

## Diffusion in a Metallic Melt at the Critical Temperature of Mode Coupling Theory

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According to mode coupling theory, liquidlike motion becomes frozen at a critical temperature  $T_c$  well above the caloric glass transition temperature  $T_g$ . Here, for the first time, we report on radiotracer diffusion in a supercooled  $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$  alloy from  $T_g$  to the equilibrium melt. Liquidlike motion is seen to set in exactly above  $T_c$  as evidenced by a gradual drop of the effective activation energy. This strongly supports the mode coupling scenario. Isotope effect measurements, which have never been carried out near  $T_c$  in any material, show atomic transport up to the equilibrium melt to be far away from the hydrodynamic regime of uncorrelated binary collisions.

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Transport in simple liquids at high temperatures is well understood. In the hydrodynamic regime, all atoms contribute continuously to the mean square atomic displacement, and diffusion takes place similar to viscous flow, as described by the Stokes-Einstein equation [1]. Transport in the hydrodynamic regime is governed by uncorrelated binary collisions of atoms. Here kinetic theories predict the diffusivity  $D$  to obey a

$$D \propto \frac{1}{\sqrt{m}} T^n \quad (1)$$

temperature dependence, where  $m$  is the atomic mass and  $n$  is close to 2 according to experiments and molecular dynamic simulations [1–3]. In contrast, diffusion in the glassy state is solidlike; i.e., it takes place by thermally activated local hopping events over frozen-in barriers. Isotope effect measurements [4,5] and molecular dynamic simulations [6,7] suggest diffusion in metallic glasses to occur by highly collective jumps involving many atoms.

The transition from the liquid to the glassy state has often been described as a thermodynamic phenomenon [8]. Although it is now well established that the glass transition is no classical thermodynamic phase transition and has strongly kinetic features [9,10], its nature and the underlying atomic dynamics are still discussed controversially [11–14].

At present, the most advanced description of the arrest of liquidlike motion is provided by the mode coupling theory (MCT) which describes the evolution of density-density correlations of finite wavelengths upon (super)cooling a liquid or melt [15]. The central prediction of the theory is that the transition from liquidlike motion to solidlike hopping does not occur at the caloric glass transition temperature  $T_g$ , which marks the onset of macroscopic viscous flow (softening temperature). The atoms

are rather trapped in their nearest neighbor cages already at the critical temperature, well above  $T_g$  as a consequence of the increase in density upon cooling. Below  $T_c$ , liquidlike motion is frozen in, and only hopping which is envisioned as a highly collective process can take place [16]. The predictions of mode coupling theory have been tested by neutron scattering and other techniques as well as by molecular dynamic simulations in several glass forming systems resulting in qualitative and sometimes even quantitative agreement [for a review, see [17]]. Metallic systems, however, which have often been regarded as ideal model systems of dense random packing, have not yet been accessible in the range near and above  $T_c$  due to the onset of crystallization. This even holds for the new bulk glass forming alloys introduced by Inoue [18] and Johnson [19].

For the present studies, we used a novel  $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$  glass forming alloy, which has been discovered very recently and is particularly stable against crystallization [20]. We determined the caloric glass transition temperature  $T_g$  as 582 K by means of differential scanning calorimetry at 20 K/min. The quasieutectic melting temperature  $T_m$  is 802 K. Microscopic dynamics in the equilibrium liquid of PdNiCuP as studied by inelastic neutron scattering is in accordance with the MCT which describes predictions. The temperature dependence of the structural relaxation times as well as the temperature dependence of amplitude and time scale of a localized cage motion (fast beta relaxation) extrapolate consistently to a  $T_c$  at 710 K [21].

We were able to measure diffusivities from close to the caloric glass transition temperature up to far above the quasieutectic melting temperature using an elaborate encapsulation technique in a graphite container. We employed the radiotracer technique in conjunction with serial sectioning for diffusion measurements involving a  $^{57}\text{Co}/^{60}\text{Co}$  isotope mixture. Cobalt is well known to probe

the self-diffusion behavior of Ni [14]. This allowed us to measure the diffusivities of both isotopes simultaneously [4] and to determine the isotope effect defined as

$$E = (D_\alpha/D_\beta - 1)/(\sqrt{m_\beta/m_\alpha} - 1), \quad (2)$$

where  $m_i$  is the mass and  $D_i$  the diffusivity of isotope  $i$ .  $E$  measures the mass dependence of diffusion and is defined such that  $E = 1$  for an ideal  $1/\sqrt{m}$  dependence as predicted by Eq. (1). Serial sectioning was performed by ion-beam sputtering or mechanical grinding, depending on the penetration depth of the tracers. A typical resulting penetration profile is given in Fig. 1. All samples were checked for crystallization by x-ray diffraction after annealing. Details will be given elsewhere. Tracer diffusivities were obtained by fitting the thin film solution of

Fick's second law [1],

$$c(x, t) = \frac{I_0}{\sqrt{\pi Dt}} e^{-x^2/(4Dt)}, \quad (3)$$

to the profiles (neglecting data very near the surface). In Eq. (3),  $t$  denotes the annealing time,  $x$  the penetration depth, and  $I_0$  is a constant. The isotope effect was obtained by plotting  $\ln c_\alpha/c_\beta$  versus  $\ln c_\alpha$  [Fig. 1(b)]. The slope directly yields  $(D_\alpha/D_\beta - 1)$  and, hence,  $E$  via Eq. (2).

