

Slow Motion in a Metallic Liquid

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Liquid $\text{Zr}_{46.8}\text{Ti}_{8.2}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ has been studied by quasielastic neutron scattering. The microscopic dynamics of this bulk glass forming alloy deviates qualitatively from simple metallic liquids; it shows two-step structural relaxation like other liquids in their supercooled state. Unexpectedly for a nonfragile system, fast β relaxation is in full accord with the mode-coupling theory of the liquid to glass transition. The long-time α relaxation suggests failure of the Stokes-Einstein relation. [S0031-9007(98)06113-4]

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Novel multicomponent Zr-based alloys like $\text{Zr}_{46.8}\text{Ti}_{8.2}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ (vitr alloy V4) can be easily quenched into an amorphous solid. Cooling rates as low as 10 K/min allow for the production of bulk metallic glass [1]. The stability against crystallization seems basically due to a deeply eutectic composition ($T_{\text{sol}} = 905$ K, $T_{\text{liq}} = 1050$ K), and comes along with a surprisingly high viscosity ($\eta \approx 100$ P) at the liquidus temperature [2], 4–5 orders of magnitude larger than in simple metallic liquids. As a consequence, molecular motion in the liquid state cannot be described by the concepts developed and tested in much detail, e.g., for alkali melts [3]. Instead, we will show that the microscopic dynamics of V4 at and above T_{liq} bears strong resemblance to the behavior of certain molecular or ionic liquids in their supercooled state.

We investigate the fast dynamics by inelastic neutron scattering using a cold neutron time-of-flight spectrometer (IN6 of the ILL, Grenoble). With an incoming wavelength of 4.1 Å, an energy resolution of $\delta E = 170$ μeV (FWHM) can be reached; the accessible wave-number range (at zero energy transfer) extends then from $q = 0.4$ to 2.4 Å⁻¹. At one temperature (1065 K), additional spectra were measured with $\lambda = 5.1$ Å, yielding an even higher resolution $\delta E = 97$ μeV over a reduced wave-number range $q = 0.3$ –2.0 Å⁻¹.

V4 was alloyed by arc melting under argon atmosphere and sealed in a SiC container giving a flat plate with a sample thickness of 1.5 mm. Spectra of the equilibrium liquid were taken at four temperatures between 1065 and 1200 K; consistent results are also obtained from a 1020 K scan although a 5% crystalline fraction appears in the elastic structure factor. A measurement in the fully crystalline state at 870 K gave the instrumental resolution profile. For comparison, spectra of the glass at 293 K are also available [4]. After normalization to a vanadium standard, correction for self-absorption and container scattering, and interpolation to constant wave numbers q , we obtained the scattering law $S(q, \omega)$ (Fig. 1).

By formally summing the scattering cross sections of the individual elements, one finds that V4 is a 90% coherent scatterer. However, with the large wavelengths required for high energy resolution, the structure factor maximum at $q_0 = 2.7$ Å⁻¹ is out of reach. Our spectra are likely to be dominated by incoherent contributions, which is supported by the wave-number dependence of the elastic structure factor $S(q, \omega = 0)$ [Fig. 1(a)]. The scattering lengths of all five components are roughly of the same magnitude so that no element is especially emphasized in the total cross section.

