H. Chen

PACS. 61.20.Lc Time-dependent properties of liquid structure; relaxation – 61.12.Ex Neutron scattering

Abstract. Using three different quasielastic neutron spectrometers with widely different resolutions, we have been able to study the microscopic translational and rotational dynamics of water, in a mesoporos silica matrix MCM-48-S, from $T = 300$ K to 220 K, with a single consistent model. We formulated our fitting routine using the relaxing cage model. Thus, from the fit of the experimental data, we extracted the fraction of water bound to the surface of the pore, the characteristic relaxation times of the long-time translational and rotational decays, the stretch exponent describing the shape of the relaxation processes, and the power exponent determining the Q-dependence of the translational relaxation time. A tremendous slowing-down of the rotational relaxation time, as compared to the translational one, has been observed.

Eur. Phys. J. E 12, s01 (2003) 016
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-016-2

Received January 2003
Published online 5 November 2003

Structure and dynamics of water confined in silica hydrogels: X-ray scattering and dielectric spectroscopy studies

M. Cammarata, M. Levantino, A. Cupane, A. Longo, A. Martorana, F. Bruni

PACS. 77.84.Nh Liquids dielectric properties – 61.10.Eq X-ray scattering (include small-angle scattering – 77.22.Gm Relaxation processes in dielectrics

Abstract. We have used a sol-gel technique to obtain optically transparent hydrogels in which water is confined within a 3D silica matrix. In this work we report X-ray scattering and dielectric spectroscopy measurements on samples having different aging times and compare them with previously obtained results with near-infrared (NIR) absorption spectroscopy. X-ray scattering at room temperature enables to characterize the structure and size of the matrix pores and the non-uniform distribution of water inside the hydrogel. Broad band dielectric spectroscopy in the temperature range 130–280 K enables

to study water dynamics. In aged hydrogels two relaxations are clearly evident and show characteristic temperature dependence. The faster relaxation has an Arrhenius behavior in the whole temperature range investigated with an activation enthalpy of $\sim$ 50 kJ/mol; it is attributed to water molecules strongly interacting with the silica matrix. The slower relaxation has a markedly non-Arrhenius behavior which can be fitted with a Vogel-Fulcher-Tamman (VFT) relation with critical temperature of $\sim$ 100 K and activation enthalpies of 35 and 95 kJ/mol at 300 and 170 K, respectively; it is attributed to water molecules within the pores that do not interact strongly with the matrix and behave collectively. The VFT temperature dependence of the dielectric relaxation time suggests that this water does not crystallize, in agreement with previous results from NIR spectroscopy.

Eur. Phys. J. E 12, s01 (2003) 017
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-017-1

Received January 2003
Published online 5 November 2003

Confinement effect on thermodynamic and structural properties of water in hydrophilic mesoporous silica

J. Puibasset, R.J.-M. Pellenq

PACS. 68.43.De Statistical mechanics of adsorbates – 61.43.Gt Powders, porous materials

Abstract. The adsorption of water on porous silica surfaces at 300 K, has been qualitatively reproduced by Grand Canonical Monte Carlo simulations (GCMC) without any adjustment of adsorbate/substrate potential parameter. The simulated adsorption isotherm and isosteric differential enthalpy of adsorption compare well to experimental data for Vycor, showing the ability of the model in describing hydrophilic properties of silica surfaces. The analysis of fluid structure in the mesoporous glass gives detailed insights into confinement and disorder effects on water adsorbed on the hydrophilic surface of a porous glass. It is shown that hydrophilic properties are not simply related to surface hydroxyl density but are also related to local structure of the silica surface.

Eur. Phys. J. E 12, s01 (2003) 018
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-018-0

Received January 2003
Published online 5 November 2003

Evidence of shear-dependent boundary slip in Newtonian liquids

C. Neto, V.S.J. Craig, D.R.M. Williams

PACS. 47.45.Gx Slip flows – 68.37.Ps Atomic Force Microscopy – 82.70.Dd Colloids

Abstract. The flow of Newtonian fluids was studied by directly measuring the hydrodynamic drainage force acting on a sphere approaching a flat surface. Our force measurements provide clear evidence of boundary slip and show that the degree of boundary slip is a function of the liquid viscosity and the shear rate. A shear-dependent boundary slippage was also observed in experiments with a polymer (PDMS). The liquids wetted the bounding surfaces either partially or completely. Our results have important consequences for the design of microfluidic devices, and in technological processes, such as lubrication and permeability of microporous media.