The temperature dependence of the Co diffusivity is shown in Fig. 2(a). Above  $T_g$ , the diffusivity follows an Arrhenius-type behavior with  $D(T) = 10^{10.2(\pm 0.2)} \text{ m}^2 \text{ s}^{-1} \exp[-3.3(\pm 0.1) \text{ eV}/k_B T]$  as observed in previous diffusion studies in supercooled metallic melts below  $T_c$  [14]. Arrhenius behavior is not necessarily expected for diffusion in the supercooled equilibrium state where any change in temperature also gives rise to structural changes. Therefore the activation energy has to be regarded as an effective quantity not reflecting the barrier height.

Our data clearly provide evidence of a change in the atomic dynamics: At  $T_c = 710$  K, the effective activation

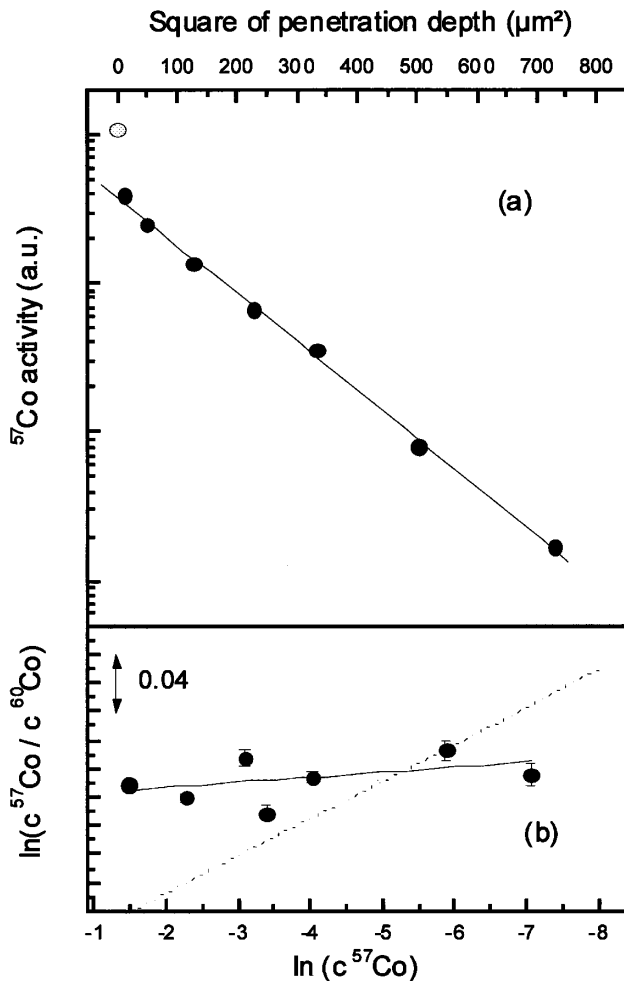


FIG. 1. (a) Typical penetration profile for Co diffusion in  $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$  at 748 K and 1 h annealing. The activity is plotted vs the square of penetration depth. (b) Corresponding isotope effect profile. The activity ratio of  $^{57}\text{Co}$  and  $^{60}\text{Co}$  is plotted vs the  $^{57}\text{Co}$  activity on a logarithmic scale. The dotted line below yields an isotope effect of  $E = 1$  and is shown for comparison.

