

LECTURE NOTES
IN PHYSICS

M. Ferrario
G. Ciccotti
K. Binder
(Eds.)

Computer Simulations in Condensed Matter: From Materials to Chemical Biology – Vol.2

Mauro Ferrario Giovanni Ciccotti Kurt Binder

Computer Simulations
in Condensed
Matter Systems:
From Materials
to Chemical Biology
Volume 2

 Springer

Editors

Professor Mauro Ferrario
Dipartimento di Fisica
Università di Modena e Reggio Emilia
Via Campi, 213/A
41100 Modena, Italy
E-mail: mauro.ferrario@unimore.it

Professor Kurt Binder
Institut für Physik
Universität Mainz
Staudinger Weg 7
55128 Mainz, Germany
E-mail: kurt.binder@uni-mainz.de

Professor Giovanni Ciccotti
Dipartimento di Fisica, INFN
Università di Roma La Sapienza
Piazzale Aldo Moro 2
00185 Roma, Italy
E-mail: giovanni.ciccotti@roma1.infn.it

M. Ferrario et al., *Computer Simulations in Condensed Matter Systems: From Materials to Chemical Biology Volume 2*, Lect. Notes Phys. 704 (Springer, Berlin Heidelberg 2006), DOI 10.1007/b11761754

Library of Congress Control Number: 2006927292

ISSN 0075-8450

ISBN-10 3-540-35283-X Springer Berlin Heidelberg New York

ISBN-13 978-3-540-35283-9 Springer Berlin Heidelberg New York

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilm or in any other way, and storage in data banks. Duplication of this publication or parts thereof is permitted only under the provisions of the German Copyright Law of September 9, 1965, in its current version, and permission for use must always be obtained from Springer. Violations are liable for prosecution under the German Copyright Law.

Springer is a part of Springer Science+Business Media
springer.com

© Springer-Verlag Berlin Heidelberg 2006

The use of general descriptive names, registered names, trademarks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

Typesetting: by the authors and techbooks using a Springer L^AT_EX macro package

Cover design: WMXDesign & production GmbH, Heidelberg

Printed on acid-free paper SPIN: 11761754 54/techbooks 5 4 3 2 1 0

Preface

The school that was held at the Ettore Majorana Foundation and Center for Scientific Culture (EMFCSC), Erice (Sicily), in July 2005, aimed to provide an up-to-date overview of almost all technical advances of computer simulation in statistical mechanics, giving a fair glimpse of the domains of interesting applications. Full details on the school programme and participants, plus some additional material, are available at its Web site, <http://cscm2005.unimore.it>

Computer simulation is now a very well established and active field, and its applications are far too numerous and widespread to be covered in a single school lasting less than 2 weeks. Thus, a selection of topics was required, and it was decided to focus on perspectives in the celebration of the 65th birthday of Mike Klein, whose research has significantly pushed forward the frontiers of computer simulation applications in a broad range, from materials science to chemical biology. Prof. M. L. Klein (Dept. Chem., Univ. Pennsylvania, Philadelphia, USA) is internationally recognized as a pioneer in this field; he is the winner of both the prestigious Aneesur Rahman Prize for Computational Physics awarded by the American Physical Society, and its European counterpart, the Berni J. Alder CECAM Prize, given jointly with the European Physical Society. The festive session held on July 23rd, 2005, highlighting these achievements, has been of a particular focus in this school. In the framework of the EMFCSC International School of Solid State Physics Series, the present school was the 34th course of its kind.