Eur. Phys. J. E 12, s01 (2003) 019
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-019-y

Received January 2003
Published online 5 November 2003

Anisotropic diffusion of single molecules in thin liquid films

J. Schuster, F. Cichos, Ch. von Borczyskowski

PACS. 68.08.-p Liquid-solid interfaces – 82.45.Mp Thin layers, films, monolayers, membranes

Abstract. Single molecule wide field imaging is applied to study the diffusion in ultrathin liquid films on solid surfaces. The results show a broad distribution of diffusion coefficients. This is tentatively ascribed to an anisotropy of the diffusion coefficient perpendicular to the surface and a slow exchange of molecules between regions of different diffusion coefficients. We have evidence that these changes as well as the slow motion perpendicular to the surface are related to the molecular layering of the liquid close to the surface.

Eur. Phys. J. E 12, s01 (2003) 020
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-020-6

Received January 2003
Published online 5 November 2003

Ion crater healing and variable temperature ellipsometry as complementary probes for the glass transition in thin polymer films

Y. Grohens, R.M. Papalo, L. Hamon

PACS. 05.70.NP Interface and surface thermodynamics – 34.50.Dy Interactions of atoms and molecules with surfaces; photon and electron emission; neutralization of ions

Abstract. Poly(methyl methacrylate) (PMMA) thin films of various tacticity and thickness were bombarded at grazing angles by 20 MeV Au ions at different temperatures. The shape of the tracks was investigated by scanning force microscopy (SFM) after annealing for various time at different temperatures and constant quenching rate. The thickness dependent glass transition temperature, $T_g(h)$, was estimated from the temperature of relaxation of ion-caused nanodeformations in the films. $T_g(h)$ obtained from the thermal healing of the holes and hillocks is found in good agreement with the one determined by variable temperature ellipsometry for PMMA film thickness of 80 nm and corresponds to the T_g of each bulk PMMA stereoisomer. Below this thickness, some significant divergences are observed between the T_g measured by the two techniques. We propose that the healing of ion crater hillock and the kink in the thermal expansion arise from the different nature of chains motions which are perturbed to different extents according to the main polymer chain preferential orientation in the thin film. This can be tentatively interpreted by a so-called "anisotropic" character of the glass transition.

Eur. Phys. J. E 12, s01 (2003) 021
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-021-5

Received January 2003
Published online 5 November 2003

Influence of the glass transition on solvent loss from spin-cast glassy polymer thin films

H. Richardson, M. Sferrazza, J.L. Keddie

PACS. 64.70.Pf Glass transitions – 82.60.Lf Thermodynamics of solutions – 61.41.+e Polymers, elastomers and plastics

Abstract. The interdependence of solvent loss and vitrification in spin-cast poly(methyl methacrylate) thin films is explored. Fast measurements of decreases in film thickness, achieved with ellipsometry, indicate that the rate of solvent (toluene) loss decreases sharply when the solvent volume fraction $\phi_{\rm solv}$ falls below about 0.15 and the film vitrifies. Ellipsometry and microgravimetry show that solvent is lost from a glassy thin film (150 nm thick) over of a period of more than ten hours, which is much longer than would be required if it was limited by diffusion in the glass. These results support the recently proposed idea that the compression of the glass creates an energy barrier that slows down solvent loss.