With a width Γ of a few 10 μeV at $q = 2$ Å⁻¹ [Fig. 1(b)], the quasielastic line is about 2 orders of magnitude narrower than in simple liquids at the melting point—but at least 2 orders wider than expected from viscosity [5]. This expectation is based on relating linewidth and viscosity through the diffusivity D . The Stokes-Einstein relation $D = kT/6\pi\eta r$ with a hydrodynamic radius of the order $r \approx 1$ Å suggests that the diffusivity of any component of our alloy is smaller than 10⁻¹² m² s⁻¹. For small q the incoherent scattering law will be a sum of quasielastic lines with widths $\Gamma = D\hbar q^2$. Even outside the hydrodynamic limit, we still observe $\Gamma \propto q^2$ [6]. This allows us to read off an average diffusivity. At T_{liq} we obtain $D \approx 10^{-10}$ m² s⁻¹: all components of our alloy are highly mobile; the friction they experience is about 2 orders weaker than the macroscopic viscosity. This is in marked contrast to simple as well as to molecular liquids where the Stokes-Einstein relation holds with reasonable values of r [3,7]. The Stokes-Einstein relation fails also with respect to the temperature dependence: On heating from 1020 to 1200 K, the interpolated viscosity [8] decreases by a factor of 8, while Γ increases by only a factor of 4.

Failure of the Stokes-Einstein relation has been reported previously for the metastable melt: Measured diffusivities of Be [9] or Al [10] do not follow the temperature dependence of viscosity [11]. Close to the glass transition, such decoupling is unsurprising and known from many other supercooled liquids [12]. On

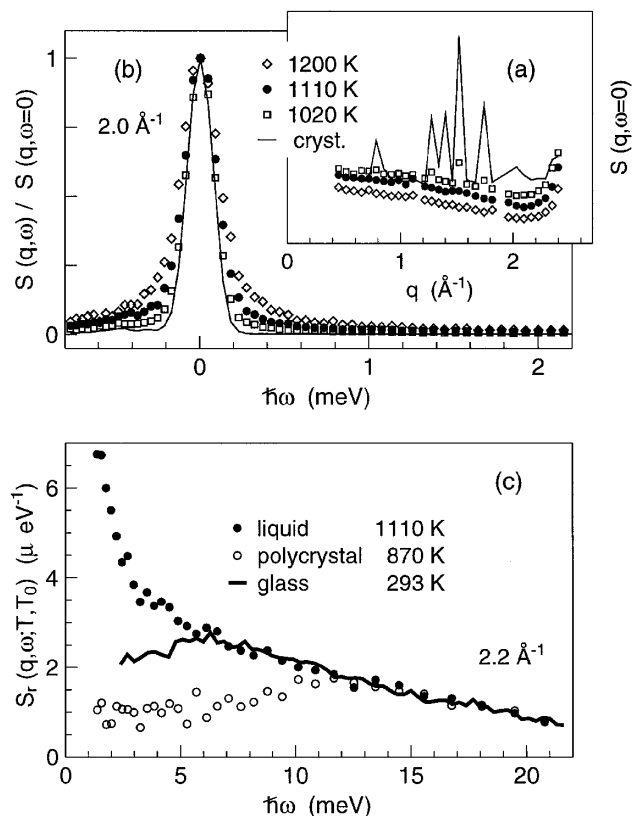


FIG. 1. Scattering law $S(q, \omega)$ of $\text{Zr}_{46.8}\text{Ti}_{8.2}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ (V4) as measured on the time-of-flight spectrometer IN6. (a) Elastic structure factor $S(q, \omega = 0)$ in the liquid and crystalline state. (b) Quasielastic part of the spectra. The crystalline sample yields the instrumental resolution. From a broadening in the order of $10 \mu\text{eV}$ we estimate a diffusivity of $10^{-10} \text{m}^2 \text{s}^{-1}$ at T_{liq} , 2 orders of magnitude larger than expected from the Stokes-Einstein relation. (c) Inelastic spectra of the glassy, crystalline, and liquid sample, plotted as temperature reduced structure factor $S_r(q, \omega; T, T_0) = S(q, \omega)n(\omega, T_0)/n(\omega, T)$ with arbitrary $T_0 = 1100 \text{K}$. At high energies, all data coincide. The boson peak around $\sim 6 \text{meV}$, characteristic of the glass, persists in the liquid phase.

heating towards the normal liquid state, however, quasielastic linewidths or directly measured diffusion constants of ionic [13], molecular [14], or even polymeric [15] liquids become consistent with the Stokes-Einstein relation. Although V4 is a more complicated multi-component liquid, a deviation by 2 orders of magnitude remains surprising.

