

**Atomic transport in dense multicomponent metallic liquids**

A. Meyer\*

*Physik Department E13, Technische Universität München, 85747 Garching, Germany*

(Received 19 June 2002; published 21 October 2002)

$\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$  has been investigated in its equilibrium liquid state with incoherent, inelastic neutron scattering. As compared to simple liquids, liquid  $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$  is characterized by a dense packing with a packing fraction above 0.5. The intermediate scattering function exhibits a fast relaxation process that precedes structural relaxation. Structural relaxation obeys a time-temperature superposition that extends over a temperature range of 540 K. The mode-coupling theory of the liquid to glass transition [mode-coupling theory (MCT)] gives a consistent description of the dynamics that governs the mass transport in liquid Pd-Ni-Cu-P alloys. MCT scaling laws extrapolate to a critical temperature  $T_c$  at about 20% below the liquidus temperature. Diffusivities derived from the mean relaxation times compare well with Co diffusivities from recent tracer diffusion measurements and diffusivities calculated from viscosity via the Stokes-Einstein relation. In contrast to simple metallic liquids, the atomic transport in dense, liquid  $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$  is characterized by a drastic slowing down of dynamics on cooling and a  $q^{-2}$  dependence of the mean relaxation times at intermediate  $q$  as a result of a highly collective transport mechanism. At temperatures as high as  $2T_c$  diffusion in liquid  $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$  is as fast as that in simple liquids at the melting point. However, the difference in the underlying atomic transport mechanism indicates that the diffusion mechanism in liquids is not controlled by the value of the diffusivity but rather by that of the packing fraction.

DOI: 10.1103/PhysRevB.66.134205

PACS number(s): 61.25.Mv, 61.20.Lc, 61.12.-q

**I. INTRODUCTION**

We investigate microscopic dynamics in liquid Pd-Ni-Cu-P melts with inelastic neutron scattering. Our results show that Pd-Ni-Cu-P can in good approximation be regarded as multicomponent hard-sphere-like system. As compared to liquid alkali metals packing in liquid Pd-Ni-Cu-P is much more dense. As a consequence, dynamics in liquid Pd-Ni-Cu-P cannot be described by concepts developed for simple liquids. Instead, atomic transport in Pd-Ni-Cu-P melts is in excellent accordance with concepts developed in the context of glass formation.

Because of the short range nature of the interatomic potential with a strong repulsive core, the potential in simple metals can in good approximation be condensed to an effective hard-sphere radius  $R$ .<sup>1</sup> Therefore, the packing fraction  $\varphi = \frac{4}{3}\pi nR^3$  ( $n$  is the number density in unit volume) is an important parameter for the discussion of the transport mechanism.<sup>2</sup> Liquid alkali metals are a paradigm of hard-sphere-like fluids and their microscopic dynamics have been investigated in great detail.<sup>3,4</sup> At low packing fraction, e.g., at temperatures well above the melting temperature, atomic transport is dominated by binary collisions. This reflects itself in a Gaussian line shape of the quasielastic neutron scattering signal in the free particle limit towards large wave numbers  $q$ . With increasing packing fraction, i.e., by approaching the melting temperature  $T_m$ , fluid dynamics play a more important role and towards small but finite  $q$  the quasielastic line is well approximated by a Lorentzian function.<sup>3,5</sup> Alkali melts exhibit a packing fraction of about 0.4 at the melting point.

Colloidal suspensions<sup>6</sup> and molecular dynamics simulated binary metallic melts<sup>7,8</sup> that have a significantly higher packing fraction above 0.5 exhibit microscopic dynamics that is not governed by binary collisions and is typical for glass-

forming, molecular liquids.<sup>9-11</sup> Their dynamics has been described by predictions of the mode-coupling theory (MCT) of the liquid to glass transition:<sup>12</sup> Atomic transport slows down by orders of magnitude on a small change in temperature or pressure. The slowing down of the dynamics goes along with a spread of the quasielastic line as compared to the Lorentzian found in simple liquids corresponding to a stretching in time of correlation functions over a wider time range than expected for an exponential decay.

Mode-coupling theory gives a microscopic explanation for this behavior in terms of a non linear coupling of density fluctuations caused by feedback effects in the dense liquid. Atomic transport is envisioned as a highly collective process. At a critical packing fraction  $\varphi_c$  or a critical temperature  $T_c$ , MCT predicts a change in the transport mechanism from liquidlike flow to glasslike activated hopping processes. MCT calculations for a hard-sphere system exhibit a critical packing fraction of 0.525.<sup>13</sup> In a colloidal suspension  $\varphi_c \approx 0.58$  has been found.<sup>6</sup> Whereas in alkali melts the packing fractions are well below 0.5, new multicomponent alloys in a Zr basis<sup>14</sup> and Pd basis<sup>15-17</sup> at quasieutectic compositions exhibit packing fractions at their liquidus temperature  $T_{\text{liq}}$  of some 0.52.<sup>18,19</sup> These alloys, known for their bulk glass-forming ability, exhibit viscosities at their melting temperatures that are 2-3 orders of magnitude larger than in simple metals and most alloys.<sup>20,21</sup>

In previous neutron scattering experiments fast dynamics in viscous  $\text{Zr}_{46.8}\text{Ti}_{8.2}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$  have been investigated: Data analysis in the framework of MCT is in full agreement with the predicted scaling functions and gives a  $T_c$  some 20% below  $T_{\text{liq}}$ .<sup>22</sup> In an experiment on viscous  $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$  (Pd40) the focus was on slow dynamics:<sup>23</sup> The long-time decay of correlations exhibits the common features of glass-forming liquids, i.e., structural relaxation

obeys a stretching in time and a universal time-temperature superposition.

Here, inelastic neutron scattering results on liquid  $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$  ( $\text{Pd}_{43}$ ) are reported. The small change in composition compared to  $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$  results in an improved stability with respect to crystallization<sup>16</sup>—a cooling rate as low as 0.09 K/s is sufficient to avoid crystallization and to form bulk metallic glass.<sup>24</sup> This allows measurements of transport coefficients at temperatures around the mode coupling  $T_c$  with experimental techniques that only require heat treatment for some minutes, e.g., rheometry<sup>20</sup> or radio tracer diffusion measurements.<sup>25</sup>

Compared to previous neutron scattering measurements<sup>22,23</sup> a different experimental setup has been used that covers an extended range of momentum transfers  $q$ . This allows a detailed investigation of the fast MCT  $\beta$  relaxation and the correlation between structural relaxation and long range atomic transport. In addition, the temperature range has been extended by several 100 K up to temperatures at which the diffusion of the atoms is of the order of that in simple monatomic metals. The results are set in context with macroscopic transport coefficients, the dynamics in simple liquids, and the predictions by the mode coupling theory of the liquid to glass transition.