Eur. Phys. J. E 12, s01 (2003) 022
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-022-4

Received January 2003
Published online 5 November 2003

First inelastic neutron scattering studies on thin free standing polymer films

B. Frick, K. Dalnoki-Veress, J.A. Forrest, J. Dutcher, C. Murray, A. Higgins

PACS. 82.35.Lr Physical properties of polymers – 64.70.Pf Glass transitions – 68.60.Bs Mechanical and acoustical properties

Abstract. Glass transition studies in free standing polymer films have revealed values of the transition temperature, T_g, which were substantially reduced below the bulk for sufficiently thin films. Here we report on the preparation of two stacks of free standing polystyrene films: 70 films with a thickness of $h \sim 107$ nm and 140 films with $h \sim 55$ nm with equivalent *total* sample thicknesses of approximately 7.5 μm. We have performed the first measurements on such samples using inelastic neutron scattering, and demonstrate that inelastic neutron scattering experiments, performed on the time-of-flight spectrometer IN6 and the backscattering spectrometer IN16 at the Institut Laue-Langevin, are feasible.

Eur. Phys. J. E 12, s01 (2003) 023
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-023-3

Received January 2003
Published online 5 November 2003

Thickness dependence of the dynamics in thin films of isotactic poly (methylmethacrylate)

J.S. Sharp, J.A. Forrest

PACS. 61.41.+e Polymers, elastomers, and plastics – 61.43.Fs Glasses – 64.70.Pf Glass transitions – 65.60.+a Thermal properties of amorphous solids and glasses: heat capacity, thermal expansion, etc. – 68.15.+e Liquid thin films – 68.35.Ja Surface and interface dynamics and vibrations

Abstract. The film thickness dependence of both the glass transition temperature (T_g) and the 1 kHz alpha relaxation were studied for thin films of isotactic Poly (methylmethacrylate) (i-PMMA) supported on aluminium substrates. Films in the thickness range 7–200 nm were studied. The ellipsometrically determined T_g was found to show reductions for films thinner than 60 nm, with the largest observed reduction being 12 K for a 7 nm thick film. Measurements of the T_g were also performed on i-PMMA films supported on silicon substrates. Dielectric studies of the temperature dependent 1 kHz alpha relaxation peak, showed that the position (T_α) and shape of the peak have no film thickness dependence. This was

shown to hold for films with one free surface and films with a 30 nm thermally evaporated capping layer. Capping the films was shown to have no effect on the thickness dependence of either T_g or T_α. The implications of these results are discussed further and the different film thickness dependencies of T_g and T_α are discussed. This is done within the framework of the Vogel-Fulcher-Tamann (VFT) theory of glass forming materials and also in the context of the existence of a dynamic correlation length ξ.

Eur. Phys. J. E 12, s01 (2003) 024
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-024-2

Received January 2003
Published online 5 November 2003

Glass transition temperature of freely-standing films of atactic poly(methyl methacrylate)

C.B. Roth, J.R. Dutcher

PACS. 36.20.-r Macromolecules and polymer molecules – 64.70.Pf Glass transitions – 68.60.Bs Mechanical and acoustic properties of thin films

Abstract. We have used ellipsometry to measure the glass transition temperature T_g of high molecular weight ($M_w = 790 \times 10^3$), freely-standing films of atactic poly(methyl methacrylate) (a-PMMA), as well as films of the same polymer supported on two different substrates: the native oxide layer of silicon (Si) and gold-covered Si. We observe linear reductions in T_g with decreasing film thickness h for the freely-standing PMMA films with 30 nm $< h <$ 100 nm, which is qualitatively similar to previous results obtained for freely-standing polystyrene (PS) films. However the magnitude of the T_g reductions for PMMA is much less than for freely-standing films of PS of comparable molecular weight and thickness. We also find that for films supported on either substrate, with thicknesses as small as 30 nm, the T_g values do not deviate substantially from the value measured for thick films.

Eur. Phys. J. E 12, s01 (2003) 025
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-025-1

Received January 2003
Published online 5 November 2003

Dielectric relaxations in ultrathin isotactic PMMA films and PS-PMMA-PS trilayer films