However, this school can be considered as being the third (and perhaps last?) event in a series of comprehensive schools on computer simulation, 10 years after the COMO Euroconference on “Monte Carlo and Molecular Dynamics of Condensed Matter systems,” and 20 years after the VARENNA Enrico Fermi Summer School on “Molecular Dynamics of Statistical Mechanical Systems.” Comparing the topics emphasized upon in these schools, both the progress in achieving pioneering applications to problems of increasing complexity, and the impressive number of new methodological developments are evident. While the focus of the Varenna School was mostly on Molecular Dynamics (MD) and its applications from simple to complex fluids, the Como school included both Monte Carlo (MC) simulations of lattice systems (from

quantum problems to the advanced analysis of critical phenomena in classical systems like the simple Ising model), and the density functional theory of electronic structure up to the Car-Parrinello *ab initio* Molecular Dynamics techniques (CPMD). At the Erice school, a new focus was put on the paradigm of “Multiscale Simulation”, i.e. the idea to combine different methods of simulation on different scales of length and time in a coherent fashion. This method allow us to clarify the properties of complex materials or biosystems where a single technique (like CPMD or MD or MC etc.) due to excessive needs of computer resources is bound to fail. Good examples presented at this school for such multiscale simulation approaches included MD studies of polymers coupled with a solvent, which is described only in a coarse-grained fashion by the lattice Boltzmann technique and hybrid quantum mechanical/molecular mechanics (QM/MM) methods for CPMD simulations of biomolecules, etc.

As a second “leitmotif,” emphasis has been put on rapidly emerging novel simulation techniques. Techniques that have been dealt with at this school include the methods of “transition path sampling” (i.e. a Monte Carlo sampling not intending to clarify the properties of a state in the space of thermodynamic variables, but the properties of the dominating paths that lead “in the course of a transition” from one stable state to another), density of state methods (like Wang-Landau sampling and multicanonical Monte Carlo, allowing an elegant assessment of free energy differences and free energy barriers, etc.) and so on. These techniques promise substantial progress with famous “grand challenge problems” like the kinetics of protein folding, as well as with classical ubiquitous problems like the theory of nucleation phenomena. Other subjects where significant progress in methodological aspects was made included cluster algorithms for off-lattice systems, evolutionary design in biomedical physics, construction of coarse-grained models describing the self-assembly and properties of lipid layers or of liquid crystals under confinement and/or shear, glass simulations, novel approaches to quantum chemistry, formulation of models to correctly describe the essence of dry friction and lubrication, rare event sampling, quantum Monte Carlo methods, etc. The diversity of this list vividly illustrates the breadth and impact that simulation methods have today.

While the most simple MC and MD methods have been invented about 50 years ago (the celebration of the 50th anniversary of the Metropolis algorithm was held in 2003, the 50th anniversary of the Alder-Wainwright spectacular first discovery by MD of the (then unexpected) phase transition in the hard sphere fluid is due in 2007), even the “second generation” of scientists, who started out 30-40 years ago as “simulators” are now already the “old horses” of the field, either close to the end of their scientific career, or, in the best case, near it. Thus, we can clearly observe that the task of developing the computer simulation methodology is further taken over with vigor by the “third generation” of well-established younger scientists who have emerged in the field. Because two of the organizers of the school (KB, GC) do belong to the “old horse” category, it was clearly necessary to get an energetic younger

co-organizer involved (MF), and we also felt it was the appropriate time that the most senior experts need not give the main lectures of the school, but rather the younger generation who are now most actively driving forward the frontier of research. Of course, it was crucial to involve the very valuable experience and knowledge of our senior colleagues into the school as well, and we are very glad that so many of them have accepted our invitation to give one-hour seminars providing tutorial introductions to various advanced research topics, which is at the heart of the research interests of the speakers. In this way, it was possible to produce an exciting event on the forefront of research on computer simulation in condensed matter, in a very stimulating and interactive atmosphere, with plenty of fruitful discussions.

It is with great pleasure that we end this preface with several acknowledgments. This school, of which the lecture notes are collected here, could not have taken place without the generous support of the European Community under the Marie Curie Conference and Training Courses, Contract No. MSCF-CT-2003-503840. We are grateful to the coordinators of this program, Michel Mareschal and Berend Smit, for their help in securing this support. We also wish to thank the CECAM secretaries, Emmanuelle Crespeau and Emilie Bernard.