Resuming the data analysis, we note that the wing of the quasielastic line extends up to meV energies. In Fig. 1(c), it is compared to the inelastic spectra of crystal and glass; the measured $S(q, \omega)$ are rescaled in intensity by the Bose occupation $n(\omega, T) = [\exp(\hbar\omega/k_B T) - 1]^{-1}$ expected for harmonic vibrations in lowest-order mass expansion [16]. The maximum in $S(q, \omega)$, commonly denoted the “boson peak,” is situated at 6 meV, considerably higher than in most other model glasses [17]. This makes V4 particularly suited for the study of relaxational dynamics, since the quasielastic scattering ap-

pears comparatively well separated from the vibrational spectrum.

Above 10 meV, all data coincide: the high-lying modes in which near neighbors oscillate against each other are sensitive neither to the presence or absence of long-range crystalline order nor to the onset of liquidlike long-time dynamics. Previous scattering experiments on V4 and related alloys up to the metastable melt had already discovered astonishing harmonicity [4,18], in marked contrast to the behavior of simple metals.

These results suggest that harmonic theory is even the right starting point for the description of microscopic dynamics in the viscous liquid. Such a view is indeed taken by mode-coupling theory (MCT) which tries to explain the long-time evolution of density correlations starting from oscillatory short-time behavior. Available formulations of MCT differ in the manner they approximate memory effects. The MCT’s developed for simple liquids near the melting point [3] cannot account for the shape of our quasielastic signal. Instead, we refer to a self-consistent variant of MCT originally invented [19] for the description of ergodicity breaking in the glass transition which in recent years [20] has been found to correctly describe fast dynamics and structural relaxation in various viscous liquids [21–24]. Molecular dynamics simulations of $\text{Ni}_{0.5}\text{Zr}_{0.5}$ suggest that it might also apply to certain alloys [25].

In order to analyze spectral line shapes in terms of MCT, we symmetrize measured spectra $S(q, \omega)$ with the detailed-balance factor $\exp(-\hbar\omega/2k_B T)$, Fourier transform them, and divide by the Fourier transform of the instrumental resolution. Normalization to the $t = 0$ value yields the time correlation function $\Phi(q, t)$ from $t \approx 0.1$ up to 4 psec (8 psec for 5.1\AA spectra). The information density in the short-time regime is basically restricted by the Nyquist theorem: Phononic excitations are better analyzed in terms of the measured $S(q, \omega)$, without passing through Fourier deconvolution. However, removal of the resolution function is essential for a quantitative analysis of dynamics in the psec regime.

In semilogarithmic representation (Fig. 2) one recognizes a two-step decay: Between 0 and some 0.1 psec, the broad distribution of vibrations leads to a rapid dephasing of neighboring atoms, so that $\Phi(q, t)$ falls from 1 towards an intermediate value f_q . On approaching f_q retardation sets in, before $\Phi(q, t)$ decays towards zero in the much slower process of α relaxation. For the psec dynamics around f_q , labeled the fast β -relaxation regime, MCT makes its most prominent prediction: Asymptotically, any correlation function is expected to follow

$$\Phi(q, t) = f_q + h_q g_\lambda(t/t_\sigma). \quad (1)$$

The scaling function $g_\lambda(\tilde{t})$ which is fully defined by just one shape parameter λ can be computed using tabulated expansion coefficients [26].