M. Wübbenhorst, C.A. Murray, J.R. Dutcher

PACS. 64.70.Pf Glass transition – 77.22.Gm Dielectric loss and relaxation

Abstract. The local and cooperative dynamics of supported ultrathin films (L = 6.4–120 nm) of isotactic poly(methyl methacrylate) (i-PMMA, $\overline{M}_n = 118 \times 10^3$ g/mol) was studied using dielectric relaxation spectroscopy for a wide range of frequencies (0.1 Hz to 10^6 Hz) and temperatures (250–423 K). To assess the influence of the PMMA film surfaces on the glass transition dynamics, two different sample geometries were employed: a single layer PMMA film with the film surfaces in direct contact with aluminum films which act as attractive, hard boundaries; and a stacked polystyrene-PMMA-polystyrene trilayer film which contains diffuse PMMA−PS interfaces. For single layer films of i-PMMA, a decrease of the glass transition temperature T_g by up to 10 K was observed for a film thickness $L < 25$ nm (comparable to R_{EE}), indicated by a decrease of the peak temperature T_α in the loss $\epsilon''(T)$ at low and high frequencies and by a decrease in the temperature corresponding to the maximum in the apparent activation energy $E_a(T)$ of the α-process. In contrast, measurements of i-PMMA sandwiched between PS-layers revealed a slight (up to 5 K) increase in T_g for PMMA film thickness values less than 30 nm. The slowing-down of the glass transition dynamics for the thinnest PMMA films is consistent with an increased contribution from the less mobile PMMA-PS interdiffusion regions.

Eur. Phys. J. E 12, s01 (2003) 026
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-026-0

Received January 2003
Published online 5 November 2003

Dielectric relaxation studies of poly(propylene glycol) confined in vermiculite clay

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PACS. 77.22.Gm Dielectric loss and relaxation – 68.35.Ja Surface and interface dynamics and vibrations – 61.25.Hq Macromolecular and polymer solutions; polymer melts; swelling

Abstract. The molecular dynamics of oligomeric poly(propylene glycol) (PPG) liquids (M_w = 1200, 2000 and 4000 g/mol) confined in a two-dimensional layer-structured Na-vermiculite clay has been studied by broadband dielectric spectroscopy. In addition to the α-relaxation, the normal mode relaxation process was studied for all samples both in bulk and confinement. For the normal mode process the relaxation rate in the clay is drastically shifted to lower frequencies compared to that of the bulk material in contrast to the α-process whose relaxation time is only slightly affected by the confinement. Also the temperature dependence of the relaxation time for the normal mode process is strongly affected by the confinement. Moreover, in the clay the intensity of the

normal mode is stronger than that of the α-process, in contrast to the bulk samples where the opposite is observed.

Eur. Phys. J. E 12, s01 (2003) 027
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-027-y

Received January 2003
Published online 5 November 2003

Some remarks on the chain segment dynamics in confined polymers

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PACS. 68.08.-p Liquid-solid interfaces – 82.35.Jk Copolymers, phase transitions, structure – 76.60.-k Nuclear magnetic resonance and relaxation

Abstract. Recently, the chain dynamics of molten polymers in confined geometries has been investigated, using NMR. Some of these experiments have been performed on poydimethylsiloxane (PDMS) confined in planar nanolayers involving non-adsorbant solid surfaces. Here the data obtained on various PDMS systems are compared. The common property to these systems is that the local dynamics is anisotropic and the chain segments are undergoing uniaxial fluctuations around the normal $\vec{n}$ to the layers. Our data clearly show that the sign of the degree of orientational order S (*i.e.* the direction of the fluctuations around $\vec{n}$) and the broadening of the order distribution $P(S)$ both result from the relative influence of the impenetrable interfaces and anchoring junctions on the segment behaviour.

Eur. Phys. J. E 12, s01 (2003) 028
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-028-x

Received January 2003
Published online 5 November 2003

Segmental order and dynamics of polymer chains confined in block copolymer lamellar mesophases: NMR and dielectric relaxation studies

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PACS. 82.35.Jk Copolymers, phase transitions, structure – 76.60.-k Nuclear magnetic resonance and relaxation – 77.22.Gm Dielectric loss and relaxation

Abstract. The PDMS lamellar sublayers of a poly(styrene)-poly(dimethylsiloxane) diblock (PS-PDMS) and PS-PDMS-PS triblocks are investigated by NMR and dielectric spectroscopy. Some segments of the confined PDMS chains display anisotropic orientational fluctuations along the interfaces with the PS glassy blocks, whereas the others display fluctuations rather parallel to the lamellae normal. This coexistence results from a competitive ordering effect induced by the glassy interfaces and the chain-end anchoring junctions. The distribution of PDMS relaxation times within the sublayers is also examined: in particular, a slowing-down of the segmental motions, together with a broadening of this distribution, are detected.