## II. EXPERIMENT

$\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$  was prepared from a mixture of pure elements by induction melting in a silica tube. The melt was subject to a  $\text{B}_2\text{O}_3$  flux treatment in order to remove oxide impurities. Differential scanning calorimetry with a heating rate of 40 K/min resulted in a  $T_g$  at 578 K and a  $T_{\text{liq}}$  at 863 K in accordance with literature values.<sup>16,24</sup> For the neutron time-of-flight experiment a thin-walled  $\text{Al}_2\text{O}_3$  container has been used giving a hollow cylinder sample geometry of 22 mm in diameter and a thickness of 1 mm. During the measurement the liquid was covered by a thin layer of  $^{11}\text{B}_2\text{O}_3$  flux material. For the chosen geometry and neutron wavelength the sample scatters less than 2%. Therefore, multiple scattering, which would alter the data especially towards low  $q$ ,<sup>26</sup> only has a negligible effect.

Microscopic dynamics in liquid Pd-Ni-Cu-P has been investigated on the neutron time-of-flight spectrometer IN 6 at the Institut Laue-Langevin in Grenoble. An incident neutron wavelength of  $\lambda = 5.1 \text{ \AA}^{-1}$  yielded an accessible wave number range at zero energy transfer of  $q = 0.75 - 1.95 \text{ \AA}^{-1}$  at an energy resolution of  $92 \mu\text{eV}$  [full width at half maximum (FWHM)]. Regarding the scattering cross sections of the individual elements Pd-Ni-Cu-P is a 90% coherent scatterer. However, with the first structure factor maximum at  $q_0 \approx 2.9 \text{ \AA}^{-1}$  our spectra are dominated by incoherent scattering, that is dominated by the contributions from Ni with  $\approx 73\%$  and Cu with  $\approx 20\%$ .

The alloy was measured at room temperature to obtain the instrumental energy resolution function. Data were collected in the liquid between 833 K and 913 K in steps of 40 K and between 973 K and 1373 K in steps of 100 K with a duration between 2 and 5 h each. At each temperature empty cell runs were performed. The data at 833 K, 30 K below the liquidus,

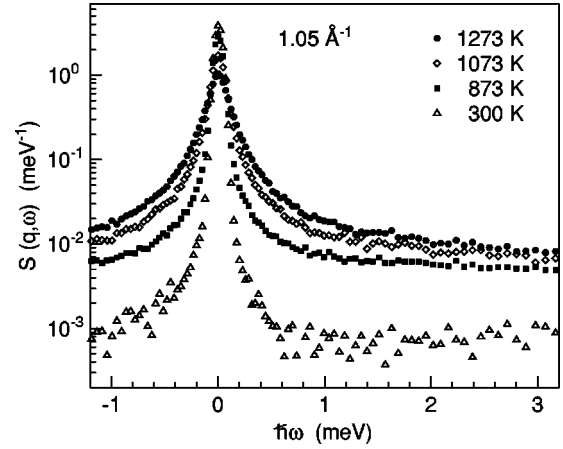


FIG. 1. Scattering law  $S(q, \omega)$  (logarithmic scale) of liquid  $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$  obtained on the neutron time-of-flight spectrometer IN 6. The signal is dominated by the incoherent scattering from Ni and Cu. The data at 300 K represent the instrumental energy resolution. Measurements in the liquid ( $T_{\text{liq}} = 863 \text{ K}$ ) show a broad quasielastic signal.

do not show signs of crystallization, which is in accordance with the time-temperature transformation of the undercooled liquid.<sup>24</sup> In order to obtain the scattering law  $S(q, \omega)$  (Fig. 1), raw data were normalized to a vanadium standard, corrected for self-absorption and container scattering, interpolated to constant  $q$ , and symmetrized with respect to energy with the detailed balance factor. Fourier deconvolution of  $S(q, \omega)$  and normalization to 1 for  $t=0$  gives the self correlation function  $\Phi(q, t)$ .

## III. MODE-COUPLING THEORY ASYMPTOTICS

The mode-coupling theory of the liquid to glass transition<sup>11,12</sup> (MCT) is developed in the well-defined frame of molecular hydrodynamics.<sup>27</sup> Starting with the particle density,  $\vec{\rho}_r(t) = \sum_i \delta(\vec{r} - \vec{R}_i(t))$ , i.e., the positions,  $\vec{R}_i$ , of each particle,  $i$ , at time  $t$ , the Zwanzig-Mori formalism provides an exact equation of motion for the density correlation function,  $\Phi_q(t) = \langle \rho_q(t) * \rho_q \rangle / \langle |\rho_q|^2 \rangle$ :

$$\ddot{\Phi}_q(t) + \Omega_q^2 \Phi_q(t) + \int_0^t M_q(t-t') \dot{\Phi}_q(t') dt' = 0, \quad (1)$$

where  $\Omega_q$  represents a phonon frequency at wave number  $q$  and  $M_q(t)$  a correlation function of force fluctuations, which in turn is a functional of density correlations. The static part of the fluctuating force is a linear combination of density fluctuation pairs and depends therefore only on the interaction potential.

Since MCT does not aim to describe the detailed microscopic phonon distribution, but rather to give a universal picture of relaxational dynamics at longer times, the integral kernel is split into

$$M_q(t) = \nu_q \delta(t) + \Omega_q^2 m_q(t), \quad (2)$$

where  $\nu_q$  models the damping by “fast” modes and  $m_q(t)$  accounts for memory effects through the coupling of “slow”

modes. The basic idea of the mode-coupling theory of the liquid to glass transition is to consider as “slow” all products of density fluctuations. By derivation,  $m_q(t)$  contains no terms linear in  $\Phi_q(t)$ . Therefore, in lowest order, it is a quadratic functional

$$m_q(t) = \sum_{q_1+q_2=q} V_q(q_1, q_2) \Phi_{q_1}(t) \Phi_{q_2}(t). \quad (3)$$

In this approximation, the coupling coefficients  $V_q$  are specified in terms of the static structure of the liquid.

Equations (1)–(3) lead to the following scenario: a fast  $\beta$ -relaxation process, which can be visualized as a rattling of the atoms in the cages formed by their neighboring atoms, precedes a structural  $\alpha$  relaxation, responsible for viscous flow. At an ideal glass transition temperature  $T_c$  the transport mechanism crosses over from glasslike activated hopping processes to liquidlike collective motion. In other words, at  $T_c$ , the cages are no longer stable on the time scale of a diffusive jump.

A common feature of structural  $\alpha$  relaxation in glass forming liquids is a stretching in correlation functions over a wider time range than expected for exponential relaxation.<sup>9,10</sup> Experimental data in the  $\alpha$ -relaxation regime can usually be well described by a stretched exponential function

$$F(q, t) = f_q^c \exp[-(t/\tau_q)^{\beta_q}] \quad (4)$$

with an exponent  $\beta_q < 1$ .  $\tau_q$  is the relaxation time and  $f_q^c < 1$  accounts for the initial decay of correlations due to phonons and the fast relaxation process. For temperatures above  $T_c$  mode-coupling theory predicts a universal time-temperature superposition of structural relaxation resulting in a temperature independent stretching exponent  $\beta_q$ . Many glass-forming liquids in contrast exhibit a temperature dependence of  $\beta$ —in some  $\beta$  is decreasing, in others increasing on temperature increase.