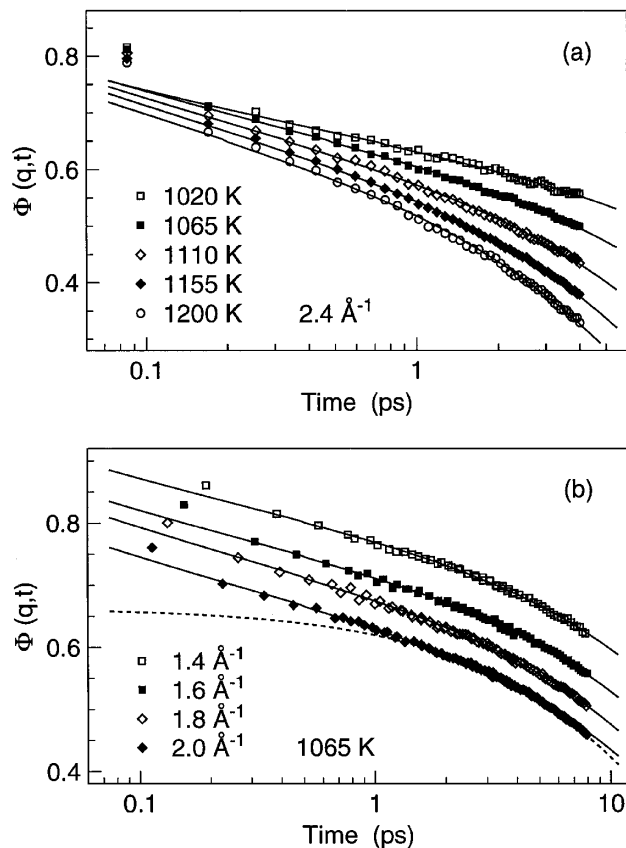


FIG. 2. Normalized time correlation function $\Phi(q, t)$ obtained by Fourier deconvolution of measured $S(q, \omega)$. Solid lines are fits with the β -relaxation scaling function of mode-coupling theory (1) with $\lambda = 0.77$. The broken line in (b) shows that the long-time asymptote can be described by a Kohlrausch function (3) with a stretching exponent $\beta \approx 0.8$.

The data were fitted in an iterative procedure: Starting with an arbitrary λ , fits to individual curves were used to estimate the scaling factors f_q , h_q , and t_σ which physically represent the amplitude of α relaxation, the amplitude of β relaxation, and a characteristic time of β relaxation. Using these values, the $\Phi(q, t; T)$ measured at different temperatures were superimposed onto master curves $[\Phi(q, t/t_\sigma) - f_q]/h_q$. After fixing a q -independent average t_σ , a global fit yielded an improved value of λ . After few iterations, we consistently obtained $\lambda = 0.77 \pm 0.04$. This result is very close to the hard spheres value 0.766 [27], and of the same order as the experimental finding in most other liquids.

The resulting α -relaxation amplitude f_q varies only weakly with temperature. In contrast, amplitude and time scale of β relaxation strongly reflect the slowing down of microscopic dynamics on cooling. In Fig. 3 both parameters are found to follow accurately mode-coupling predictions

$$t_\sigma \propto (T - T_c)^{-1/2a} \quad \text{and} \quad h_q \propto (T - T_c)^{1/2}, \quad (2)$$

where the exponent $a = 0.295$ is fully determined by λ . Within mode coupling, T_c is the temperature around which

liquidlike motion freezes and activated hopping becomes the dominant transport mechanism [28]. From extrapolation into the experimentally inaccessible metastable liquid below T_{liq} , we obtain consistent estimates $T_c \approx 875 \pm 6$ K, about 50% above the conventional glass transition temperature $T_g = 592$ K determined from viscosity [2].

Previously, we had searched for the mode-coupling crossover at far lower temperatures in the metastable melt up to the crystallization temperature. An anomalous decrease of the Debye-Waller and Lamb-Mössbauer factors indicated the onset of β relaxation, and suggested a mode-coupling crossover at a T_c somewhere above 700 K [4,18]. These conclusions are confirmed by the present direct observation of β relaxation.