Eur. Phys. J. E 12, s01 (2003) 029
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-029-9

Received January 2003
Published online 5 November 2003

Self-confined polymer dynamics in miscible binary blends

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PACS. 83.80.Tc Polymer blends – 61.41.+e Polymers, elastomers, and plastics – 77.22.Gm Dielectric loss and relaxation

Abstract. The segmental dynamics of PVME within the single-phase state of poly(styrene)/poly(vinyl methyl ether) blends (PS/PVME) was examined by dielectric spectroscopy. A particular attention has been given to the high PS concentration regime. In this latter, rather localized, weakly cooperative motions of the PVME segments are detected at low temperatures, in addition of the secondary relaxation processes. This feature is attributed to confinement effects induced by the PS chains on the PVME.

Eur. Phys. J. E 12, s01 (2003) 030
Digital Object Identifier (DOI):
10.1140/epjed/e2003-01-030-4

Received January 2003
Published online 5 November 2003

Characterization of porous structure through the dynamical properties of ions confined in sulfonated polyimide ionomers films

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PACS. 82.47.Gh Proton exchange membrane (PEM) fuel cells – 82.45.Wx Polymers and organic materials in electrochemistry – 66.10.-x Diffusion and ionic conduction in liquids

Abstract. The structure of sulfonated PolyImide (sPI) ionomer membrane has been investigated *via* the transport properties of ions confined inside. Transport coefficients of $N(CH_3)_4^+$ and Na^+ ions have been determined by several techniques in order to get a range of time/space scale as wide as possible: a method using radiotracers, conductivity, pulsed field gradient NMR and NMR quadrupolar relaxation rates determination. For $N(CH_3)_4^+$, the self-diffusion has been measured in the direction of membrane plan (parallel) and in the perpendicular direction (transverse), whereas for Na^+ only transverse self-diffusion has been measured. The conductivity of both ions has been measured in the transverse direction. The results show a anisotropic and multiscale structure with a separation phase between hydrophilic and hydrophobic domains that is not well-defined.

Eur. Phys. J. E 12, s01 (2003) 031
Digital Object Identifier (DOI): 10.1140/epjed/e2003-01-031-3

Received January 2003
Published online 5 November 2003

Molecular dynamics simulations of a mixed DOPC/DOPG bilayer

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PACS. 31.15.Qg Molecular dynamics and other numerical methods – 81.16.Fg Supramolecular and biochemical assembly – 83.85.Hf X-ray and neutron scattering – 87.16.Dg Membranes, bilayers, and vesicles

Abstract. We have constructed a mixed dioleoylphosphatidylcholine (DOPC) and dioleoylphosphatidylglycerol bilayer (DOPG) bilayer utilizing MD simulations. The aim was to develop an explicit molecular model of biological membranes as a complementary technique to neutron diffraction studies that are well established within the group. A monolayer was constructed by taking a previously customised PDB file of each molecule and arranging them in a seven rows of ten molecules and duplicated and rotated to form a bilayer. The 140-molecule bilayer contained 98 DOPC molecules and 42 DOPG molecules, in a 7:3 ratio in favour of DOPC. Sodium counter ions were placed near the phosphate moiety of DOPG to counteract the negative charge of DOPG. This was representative of the lipid ratio in a sample used for neutron diffraction. The MD package *GROMACS* was used for confining the bilayer in a triclinic box, adding Simple Polar Charge water molecules, energy minimization (EM). The bilayer/solvent system was subjected to EM using the steepest descent method to nullify bad contacts and reduce the potential energy of the system. Subsequent MD simulation using an initial NVT (constant number of particles, volume and temperature) for a 20 ps MD run followed by a NPT (constant number of particles, pressure and temperature) was performed. Structural parameters including volume of lipid, area of lipid, order parameter of the fatty acyl carbons and electron density profiles generated by the MD simulation were verified with values obtained from experimental data of DOPC, as there are no comparable experimental data available for the mixed bilayer.