Solutions of the mode-coupling equations for a hard-sphere system confirm that the MCT  $\alpha$  relaxation is well described by a stretched exponential function and Eq. (4) becomes a special, long-time solution of mode-coupling theory.<sup>13</sup> For the mean relaxation times

$$\langle \tau_q \rangle = \int_0^\infty dt F(q, t) / f_q^c = \tau_q \beta^{-1} \Gamma(\beta^{-1}), \quad (5)$$

mode-coupling theory predicts that  $\langle \tau_q(T) \rangle$  is inversely proportional to the diffusivity  $D(T)$  and obeys an asymptotic scaling law for temperatures above but close to  $T_c$ :

$$\langle \tau_q \rangle \propto 1/D \propto [(T - T_c)/T_c]^{-\gamma}. \quad (6)$$

Asymptotic expansions of Eqs. (1) and (3) show that in the intermediate  $\beta$ -relaxation regime around a crossover time,  $t_\sigma$ , and for temperatures close to  $T_c$ , the asymptotic form of the correlation function is independent of the detailed structure of the coupling coefficients and exhibits a universal factorization property:

$$\Phi(q, t) = f_q^c + h_q g_\lambda(t/t_\sigma), \quad (7)$$

where  $f_q$  represents the Debye-Waller factor and  $h_q$  an amplitude. The scaling function  $g_\lambda(\tilde{t})$  is defined by just one shape parameter  $\lambda$ . Close to  $T_c$  mode-coupling theory predicts the temperature dependence of  $t_\sigma$  and  $h_q$  with the asymptotic scaling functions:

$$t_\sigma \propto (T - T_c)^{-1/2a} \quad \text{and} \quad h_q \propto (T - T_c)^{1/2}. \quad (8)$$

There are tables providing  $a$ ,  $\gamma$ , and  $g_\lambda$  as a function of  $\lambda$ .<sup>28</sup>

## IV. RESULTS

Figure 1 shows the scattering law  $S(q, \omega)$  of liquid Pd-Ni-Cu-P at  $q = 1.05 \text{ \AA}^{-1}$ . The signal is dominated by the incoherent scattering from Ni and Cu.  $S(q, \omega)$  displays a quasielastic line with an increasing width on temperature increase and with wings extending up to several meV. Above some 3 meV the quasielastic signal merges into a constant as expected for an ideal Debye solid and found in liquid  $\text{GeO}_2$ .<sup>29</sup> The quasielastic signal of  $S(q, \omega)$  is fairly well separated from vibrations.

### A. Vibrations

There is no general understanding of the influence of phonons on the atomic transport in liquids. Whereas in monatomic alkali melts one finds low-lying collective phonon modes that mediate mass transport,<sup>30,31,3</sup> the mode-coupling theory of the liquid to glass transition does not consider the detailed phonon dynamics for its description of atomic transport in viscous liquids [Eq. (2)]. In particular, dynamics in hard-sphere-like colloidal suspensions that do not exhibit vibrations, are in excellent agreement with MCT predictions.<sup>6</sup>

In most molecular liquids broad phonon distributions overlap with the quasielastic signal. The phonon density of states exhibits a first maximum usually between 4 and 8 meV.<sup>32,33</sup> This aggravates the theoretical description of the relaxational dynamics. Figure 2 displays the vibrational density of states  $g(\omega)$  representing mainly the incoherent contributions of the Ni and Cu atoms of liquid Pd-Ni-Cu-P.  $g(\omega)$  has been derived from the scattering law  $S(q, \omega)$  using a procedure that assumes pure incoherent scattering and uses the multiphonon correction as described in Ref. 34.

$g(\omega)$  displays a weak temperature dependence, indicating that anharmonic contributions to the interatomic potential are minor. This is in accordance with an expansion coefficient of only  $4 \times 10^{-5} \text{ K}^{-1}$ ,<sup>19</sup> which is an order of magnitude smaller than that of most molecular glass-forming liquids. With a maximum in  $g(\omega)$  at some 17 meV, vibrations are fairly well separated from the quasielastic signal that extends up to several meV. In addition, Pd-Ni-Cu-P does not exhibit a “boson peak”—a maximum in  $S(q, \omega)$  that is found in other glasses usually at a few meV—in the  $q$  range investigated. This allows a detailed investigation of the atomic transport in liquid Pd-Ni-Cu-P.

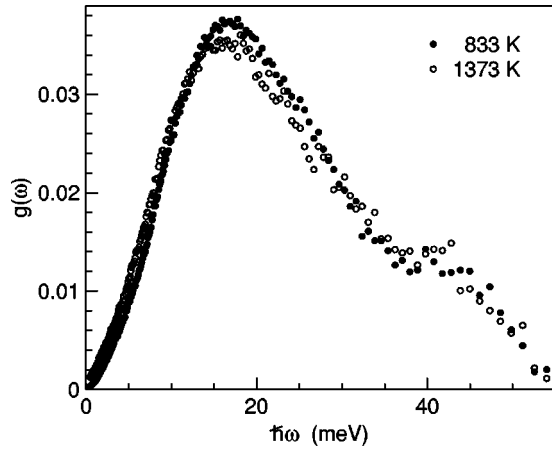


FIG. 2. Density of states  $g(\omega)$  representing mainly the Ni and Cu vibrations in liquid  $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$ . With a maximum at some 17 meV (corresponding to some 0.04 ps) vibrations are fairly well separated from the fast relaxational dynamics around 1 ps. The small expansion coefficient reflects itself in a weak temperature dependence of  $g(\omega)$ .

### B. Structural relaxation

The quasielastic signal is best analyzed in the time domain with a removal of the instrumental resolution function. The density correlation function  $\Phi(q, t)$  has been obtained by Fourier transformation of measured  $S(q, \omega)$ , division of the instrumental resolution function, and normalization with the value at  $t=0$ . Between 0 and  $\approx 1$  ps phonons and a fast process lead to a decrease in  $\Phi(q, t)$  from 1 towards a plateau. Figure 3 displays the long-time decay of  $\Phi(q, t)$  at  $q = 1.05 \text{ \AA}^{-1}$  from this plateau towards zero in a semilogarithmic representation.

In contrast to simple metallic liquids, liquid Pd-Ni-Cu-P exhibits a structural relaxation that shows stretching in time. The lines are fits with the stretched exponential function [Eq. (4)]. In a first fitting process the stretching exponent  $\beta_q(T)$

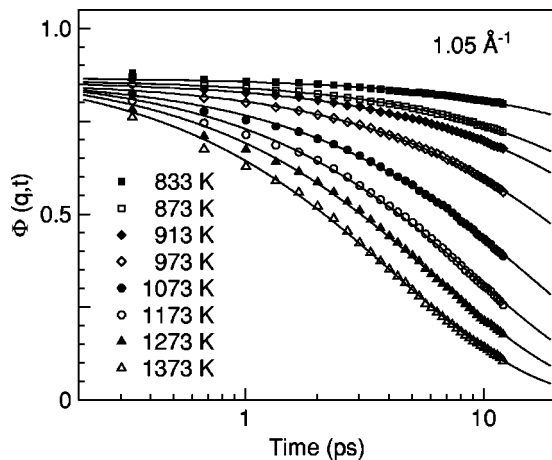


FIG. 3. Normalized density correlation function  $\Phi(q, t)$  of liquid Pd-Ni-Cu-P at  $1.05 \text{ \AA}^{-1}$  as obtained by Fourier deconvolution of measured  $S(q, \omega)$ . Structural relaxation causes the final decay of  $\Phi(q, t) \rightarrow 0$ . The lines are fits a stretched exponential function [Eq. (4)].