We thank the Ettore Majorana Foundation and Centre for Scientific Culture in Erice, Sicily, for providing their excellent facilities to hold this school, and also Giorgio Benedek, Director of the International School of Solid State Physics, for the opportunity to hold our school as its 34th course: for his enthusiastic support during the school, and for his personal scientific participation. We are particularly grateful to him for providing the beautiful facilities of Erice.

MF thanks Davide Calanca, INFM-S3, Modena, for his valuable help in setting up the Web site of the school.

We thank the director of the physics department of the University of Rome "La Sapienza", Guido Martinelli, and the Administrative Secretary of the Department, Mrs. Maria Vittoria Marchet and her assistant, Mrs. Maria Proietto, for helping us in the difficult duty of managing all the financial matters. Mrs. Fernanda Lupinacci deserves grateful appreciation for her devoted and untiring presence and skillful help in overcoming all practical difficulties related to the organizational needs, and for providing a hospitable atmosphere to all the participants.

We are very grateful to Daan Frenkel, Mike Klein, and Peter Nielaba for their very valuable input when setting up the scientific program of the school, to all the lecturers, for their willingness to engage in the endeavor, and to all the participants, for their engagement and enthusiasm.

May 2006

*Mauro Ferrario
Giovanni Ciccotti
Kurt Binder*

Contents

Computer Simulations of Supercooled Liquids <i>W. Kob</i>	1
Numerical Simulations of Spin Glasses: Methods and Some Recent Results <i>A.P. Young</i>	31
Dipolar Fluctuations in the Bulk and at Interfaces <i>V. Ballenegger, R. Blaak, and J.-P. Hansen</i>	45
Theory and Simulation of Friction and Lubrication <i>M.H. Müser</i>	65
Simulation of Nanodroplets on Solid Surfaces: Wetting, Spreading and Bridging <i>A. Milchev</i>	105
Monte Carlo Simulations of Compressible Ising Models: Do We Understand Them? <i>D.P. Landau, B. Dünweg, M. Laradji, F. Tavazza, J. Adler, L. Cannavacciolo, and X. Zhu</i>	127
Computer Simulation of Colloidal Suspensions <i>H. Löwen</i>	139
Phase Transitions of Model Colloids in External Fields <i>P. Nielaba, S. Sengupta, and W. Strepp</i>	163
Computer Simulation of Liquid Crystals <i>M.P. Allen</i>	191

Coarse-Grained Models of Complex Fluids at Equilibrium and Under Shear <i>F. Schmid</i>	211
Mesoscopic Simulations of Biological Membranes <i>B. Smit, M. Kranenburg, M. M. Sperotto, and M. Venturoli</i>	259
Microscopic Elasticity of Complex Systems <i>J.-L. Barrat</i>	287
Mesoscopic Simulations for Problems with Hydrodynamics, with Emphasis on Polymer Dynamics <i>B. Dünweg</i>	309
Polymer Dynamics: Long Time Simulations and Topological Constraints <i>K. Kremer</i>	341
Reaction Kinetics of Coarse-Grained Equilibrium Polymers: A Brownian Dynamics Study <i>C.-C. Huang, H. Xu, F. Crevel, J. Wittmer, and J.-P. Ryckaert</i>	379
Equilibration and Coarse-Graining Methods for Polymers <i>D.N. Theodorou</i>	419
Drug-Target Binding Investigated by Quantum Mechanical/Molecular Mechanical (QM/MM) Methods <i>U. Rothlisberger and P. Carloni</i>	449
Redox Free Energies from Vertical Energy Gaps: Ab Initio Molecular Dynamics Implementation <i>J. Blumberger and M. Sprik</i>	481
Advanced Car–Parrinello Techniques: Path Integrals and Nonadiabaticity in Condensed Matter Simulations <i>D. Marx</i>	507
Evolutionary Design in Biological Physics and Materials Science <i>M. Yang, J.-M. Park, and M.W. Deem</i>	541
Monte-Carlo Methods in Studies of Protein Folding and Evolution <i>E. Shakhnovich</i>	563
Index	595