For times $t \gg t_\sigma$, Eq. (1) takes the asymptotic form $\Phi(q, t) - f_q \propto t^{-b}$ with an exponent $b < 1$ given by λ . Such fractal time dependence is consistent [29] with Kohlrausch's stretched exponential

$$\Phi(q, t) \propto \exp[-(t/\tau_q)^\beta]. \quad (3)$$

From $t \approx 1$ psec up to the longest accessible times, Eq. (3) correctly describes the final decay of correlations towards zero (Fig. 2). The stretching exponent is $\beta = 0.8 \pm 0.1$.

In conclusion, the microscopic dynamics of liquid $\text{Zr}_{46.8}\text{Ti}_{8.2}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ deviates in many aspects from the established behavior of simple liquids. The traditional description of quasielastic scattering in terms of one or several Lorentzians is totally inadequate. We observe

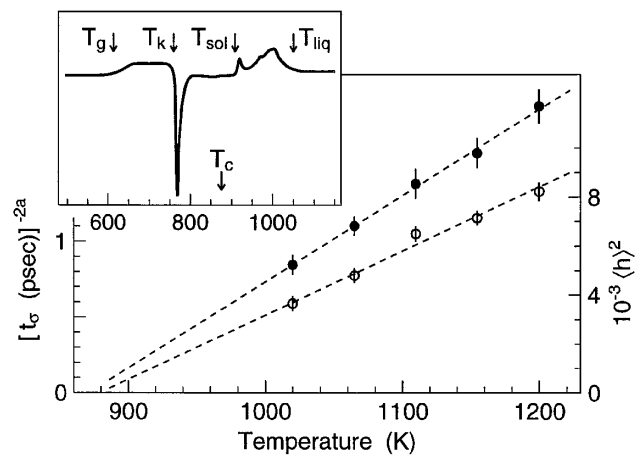


FIG. 3. Amplitude h_q (\circ) and time scale t_σ (\bullet) of β relaxation in liquid V4, rectified according to the mode-coupling prediction (2), with an exponent $a = 0.295$ obtained from $\lambda = 0.77$. Since the h_q showed no significant q dependence, they were averaged over the wave-number range 1.2 – 2.4 \AA^{-1} . Both $\langle h \rangle$ and t_σ extrapolate consistently to a crossover temperature $T_c = 875 \pm 6$ K. Inset: Characteristic temperatures of a melt-spun V4 ribbon as seen by differential scanning calorimetry with a heating rate of 40 K/min. Previous scattering experiments had searched for the onset of fast β relaxation in the metastable melt up to the crystallization temperature T_k [4,18]. In the present study, we succeeded in keeping the corrosive alloy for hours above T_{liq} without detectable traces of crystallization or reaction with the sample holder.

a two-step process which cannot be accounted for by a simple superposition of vibrational and relaxational motion. Instead, as in several other glass forming systems, the fast dynamics is in full accord with the MCT of structural relaxation; in particular, this theory accounts in all detail for the intermediate regime (1).

It has been conjectured [17] that MCT works best in fragile liquids. Characterized by a particularly sharp temperature dependence of viscosity, fragile glass formers usually have no directional bonds [12]. In fact, the best agreement with MCT has so far been reported in ionic [21], molecular [22,23], and colloidal [24] systems. In intermediate systems like glycerol [30] or $\text{NaPO}_3 \cdot \text{LiPO}_3$ [31], the short-time limit of (1) is partly covered by vibrational excitations, and in a nonfragile ("strong") network like B_2O_3 only remnants of MCT asymptotics were found [32]. This correlation is broken by the present study. Viscosity measurements [2,11] rank V4 as a relatively strong liquid, with a fragility between glycerol and B_2O_3 . A high Zr content suggests an important role of covalent directional bonds [33]. Nevertheless, the scaling laws (1) and (2) hold as well as in any neutron scattering experiment on fragile glass formers: The fast dynamics of $\text{Zr}_{46.8}\text{Ti}_{8.2}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ is in full accord with mode-coupling theory.

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