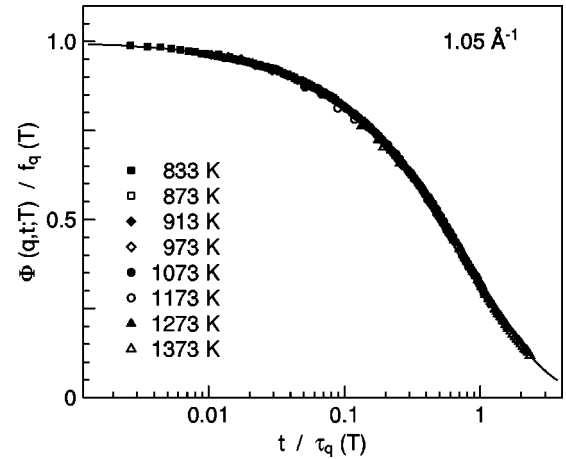


FIG. 4. Rescaling of the density correlation function in the  $\alpha$  relaxation regime (for  $t > 1$  ps) using results from fits with a stretched exponential function: a time-temperature superposition of structural relaxation holds from  $T_{\text{liq}} - 30$  K to  $T_{\text{liq}} + 510$  K. The line is a fit with Eq. (4) resulting in a stretching exponent  $\beta = 0.75$ .

was treated as a parameter:  $\beta_q(T)$  varies weakly around a mean  $\beta = 0.75$ . For the further data analysis a  $\beta = 0.75$  was used.

Structural relaxation described by mode-coupling theory displays stretching and a time-temperature superposition. Using results from the fitting procedure with Eq. (4) and a stretching exponent  $\beta = 0.75$  master curves  $\Phi(q, (t/\tau_q))/f_q$  have been constructed for the data in the structural relaxation regime above some 1 ps. Figure 4 shows rescaled  $\Phi(q, (t/\tau_q))/f_q$  at  $q = 1.05 \text{ \AA}^{-1}$ . Over the entire temperature range, which spans 540 K, the  $\Phi(q, (t/\tau_q))/f_q$  fall on a master curve: a time-temperature superposition of structural relaxation holds. We note that the validity of the time-temperature superposition up to temperatures at which the transport coefficients approach that of simple liquids (Sec. IV C) is in marked contrast to the idea that viscous liquids exhibit a transition to a liquid with the stretching exponent  $\beta$  approaching 1 with temperature increase.

Stretching of self-correlation functions is generally found to be more pronounced in fragile glass-forming liquids, characterized by a curved temperature dependence of viscosity in an Arrhenius plot;<sup>35</sup> e.g., the van der Waals liquid orthoterphenyl with  $\beta \approx 0.5$ .<sup>33</sup> In an intermediate system such as hydrogen-bond-forming glycerol a  $\beta \approx 0.6$  has been reported.<sup>36</sup> The stretching exponent in liquid Pd-Ni-Cu-P metals compares well to the value  $\beta \approx 0.75$  found in covalent-network-forming sodium disilicate melts<sup>37</sup> and indicates that the Pd-Ni-Cu-P alloy might classify as a fairly strong glass-forming liquid.

Figure 5 shows rescaled  $\Phi(q, (t/\tau_q))/f_q$  at 1073 K for  $q$  values in the range between  $0.75 \text{ \AA}^{-1}$  and  $1.95 \text{ \AA}^{-1}$ . Structural relaxation in liquid Pd-Ni-Cu-P can be described with a stretched exponential function and a  $q$ - and temperature-independent stretching exponent  $\beta = 0.75 \pm 0.02$ .  $\beta_q$  shows a small but systematic decrease with increasing  $q$  in agreement with MCT calculations for a hard-sphere system.<sup>13</sup> However,

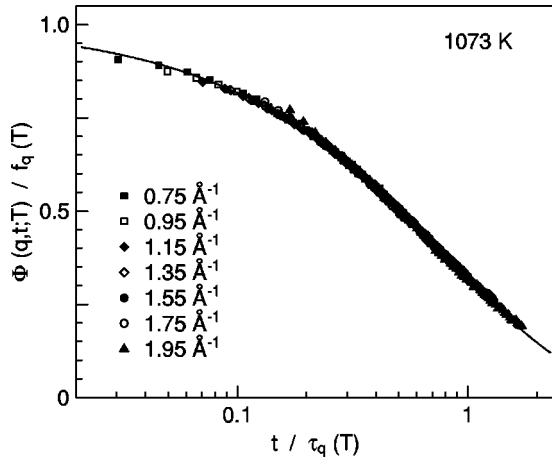


FIG. 5. Rescaling of the density correlation function  $\Phi(q,t)$  at 1073 K. Within the accessible  $q$  range the stretching of the structural relaxation is fairly  $q$  independent. The line represents a stretched exponential function [Eq. (4)] with a stretching exponent  $\beta=0.75$ .

a small variation of  $\beta_q$  in the fitting procedure has no significant effect on the resulting mean relaxation times [Eq. (5)].

### C. Diffusion

In the hydrodynamic limit for  $q \rightarrow 0$  one expects that the mean relaxation times  $\langle \tau_q \rangle$  are indirect proportional to the square of the momentum transfer  $q$ .<sup>27</sup> In liquid Pd-Ni-Cu-P the  $1/q^2$  dependence holds even up to  $1.9 \text{ \AA}^{-1}$  (Fig. 6) while the first structure factor maximum is at  $q_0 \approx 2.9 \text{ \AA}^{-1}$ . In liquid alkali metals one observes a systematic deviation from a  $q^2$  dependence of the quasielastic line width already at  $q$  values that correspond to 1/10 of their structure factor maximum  $q_0$ . This deviation is explained by low-lying phonon modes that mediate atomic transport.<sup>2,31</sup> Mean relaxation times for self motion in the MCT hard sphere system, in contrast, vary rather well proportionally to  $1/q^2$  for  $q$  values

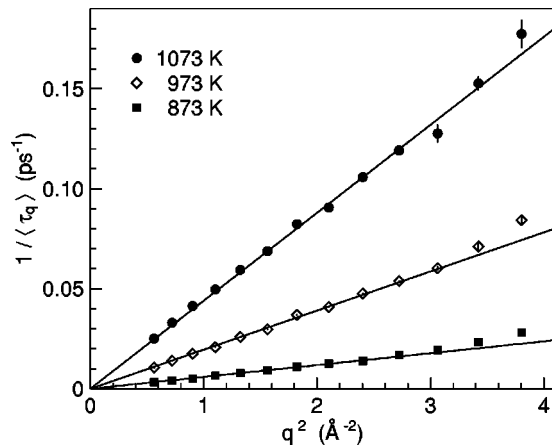


FIG. 6. Mean relaxation times  $\langle \tau_q \rangle$  of tagged particle motion in liquid Pd<sub>43</sub>Ni<sub>10</sub>Cu<sub>27</sub>P<sub>20</sub>.  $1/\langle \tau_q \rangle$  shows a  $q^2$  dependence as expected for long range atomic transport for  $q \rightarrow 0$ . The slope corresponds to the self diffusion coefficient  $D(T)$ .