Computer Simulations of Supercooled Liquids

W. Kob

Laboratoire des Colloïdes, Verres et Nanomatériaux, UMR 5587, CNRS Université
Montpellier II, Place E. Bataillon, 34095 Montpellier, France
kob@lcvn.univ-montp2.fr



Walter Kob

1	Introduction	3
2	Salient Features of Glass-Forming Systems	4
2.1	Theoretical Approaches	11
3	Computer Simulations of Glass-Forming Liquids	18
4	Conclusions	28
	References	28

We review some of the salient features of glass-forming systems. After a brief discussion of the theoretical approaches that are used to describe the slowing down of the dynamics of these system, notably the theory of Adam and Gibbs and the mode-coupling theory of the glass transition, we present some results of computer simulations that have been done to check the validity of these theories.

1 Introduction

The phenomenon of the glass transition is a feature that can be observed in a multitude of complex systems. The paradigm of this transition is of course the freezing of a glass-forming liquid such as silica, SiO_2 , into an amorphous solid if the melt is cooled with a sufficiently high cooling rate, e.g. faster than a few K/s.¹ However, it is found that also many other systems can be frozen into a disordered structure, i.e. a configuration that is very different from the one of the ground state, if an external parameter (temperature, magnetic field, chemical potential, etc.) is changed sufficiently quickly, and prominent examples include polymers, colloidal suspensions, metals, superconductors, proteins, and optimization problems. All these systems have one key feature in common: The tendency to optimize the structure on the local scale with the result that on larger scales the structure is frustrated and therefore disordered. Examples are the packing of spheres for which the densest *local* packing is an icosahedron, a geometrical structure that does not allow to fill space in a regular manner. Another important example are commissions in which the members have to find a consensus on a given subject, i.e. optimize a “cost function”: It is easy to find a good solution for a small number of people, but very often impossible to find one that satisfies everyone. (Therefore one has the golden rule for an efficient functioning of a commission that the number of members has to be odd and smaller than three.)

The presence of this frustration on large length scales (or with a large number of degrees of freedom) makes it very difficult to come up with a reliable theoretical description that goes beyond mean field concepts and therefore progress in the theory of disordered systems has been very slow. Therefore it is presently not possible to present a coherent theory that is able to describe the multitude of features that can be found in glass-forming systems. Thus the goal of the present text is to give just a concise overview of the typical features of glass-forming systems, to discuss briefly some of the theoretical approaches that have been proposed to describe these systems, and to review some of the numerical simulations that have been done to test these theories.

¹ This rate is in fact not very high and therefore silica is considered to be a “good” glass former. For other systems, such as mixtures of metals with only 2–3 components, one needs rates on the order of 10^6 K/s in order to avoid crystallization.

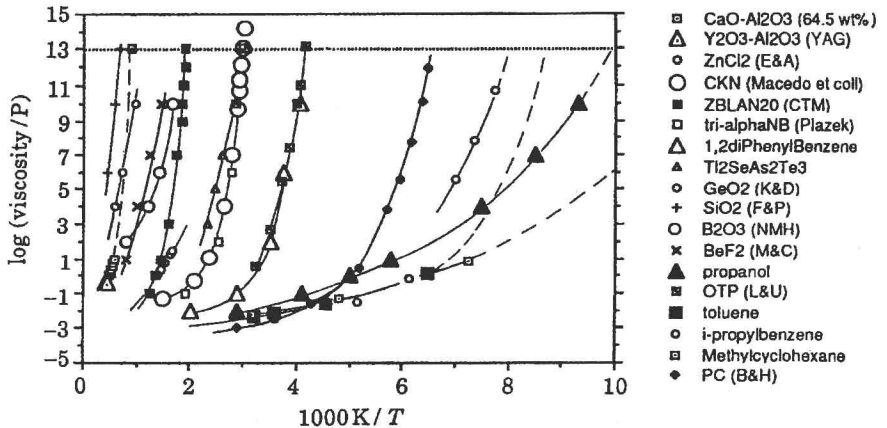


Fig. 1. Arrhenius plot of the temperature dependence of the viscosity of various glass-forming liquids. From [9]