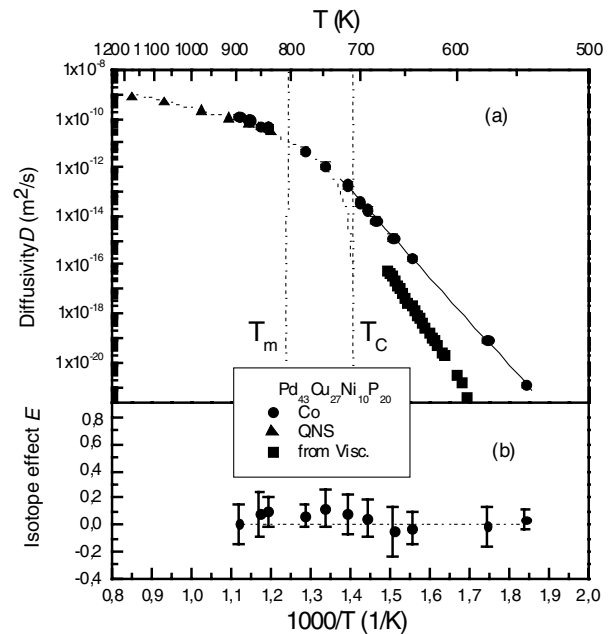


FIG. 2. Temperature dependence of (a) Co diffusivity and (b) isotope effect in  $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$ . The diffusivity is plotted on a semilogarithmic scale vs  $1/T$ . Data for Ni and Cu diffusion from quasielastic neutron scattering (QNS) [21] and diffusivities determined from viscosity data [22] by means of the Stokes-Einstein equation are shown for comparison. The breakdown of the Stokes-Einstein equation below  $T_c$  is obvious. The dotted line is a fit of the idealized mode coupling theory to the QNS data (see text). The quasicutectic melting temperature  $T_m$  and  $T_c$ , determined from the QNS, data are displayed. Below  $T_c$ , the tracer diffusivity data were fitted by an Arrhenius law.

energy  $-k\partial \ln D/\partial T^{-1}$  [slope in Fig. 2(a)] drops gradually as expected from the onset of liquidlike motion in the mode coupling scenario. Because of the increasing influence of liquidlike motion, the nearest neighbor barriers should gradually decrease as the temperature is increased above  $T_c$ . Above  $T_m$ , our Co diffusivities are within the statistical error equal to the diffusivities derived from inelastic neutron scattering [21]. We note that at  $T_m$  the diffusivity is 2 orders of magnitude smaller than that of ordinary liquids. Above  $T_c$ , the idealized MCT (that neglects mass transport below  $T_c$ ) predicts

$$1/D\alpha[(T - T_c)/T_c]^{-\gamma}. \quad (4)$$

The dashed line in Fig. 2 represents Eq. (4) using the  $T_c = 710$  K and the  $\gamma = 2.7$  from the analysis of the localized cage motion as measured by inelastic neutron scattering [21]. Our diffusion data are even in quantitative agreement with the MCT predictions.

The singularity in  $T_c$  is not expected in real systems and from recent extensions of the idealized MCT [16] that take into account hopping processes and predict a smooth transition to Arrhenius behavior exactly in the way reflected in our data (Fig. 2). We further note that the extrapolation of the diffusivities determined from viscosity data [22] by means of the Stokes-Einstein equation merge with our diffusion data above  $T_c$ . This shows the breakdown of the Stokes-Einstein equation below  $T_c$  and that its validity starts to set in above  $T_c$ , where MCT predicts the onset of liquidlike motion. Thus, the present results strongly support the extended mode coupling approach for metallic glass formers.

It has to be pointed out that other theories, including the free volume theory first introduced by Cohen and Turnbull, which already involves the cage effect, also predict a change in the slope of the Arrhenius plot in the supercooled liquid state (for reviews, see Refs. [9,10]). However, our observation that liquidlike motion sets in exactly above the critical temperature  $T_c$  of MCT is striking.

Inelastic neutron scattering measures diffusive motion of the atoms on microscopic time and length scales. The experiment on liquid Pd-Cu-Ni-P alloys [21,23] exhibits a  $q^2$  dependence of the quasielastic signal that is dominated by the incoherent contribution of the Ni and Cu atoms. This allows for the measurements of diffusivities on an absolute scale, not affected by convection that causes additional mass transport at significantly longer times. The excellent agreement between our tracer diffusion data and the diffusivities from quasielastic neutron scattering demonstrates that convection effects, which are a severe problem in diffusion measurements in ordinary liquids under gravity conditions, are negligible in dense Pd-Cu-Ni-P melts.

The isotope effect is very low ( $E \approx 0.05$ ) in the whole range investigated. Below  $T_c$ , a very low isotope effect

has been observed before in metallic glass forming alloys [24,25]. The low  $E$  values were attributed to highly collective thermally activated hopping processes as envisioned by the aforementioned extension of the mode coupling theory to the range below  $T_c$  [16] and as seen in molecular dynamics simulations [7]. The low  $E$  values in the equilibrium melt, however, are remarkable. They show that the present Pd-Cu-Ni-P melt is still far away from the hydrodynamic regime of uncorrelated binary collisions even 200 K above  $T_c$ . This contrasts strongly with simple melts such as liquid Sn, which exhibits an isotope effect of the expected order of unity [3]. Molecular dynamics simulations indicate a strong correlation of isotope effect and density of the liquid and suggest the present very low  $E$  value to be due to the small density difference between glassy and liquid state of only about 3% [26]. The strongly coordinated atomic motion evidenced by the low isotope effect value in the equilibrium liquid appears to be the key to the excellent glass forming ability.

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