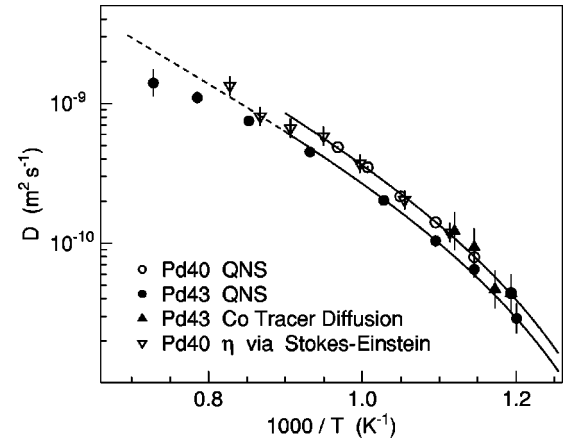


FIG. 7. Self-diffusion coefficient  $D$  of Ni and Cu in liquid Pd<sub>43</sub>Ni<sub>10</sub>Cu<sub>27</sub>P<sub>20</sub> (closed circles) and Pd<sub>40</sub>Ni<sub>10</sub>Cu<sub>30</sub>P<sub>20</sub> (open circles from Ref. 23) derived from the mean relaxation times. The lines are fits with MCT  $\tau$  scaling [Eq. (6)]. The data are well described with  $T_c = 700 \pm 30$  and  $\gamma = 2.7 \pm 0.2$ . For comparison <sup>57</sup>Co tracer diffusion in Pd<sub>43</sub>Ni<sub>10</sub>Cu<sub>27</sub>P<sub>20</sub> (Ref. 25) and diffusivities calculated from viscosity  $\eta$  of liquid Pd<sub>40</sub>Ni<sub>10</sub>Cu<sub>30</sub>P<sub>20</sub> (Ref. 21) via the Stokes-Einstein relation [Eq. (10)] are shown.

extending even above the first structure factor maximum.<sup>13</sup> We note that mixing of hard spheres with different radii should enforce this behavior even more. It appears that the validity of  $1/\langle \tau_q \rangle \propto q^2$  also for intermediate  $q$  values is a signature of the atomic transport mechanism in dense liquids.

The  $1/q^2$  dependence of the mean relaxation times, also demonstrates that structural relaxation leads to long range atomic transport with a diffusivity<sup>27</sup>

$$D = (\langle \tau_q \rangle q^2)^{-1}. \quad (9)$$

Figure 7 displays the diffusivities  $D$  in liquid Pd<sub>43</sub>Ni<sub>10</sub>Cu<sub>27</sub>P<sub>20</sub> as a function of  $1/T$ . Values range from  $3 \pm 1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$  at 833 K to  $1.4 \pm 0.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  at 1373 K. At the liquidus diffusion is about 2 orders of magnitude slower as compared to simple metallic liquids and most alloys. Diffusivities in liquid Pd40 show a similar temperature dependence but are larger by some 20%. A smaller mobility of the atoms appears to come along with the slightly better glass forming ability of the Pd43 alloy.

The lines in Fig. 7 represent fits with the MCT  $\tau$  scaling law [Eq. (6)] to the diffusivities  $D(T)$ . Although Eq. (6) is only valid close to  $T_c$ , Eq. (6) allows a rough estimate of the crossover temperature  $T_c$  and the exponent  $\gamma$ . A fit to  $D(T)$  of liquid Pd43 at temperatures up to 1073 K yields a  $T_c = 700 \pm 30$  K and a  $\gamma = 2.7 \pm 0.2$ . The exponent  $\gamma$  compares well to the  $\gamma = 2.62$  found in the MCT hard-sphere system.<sup>13</sup> The temperature dependence of the diffusivity in liquid Pd-Ni-Cu-P alloys is different from the  $D \propto T^n$  behavior (with  $n \approx 2$ ) expected for uncorrelated binary collisions of hard spheres<sup>4,38</sup> and found with inelastic neutron scattering in expanded liquid alkali metals at high temperature.<sup>39</sup>

Convection effects are a severe problem in macroscopic diffusion measurements in ordinary liquids under gravity conditions with respect to the absolute value of the self-diffusivity  $D$  and its temperature dependence. A microgravity

experiment on liquid Sn showed that well above the melting point convection even dominates the mass transport.<sup>40</sup> The microgravity data in liquid Sn obey  $D \propto T^2$  for temperatures between  $T_m$  and  $2T_m$ . Liquid Sn exhibits a packing fraction of  $\approx 0.4$  as in liquid alkali metals. Inelastic neutron scattering data are not affected by convection because it probes dynamics on significantly shorter times.

Diffusivities from recent  $^{57}\text{Co}$  tracer diffusion measurements<sup>25</sup> in liquid Pd43 are in excellent agreement with the diffusivities obtained from inelastic neutron scattering (Fig. 7). This indicates that the mobility of Co is very similar to the Ni and Cu mobility observed in the incoherent neutron scattering signal and that convection effects play no significant role in the tracer diffusion experiment. The latter is in accordance with a viscosity  $\eta$  that is two orders of magnitude larger as compared to simple metallic melts.<sup>21</sup>

In simple liquids shear viscosity  $\eta$  and the self-diffusivity  $D$  generally obey the Stokes-Einstein relation<sup>3,4,38</sup>

$$D = k_b T / (6\pi a \eta), \quad (10)$$

with reasonable values for the hydrodynamic radius  $a$ . Equation (10) even holds in most molecular liquids.<sup>41</sup> Figure 7 shows the diffusivity  $D_\eta$  calculated from the viscosity data of liquid Pd40 (Ref. 21) via Eq. (10) using  $a = 1.15 \text{ \AA}$ , which represents the Ni hard-sphere radius (Cu:  $1.17 \text{ \AA}$ ) from Ref. 1. The Stokes-Einstein relation holds with  $D_\eta = D$ . We note that  $a$  is similar to the mean next-nearest-neighbor distance displayed in the static structure factor  $d = 2\pi/q_0 \approx 1.1 \text{ \AA}$ . In multicomponent liquids that exhibit a dense packing of hard spheres with comparable hard sphere radii one expects a similar mobility of the different components. In Pd-Ni-Cu-P the hard-sphere radii of the different atoms have values within 20%. Because viscous flow represents the dynamics of all components, the validity of Eq. (10) in liquid Pd-Ni-Cu-P demonstrates that above  $T_{\text{liq}}$  the mobility of the large and numerous Pd atoms is quite similar to the Ni and Cu atoms.<sup>42</sup>

In colloidal suspensions the mean relaxation times  $\langle \tau(\varphi) \rangle$  and the inverse of the diffusivity  $1/D(\varphi)$  show the same dependence as a function of the packing fraction. The slope for  $\langle \tau(\varphi) \rangle$  and  $1/D(\varphi)$  results in a  $\gamma = 2.7$ .<sup>43</sup> In molecular dynamics simulations<sup>7</sup> on NiP, in contrast, the asymptotic MCT  $\tau$  scaling prediction [Eq. (6)] is violated:  $\langle \tau(T) \rangle$  and  $1/D(T)$  do not exhibit the same temperature dependence. Figures 7 and 10 demonstrate that in liquid PdNiCuP Eq. (6) holds quite well.