2 Salient Features of Glass-Forming Systems

In this section we will discuss some of the main features of glass-forming systems. In order to keep the language simple we will restrict ourselves to the case of structural glasses and thus will not discuss other important glassy systems such as spin glasses, protein folding, or optimization problems. In addition we will be mainly concerned with the *temperature* dependence of the properties of these systems, even if a similar behavior can be found if, e.g., one changes the pressure. More extensive discussions of these subjects can be found in [1–8].

At sufficiently high temperatures the viscosity of liquids is relatively small, i.e. η is of the order 10^{-2} Pa s, the viscosity of water at room temperature. Experimentally it is found that with decreasing temperature the viscosity increases rapidly and can reach values of the order of 10^{14} Pa s and more. This is demonstrated in Fig. 1 in which we show the logarithm of η as a function of inverse temperature for many different types of liquids. The interaction between the atoms in these various liquids can be of very different nature (van der Waals, ionic, ...) and therefore the relevant temperature scale depends also strongly on the liquid and makes a comparison of the different curves somewhat difficult. In order to overcome this problem it is customary to scale the T -axis by T_g , a temperature that is defined by requiring that $\eta(T_g) = 10^{12}$ Pa s² [10, 11]. The resulting graph, which is usually called “Angell-plot”, is shown in Fig. 2 from which we now recognize more easily that the T -dependence of η is indeed very strong but still smooth. Some of the curves (the

² The reason for choosing this somewhat arbitrary value is related to the fact that such a viscosity usually corresponds to a relaxation time that is on the order of 10s, i.e. a time scale that is well adapted to human beings.

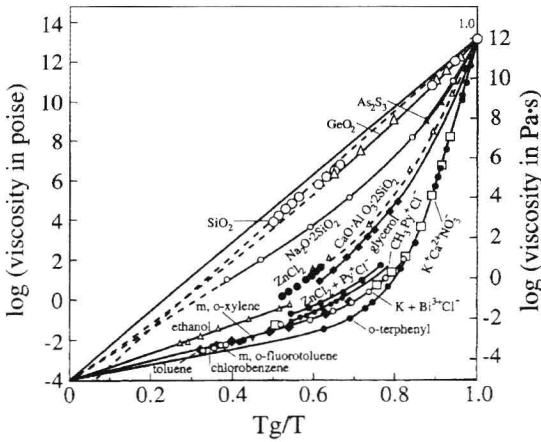


Fig. 2. Viscosity of various glass-forming liquids as a function of rescaled temperature T_g/T . After [11]

one at the bottom of the graph) seem to show a crossover from an Arrhenius dependence with a small activation energy at high T to an Arrhenius-law with a higher activation energy at low T . Liquids that show such a behavior are called “fragile glass-formers” [11]. On the other hand there are liquids that seem to show in the whole accessible temperature range an Arrhenius-law with the same activation energy (curves at the top) and these materials are called “strong glass-formers” [11].

Although Fig. 2 clearly allows to distinguish between strong and fragile glass-formers, it is presently not clear whether the different shapes of the $\eta(T)$ curves is not only due to the way the data is represented [12, 13]. E.g. Hess et al. have proposed a different type of scaling plot in which one scales the T -axis not only by T_g but in addition by a factor F that makes that the *slope* of the curves at $T = T_g$ are the same. The resulting plot is shown in Fig. 3 and it demonstrates that it is indeed possible to obtain in the regime of high η a nice collapse of the data onto a master curve, the shape of which is slightly bend. Thus this is evidence that in fact *all* $\eta(T)$ curves are bend and that the reason that in Fig. 2 this is not seen very well is just a problem of the representation of the data which makes that the high T data is squeezed in a small interval of the abscissa.

The temperature above which the data no longer falls onto this master curve has been found to be very close to the so-called critical temperature of mode-coupling theory of the glass transition (MCT) [14–17]. As we will discuss in more detail below, this theory is indeed able to rationalize many features of the dynamics of glass-forming liquids and can presently be regarded as the most successful theoretical approach to describe the dynamics of glass-forming liquids.

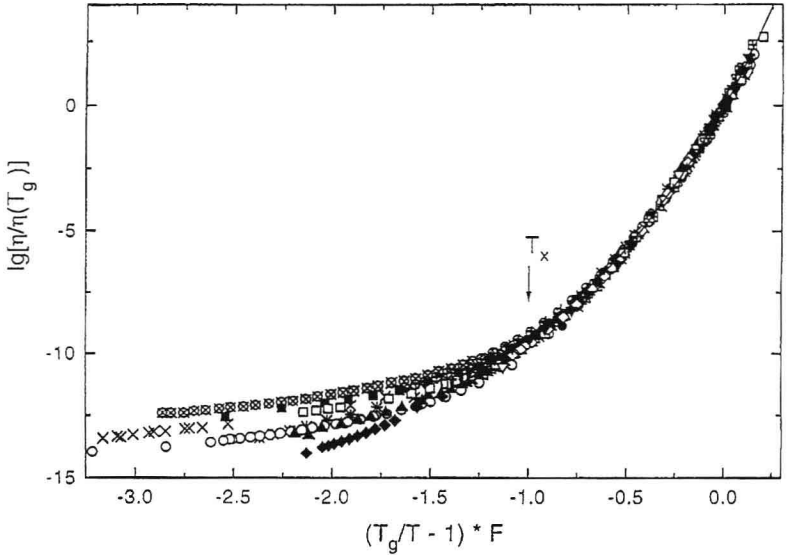


Fig. 3. The viscosity of various glass-forming systems (silica, B_2O_3 , salol, propylene carbonate, CKN ($40Ca(NO_3)_2 \cdot 60KNO_3$), etc.). T_g is the calorimetric glass transition temperature. The data is plotted as a function of $(T_g/T - 1) \cdot F$ with $F = T_x/(T_x - T_g)$. Here T_x is a temperature that has been adjusted for each liquid such that the viscosity data falls at low T on a master curve. Adapted from [13]

From Fig. 2 it also becomes clear that the T -dependence of η does not change if the temperature crosses the melting temperature T_m . Although the latter is not included in the graph, there is the rule of thumb that $T_g/T_m \approx 2/3$, i.e. in the figure T_m is located between 0.6 and $0.7 T_g/T$. Since the $\eta(T)$ curves are very smooth, it is evident that the mechanism responsible for the dramatic slowing down of the dynamics cannot be related to the fact that the liquid is supercooled. In fact, the case of SiO_2 shows that this liquid is already very viscous *at* its melting temperature ($T_m = 2000$ K and $T_g = 1450$ K, thus $T_g/T_m = 0.725$ and $\eta(T_m) \approx 10^7$ Pa s). This is the reason why it is not really appropriate to speak in the context of glass-forming liquids as the dynamics of “super-cooled liquids”. Instead one prefers to use the terms “glassy liquids” to emphasize their slow dynamics.

Figure 2 allows to recognize immediately *the* relevant question in the field: What is the reason for the strong slowing down of the dynamics (at least 15 decades!) upon a relatively mild change in temperature? The puzzling observation is that although the quantities characterizing the dynamics, such as the viscosity discussed here, or the relaxation times introduced below, show a very strong T -dependence, whereas the thermodynamic quantities (density, specific heat,...) or structural quantities (structure factor, angular distribution functions,...) show only a very mild T -dependence. This can be recognized, e.g., from Fig. 4 which shows the static structure factor of a binary