#### D. Fast $\beta$ relaxation

Within the mode-coupling theory of the liquid to glass transition, structural relaxation and therefore long range mass transport is preceded by a fast  $\beta$ -relaxation process whose time scale is typically in the order of a picosecond. For  $q$  values well below the structure factor maximum and incoherent scattering the amplitude of the  $\beta$  relaxation is increasing with increasing  $q$ . Figure 8 displays the density correlation function of liquid Pd-Ni-Cu-P at  $q = 1.95 \text{ \AA}^{-1}$ . Between 0 and  $\approx 0.2$  ps phonons lead to a rapid decay of atomic correlations [represented by the first data point in

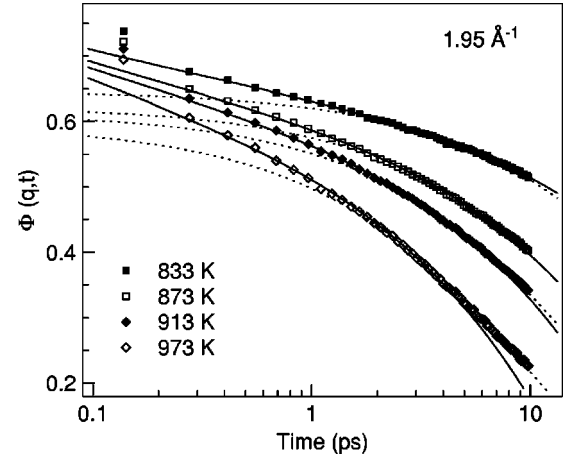


FIG. 8. Normalized time correlation function  $\Phi(q,t)$  of liquid Pd<sub>43</sub>Ni<sub>10</sub>Cu<sub>27</sub>P<sub>20</sub> in the  $\beta$  relaxation regime around 1 ps. The solid lines represent fits with the MCT  $\beta$  scaling function [Eq. (7)] giving a temperature and  $q$ -independent shape parameter  $\lambda = 0.78 \pm 0.04$ . Above  $\approx 1$  ps data are well described by a stretched exponential function [Eq. (4), dashed lines].

$\Phi(q,t)$  in Fig. 8], so that  $\Phi(q,t)$  decreases from 1 towards a plateau. On approaching this plateau a fast relaxation is clearly seen in  $\Phi(q,t)$  through an additional intensity below some 1 ps. The lines are fits with the MCT  $\beta$  scaling law [Eq. (7)]. For  $q < 1.4 \text{ \AA}^{-1}$  the limited dynamic range of the instrument prevents data analysis in the fast  $\beta$  relaxation regime. Above 973 K  $\Phi(q,t)$  cannot consistently be described with the asymptotic scaling laws [Eqs. (7) and (8)]. The dynamic range in which Eq. (7) holds increases with decreasing temperature.

The data were fitted in a two-step procedure: starting with an arbitrary line shape parameter  $\lambda$ , fits to individual curves were used to estimate the scaling factors  $f_q$ ,  $h_q$ , and  $t_\sigma$ , which physically represent the Debye-Waller factor, the amplitude of  $\beta$  relaxation, and a characteristic time of  $\beta$  relaxation. Using these values, the  $\Phi(q,t)$  measured at different temperatures were superimposed onto master curves  $[\Phi(q,t/t_\sigma) - f_q]/h_q$ . After fixing a  $q$ -independent mean  $t_\sigma$ , the fit yielded a temperature- and  $q$ -independent  $\lambda = 0.78 \pm 0.04$ .

This result compares well to the hard-sphere value  $\lambda = 0.766$  of the numerical MCT solution,<sup>13</sup> to the  $\lambda = 0.77 \pm 0.04$  found in liquid Zr<sub>46.8</sub>Ti<sub>8.2</sub>Cu<sub>7.5</sub>Ni<sub>10</sub>Be<sub>27.5</sub> (Ref. 22) and it is similar to the values in other viscous liquids.<sup>11,33</sup>  $\lambda = 0.78$  defines an exponent of the  $\tau$  scaling law [Eq. (6)] of  $\gamma = 2.7$ .<sup>28</sup> This is consistent with the temperature dependence of the mean relaxation times that give  $\gamma = 2.7 \pm 0.2$  (Fig. 7).

Figure 9 shows amplitude  $h_q$  and time scale  $t_\sigma$  of the fast  $\beta$  relaxation in liquid Pd-Ni-Cu-P rectified according to Eq. (8). The temperature dependence of  $h_q$  and  $t_\sigma$  is in accordance with the MCT predictions. Both  $h_q$  and  $t_\sigma$  extrapolate to  $T_c = 720 \pm 20$  K, which is close to the  $T_c = 700 \pm 30$  K obtained via the  $\tau$  scaling law [Eq. (6)]. The relaxational dynamics in liquid Pd<sub>43</sub>Ni<sub>10</sub>Cu<sub>27</sub>P<sub>20</sub> can consistently be described with the universal scaling functions of the mode-

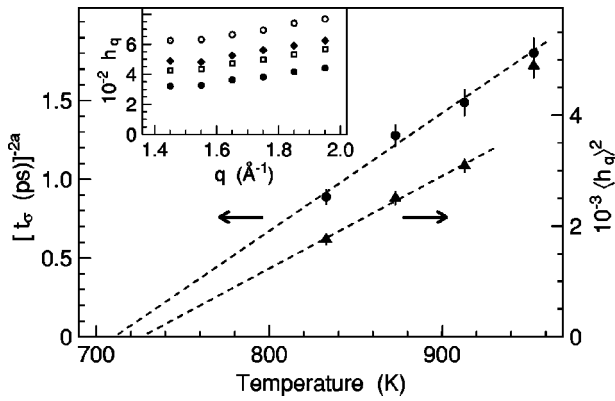


FIG. 9. Mean amplitude  $\langle h_q \rangle$  (triangles) and time scale  $t_\sigma$  (circles) of fast  $\beta$  relaxation in liquid Pd<sub>43</sub>Ni<sub>10</sub>Cu<sub>27</sub>P<sub>20</sub> rectified according the MCT predictions [Eq. (8)], with an exponent  $a=0.29$  defined by  $\lambda=0.78$ . The inset shows the  $q$  dependence of the amplitude  $h_q$  between 833 K (●) and 953 K (○). Both  $h_q$  and  $t_\sigma$  extrapolate to  $T_c=720\pm 20$  K.  $\lambda$  and  $T_c$  obtained from the analysis of the  $\beta$  relaxation regime are consistent with  $T_c=700\pm 30$  K and  $\gamma=2.7\pm 0.2$  from the analysis of the mean  $\alpha$  relaxation times [Eq. (6)].

coupling theory of the liquid to glass transition at temperatures up to  $\approx 1.3T_c$  with  $T_c=710$  K and  $\lambda=0.78$ .

### E. Atomic transport mechanism

Pd<sub>43</sub>Ni<sub>10</sub>Cu<sub>27</sub>P<sub>20</sub> exhibits an excellent glass-forming ability: a cooling rate of only 0.09 K/s is sufficient to avoid crystallization and to form a glass.<sup>24</sup> Consequently transport coefficients can continuously be measured from the equilibrium liquid down to the conventional glass transition temperature  $T_g$ . Figure 10 displays diffusivities in viscous Pd-Ni-Cu-P alloys from tracer diffusion measurements, that cover more than 13 decades,<sup>25,44</sup> derived from the mean relaxation times and from viscosity<sup>19,21</sup> calculated via Stokes-Einstein [Eq. (10)].