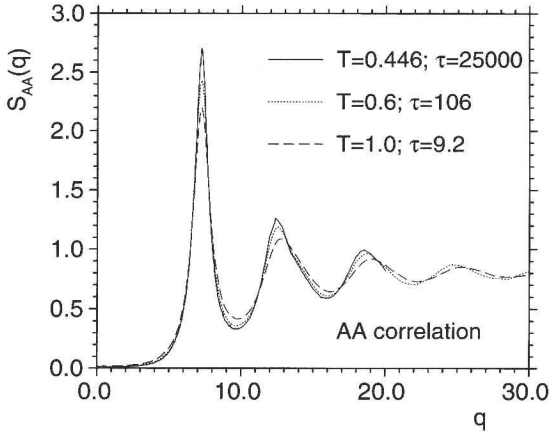


Fig. 4. Wave-vector dependence of the partial structure factor $S_{AA}(q)$ for a mixture of Lennard-Jones particles. The different curves correspond to different temperatures. Also included are the α -relaxation times τ (in reduced units)

Lennard-Jones system at various temperatures. Although the relaxation time τ , given in the figure, changes by orders of magnitude, the structure factor shows only a very weak dependence on T in that with decreasing temperature the peaks become slightly more pronounced. This weak T -dependence of the thermodynamic and structural quantities is in stark contrast to the case of second order phase transitions, another phenomenon in which one finds a strong increase of the relaxation times, and poses a real challenge to come up with a theoretical description that is able to describe the slowing down of the dynamics.

The form of the temperature dependence of η , or τ , is another important question. At low temperatures the experimental data can often be fitted very well by the so-called “Vogel-Fulcher-Tammann-law” which is given by

$$\eta(T) = \eta_0 \exp[A/(T - T_0)] , \quad (1)$$

where T_0 is the temperature at which the extrapolation (!) of the viscosity seems to diverge, and which is called “Vogel-temperature”.

In order to characterize the slowing down of the dynamics on a more microscopic level, it is useful to consider the time and temperature dependence of time correlation functions such as the van Hove function or the intermediate scattering function [8,18,19]. The typical time dependence of such a correlator Φ is shown in Fig. 5 which shows $\Phi(t)$ vs. $\log(t)$. Let us first discuss the correlator at high temperatures. At very short times $\Phi(t)$ shows a quadratic time dependence, which can be understood immediately by recalling that at short times the trajectories of the particles can be expanded in a Taylor series in time and that, due to the time reflection symmetry of Newton’s equation of motion, any time correlation function must be even in time. After this

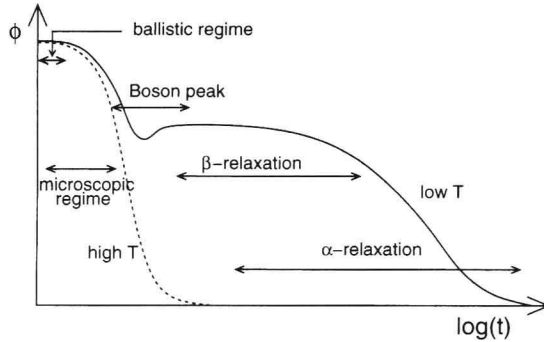


Fig. 5. Typical time dependence of a time correlation function. The curve to the left corresponds to the case of a normal liquid and the one to the right to a glassy liquid

“ballistic regime” the curve decays to zero very quickly (for atomic liquids on the time scale of pico-seconds) and the time dependence of the correlator can be approximated well by an exponential function, i.e. a Debye-law. This final decay is usually denoted by “ α -relaxation”.

Also at low temperatures the correlator show a ballistic regime at short times. However, for intermediate times $\Phi(t)$ shows a plateau, i.e. on this time scale the correlation function does not decay. The reason for this is that each particle is (temporarily) trapped in the cage formed by its neighbors, a phenomenon that is called “cage-effect” and which is in (rough) analogy to the situation found in a crystal. Although in this time window the time dependence of the correlator is weak, it is not negligible and it is usually called “ β -relaxation”. At the beginning of the mentioned plateau one often sees some strongly damped oscillations which are due to low frequency vibrational modes in the system. Although this feature is not found in all glass-forming systems, it is quite common and is referred to as the so-called “Boson-peak”, since in the dynamic susceptibility it is seen as a peak [20]³ At these temperatures the α -relaxation is no longer given by a Debye-law. Although the exact functional form is not really known, the so-called stretched exponential, or Kohlrausch-Williams-Watts function (KWW), given by

$$\Phi(t, T) = A(T) \exp[-(t/\tau(T))^{\beta(T)}], \quad (2)$$

gives often a very good description of the correlator. Here $A(T)$, $\beta(T)$, and $\tau(T)$ are fit parameters. The quantity $\tau(T)$ is often used to define a relaxation time, although other definitions, e.g. the area under the correlator, can be used as well.

³ The dynamics susceptibility $\chi''(\omega)$ of a time correlation function $\Phi(t)$ is given by the imaginary part of the time Fourier transform of $\Phi(t)$ multiplied by the frequency ω : $\chi''(\omega) = \frac{\omega}{k_B T} \Phi''(\omega)$ [18].

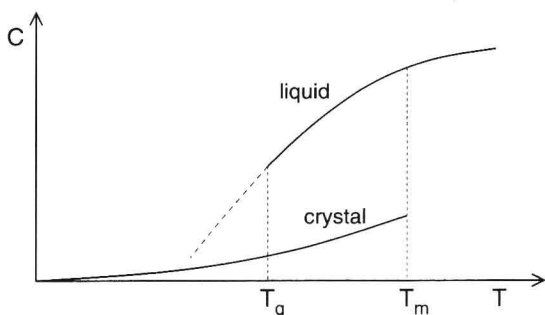


Fig. 6. Schematic plot of the temperature dependence of the specific heat of a glass-forming liquid (*upper curve*). The dashed line is an extrapolation of this curve to temperatures below the glass transition temperature T_g . The lower curve is the specific heat for the crystalline state of the same material that ends at the melting temperatures T_m

Above we have mentioned that structural and thermodynamic quantities show only a very mild variation with temperature. This observation applies also to the specific heat $C(T)$. Since at low T one has a separation of the time scale for the vibrational motion from the one for the motion giving rise to the α -relaxation, see Fig. 5, it is clear that $C(T)$ can be decomposed into two parts: One that is related to the vibrational dynamics inside the cage, $C_{\text{vib}}(T)$, and another part that is related to the configurational degrees of freedom related to the flow of the particles, $C_{\text{conf}}(T)$. It is found that $C_{\text{vib}}(T)$ is only a mild function of temperature and quite similar to the specific heat found in a crystal, i.e. $C_{\text{vib}}(T) \approx C_{\text{cryst}}(T)$, see Fig. 6. Therefore it is possible to study the T -dependence of $C_{\text{conf}} \approx C(T) - C_{\text{cryst}}(T)$ and in a seminal paper Kauzmann showed that this quantity decreases rapidly with decreasing T [21]. This observation has an important consequence for the entropy of the system which can be obtained from the relation $S(T) = S(T_m) - \int_T^{T_m} \frac{C(T)}{T} dT$, where T_m is the melting temperature. Similar to the specific heat, $S(T)$ can be split into a vibrational and configurational part and hence one can determine $\Delta S(T)$, the difference between the entropy of the liquid and the one of the crystal.

The T -dependence of ΔS , normalized by its value at the melting temperature T_m , is shown schematically in Fig. 7. Thus we recognize that, at least for fragile glass-formers, this difference decreases rapidly with decreasing temperature and if one makes an extrapolation (!) to low T the difference seems to vanish at a *finite* temperature T_K , the so-called “Kauzmann temperature”. The implication of this observation is that the dynamics of the system should come to an arrest for $T \rightarrow T_K^+$, since there are no more configurations into which the system can move. (Recall that we can expect that $S_{\text{conf}} = k_B T \ln(\Omega_{\text{conf}})$, where Ω_{conf} is the number of accessible configurations.) Interestingly the experimental data shows that often T_K is very close