At 1373 K the diffusivity in liquid Pd-Ni-Cu-P is  $1.4 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ , which is similar to diffusivities known from monoatomic liquid metals at their respective melting temperature. For example, close to the melting point inelastic neutron scattering reveals  $D=4.2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  in liquid sodium<sup>5</sup> and tracer diffusion under microgravity conditions  $D=2.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  in liquid tin.<sup>40</sup> At high temperatures the Stokes-Einstein relation holds (Fig. 7). On lowering the temperature diffusion slows down drastically. Time scales for viscous flow and Co tracer diffusion start to decouple in the vicinity of the mode coupling  $T_c \approx 710$  K and differ already by more than 3 orders of magnitude at 600 K. Also around  $T_c$  Co tracer diffusivities merge into an Arrhenius-type temperature dependence [ $D(T)=D_0 \exp(-H/k_B T)$ , where  $D_0$  is a prefactor and  $H$  the activation enthalpy] that extends down to the glass transition.<sup>25,44</sup>

The temperature dependence of the transport coefficients in Fig. 10 strongly supports the MCT prediction of a change in the atomic transport mechanism from viscous flow to glasslike hopping at  $T_c$ . There are extensive tracer diffusion measurements in supercooled Zr<sub>46.8</sub>Ti<sub>8.2</sub>Cu<sub>7.5</sub>Ni<sub>10</sub>Be<sub>27.5</sub> at

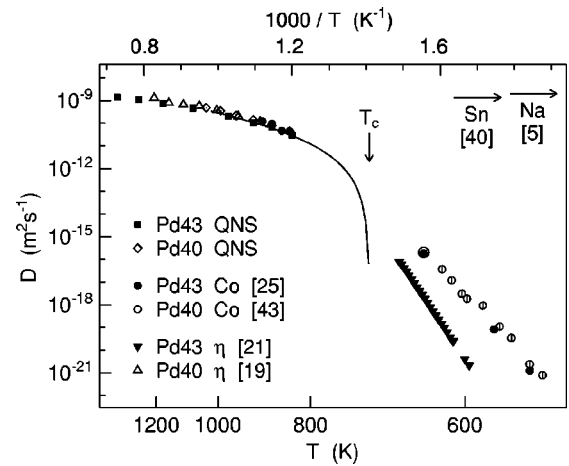


FIG. 10. Mass transport in Pd-Ni-Cu-P melts: At high temperatures diffusivities are similar to diffusivities in liquid Sn and Na close to  $T_m$  (marked by the arrows). Time scales for viscous flow and Co tracer diffusion start to decouple and Co tracer diffusivities merge into an Arrhenius-type temperature dependence that extends down to the glass transition. Both occurs in the vicinity of mode coupling  $T_c$ . The line represents the MCT  $\tau$  scaling law with  $T_c=710$  K and  $\gamma=2.7$ .

temperatures between the glass transition and about 200 K below  $T_c$ .<sup>45</sup> The diffusivities of various tracers exhibit a size dependence: the smaller the atoms the faster they diffuse and the smaller the activation enthalpy  $H$ . In viscous Zr<sub>46.8</sub>Ti<sub>8.2</sub>Cu<sub>7.5</sub>Ni<sub>10</sub>Be<sub>27.5</sub> the diffusivities of the various atoms approach each other with increasing temperature. Because in this alloy crystallization prevents access to the temperature range around  $T_c$ , one cannot conclude from the present data whether the diffusivities of the various tracers merge at the MCT  $T_c$ .

The isotope effect  $E=(D_a/D_b-1)/(\sqrt{m_b/m_a}-1)$  (diffusivity  $D$  and mass  $m$  of two isotopes  $a, b$ ) is a measure of the degree of collectivity of the atomic transport. For diffusion via single jumps in dense packed lattices  $E$  is generally in the order of unity.<sup>46</sup> For uncorrelated binary collisions one also expects  $E \rightarrow 1$ . A vanishing isotope effect indicates a collective transport mechanism involving a large number of atoms. In liquid Sn an isotope effect of about 0.4 has been reported, that is increasing with increasing temperature.<sup>40</sup> MD simulations on a binary Lennard-Jones liquid demonstrate that changes in the density in the order of 20% only result in a continuous increase in  $E$  from 0 to  $\approx 0.3$ .<sup>47</sup> In metallic glasses<sup>48</sup> as well as in supercooled Zr<sub>46.8</sub>Ti<sub>8.2</sub>Cu<sub>7.5</sub>Ni<sub>10</sub>Be<sub>27.5</sub> (Ref. 49) and Pd<sub>40</sub>Ni<sub>10</sub>Cu<sub>30</sub>P<sub>20</sub> (Ref. 44) the isotope effect is close to zero as a result of a highly collective, thermally activated hopping process. Measurements of the isotope effect in Pd<sub>43</sub>Ni<sub>10</sub>Cu<sub>27</sub>P<sub>20</sub> (Ref. 25) give  $E \approx 0.05$  in the entire temperature range from the glass transition to the equilibrium liquid.

The atomic transport mechanism in dense Pd-Ni-Cu-P remains highly collective even in the equilibrium liquid in contrast to the findings in simple metallic liquids. Viscous Pd-Ni-Cu-P exhibits an expansion coefficient of  $4 \times 10^{-5} \text{ K}^{-1}$ .<sup>19</sup> Between 1373 K and 833 K, the density and therefore, assuming a temperature independent hard-

sphere radius, the packing fraction changes only by about 2%. This small increase in the packing fraction causes a drastic slowing down of dynamics on temperature decrease. On the other side, dense packing and the resulting collective transport mechanism extend also to high temperatures, where diffusivities are similar to simple metallic liquids. This indicates that the atomic transport mechanism in liquids is not controlled by the value of the transport coefficients but rather by that of the packing fraction.

## V. CONCLUSIONS

Atomic transport in liquid Pd<sub>43</sub>Ni<sub>10</sub>Cu<sub>27</sub>P<sub>20</sub> has been investigated with inelastic, incoherent neutron scattering. The Pd-Ni-Cu-P melt is characterized by a packing fraction of about 0.52 that is some 20% larger as compared to monatomic alkali-metal melts. The self-correlation function shows a two-step decay as known from other nonmetallic glass-forming liquids: a fast relaxation process precedes structural relaxation. The structural relaxation exhibits stretching with a stretching exponent  $\beta \approx 0.75$  and a time-temperature superposition that holds for temperatures as high as  $2T_c$ . The relaxational dynamics can consistently be described within the framework of the mode-coupling theory of the liquid to glass transition with a temperature- and  $q$ -independent line shape parameter  $\lambda \approx 0.78$ . Universal MCT scaling laws extrapolate to a critical temperature  $T_c \approx 710$  K some 20% below the liquidus.

Diffusivities derived from the mean relaxation times com-

pare well with Co diffusivities from tracer diffusion measurements. Above  $T_c$  diffusivities calculated from viscosity<sup>21</sup> via the Stokes-Einstein relation are in excellent agreement with the diffusivities measured by tracer diffusion<sup>25</sup> and neutron scattering. In contrast to simple metallic liquids the atomic transport in dense liquid Pd-Ni-Cu-P is characterized by a drastic slowing down of dynamics on approaching  $T_c$  and a  $q^{-2}$  dependence of the mean relaxation times at intermediate  $q$  as a result of a highly collective transport mechanism in the dense packed liquid. At temperatures as high as  $2T_c$  diffusion in liquid Pd-Ni-Cu-P is as fast as in simple monatomic liquids at their melting points. However, the difference in the underlying atomic transport mechanism indicates that the diffusion mechanism in liquids is not controlled by the value of the diffusivity but rather by that of the packing fraction.

## ACKNOWLEDGMENTS

It is a pleasure to thank Winfried Petry and Helmut Schober for their support, Wolfgang Götze, Walter Schirmacher, and Walter Kob for a critical reading of the manuscript, Joachim Wuttke for his ingenious data analysis program, the Institut Laue-Langevin for the beamtime on IN 6, Stephan Roth for his help during the measurement and Helga Harlandt for her help with the sample preparation. This work is funded by the German DFG (SPP Phasenumwandlungen in mehrkomponentigen Schmelzen) under Project No. Me1958/2-1.

\*Electronic address: ameyer@ph.tum.de

<sup>1</sup>W. Paszkowicz, J. Phys. F: Met. Phys. **18**, 1761 (1988).

<sup>2</sup>P. Protopapas, H. C. Andersen, and N. A. D. Parlee, J. Chem. Phys. **59**, 15 (1973).

<sup>3</sup>U. Balucani and M. Zoppi, *Dynamics of the Liquid State* (Clarendon, Oxford, 1994).

<sup>4</sup>H. J. V. Tyrrell and K. R. Harris, *Diffusion in Liquids* (Butterworths, London, 1984).

<sup>5</sup>C. Morkel and W. Gläser, Phys. Rev. A **33**, 3383 (1986).

<sup>6</sup>W. van Megen and S. M. Underwood, Phys. Rev. Lett. **70**, 2766 (1993); S. R. Williams and W. van Megen, Phys. Rev. E **64**, 041502 (2001).

<sup>7</sup>W. Kob and H. C. Andersen, Phys. Rev. Lett. **73**, 1376 (1994).

<sup>8</sup>H. Teichler, Phys. Rev. Lett. **76**, 62 (1996); A. B. Mutiara and H. Teichler, Phys. Rev. E **64**, 046133 (2001).

<sup>9</sup>J. Wong and C. A. Angell, *Glass Structure by Spectroscopy* (Decker, New York, 1976).

<sup>10</sup>H. Z. Cummins, G. Li, Y. H. Hwang, G. Q. Shen, W. M. Du, J. Hernandez, and N. J. Tao, Z. Phys. B: Condens. Matter **103**, 501 (1997).

<sup>11</sup>W. Götze, J. Phys.: Condens. Matter **11**, A1 (1999).

<sup>12</sup>W. Götze and L. Sjögren, Rep. Prog. Phys. **55**, 241 (1992).

<sup>13</sup>M. Fuchs, I. Hofacker, and A. Latz, Phys. Rev. A **45**, 898 (1992).

<sup>14</sup>A. Peker and W. L. Johnson, Appl. Phys. Lett. **63**, 2342 (1993).

<sup>15</sup>A. Inoue, N. Nishiyama, and H. Kimura, Mater. Trans., JIM **38**, 179 (1997).

<sup>16</sup>I.-R. Lu, G. Wilde, G. P. Görlner, and R. Willnecker, J. Non-Cryst. Solids **250-252**, 577 (1999).

<sup>17</sup>N. Nishiyama and A. Inoue, Appl. Phys. Lett. **80**, 568 (2002).

<sup>18</sup>K. Ohsaka, S. K. Chung, W. K. Rhim, A. Peker, D. Scruggs, and W. L. Johnson, Appl. Phys. Lett. **70**, 726 (1997).

<sup>19</sup>I.-R. Lu, G. P. Görlner, H. J. Fecht, and R. Willnecker, J. Non-Cryst. Solids (to be published).

<sup>20</sup>A. Masuhr, T. A. Waniuk, R. Busch, and W. L. Johnson, Phys. Rev. Lett. **82**, 2290 (1999).

<sup>21</sup>P. H. Haumesser, J. P. Garandet, J. Bancillon, M. Daniel, I. Campbell, and P. Jackson, Int. J. Thermophys. **23**, 1217 (2002).

<sup>22</sup>A. Meyer, J. Wuttke, W. Petry, O. G. Randl, and H. Schober, Phys. Rev. Lett. **80**, 4454 (1998).

<sup>23</sup>A. Meyer, R. Busch, and H. Schober, Phys. Rev. Lett. **83**, 5027 (1999).

<sup>24</sup>J. Schroers, W. L. Johnson, and R. Busch, Appl. Phys. Lett. **77**, 1158 (2000).

<sup>25</sup>V. Zöllmer, A. Meyer, K. Rätzke, and F. Faupel (unpublished); V. Zöllmer, thesis, Universität Kiel, 2002.

<sup>26</sup>J. Wuttke, Phys. Rev. E **62**, 6531 (2000).

<sup>27</sup>J. P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, New York, 1980).

<sup>28</sup>W. Götze, J. Phys.: Condens. Matter **2**, 8455 (1990).

<sup>29</sup>A. Meyer, H. Schober, and J. Neuhaus, Phys. Rev. B **63**, 212202 (2001).

<sup>30</sup>G. Wahnström and L. Sjögren, J. Phys. C **15**, 401 (1982).

<sup>31</sup>C. Morkel, C. Gronemeyer, W. Gläser, and J. Bosse, Phys. Rev. Lett. **58**, 1873 (1987).

<sup>32</sup>J. Wuttke, W. Petry, G. Coddens, and F. Fujara, Phys. Rev. E **52**, 4026 (1995).



- <sup>33</sup>A. Tölle, Rep. Prog. Phys. **64**, 1473 (2001).
- <sup>34</sup>J. Wuttke, M. Kiebel, E. Bartsch, F. Fujara, W. Petry, and H. Sillescu, Z. Phys. B: Condens. Matter **91**, 357 (1993).
- <sup>35</sup>R. Böhmer, K. L. Ngai, C. A. Angell, and D. P. Plazek, J. Chem. Phys. **99**, 4201 (1993).
- <sup>36</sup>J. Wuttke, I. Chang, O. G. Randl, F. Fujara, and W. Petry, Phys. Rev. E **54**, 5364 (1996).
- <sup>37</sup>A. Meyer, H. Schober, and D. B. Dingwell, Europhys. Lett. **59**, 708 (2002).
- <sup>38</sup>J. S. Kirkaldy and D. Y. Young, *Diffusion in the Condensed State* (The Institute of Metals, London, 1987).
- <sup>39</sup>R. Winter, C. Pilgrim, F. Hensel, C. Morkel, and W. Gläser, J. Non-Cryst. Solids **156-158**, 9 (1993).
- <sup>40</sup>G. Froberg, K.-H. Kraatz, and H. Wever, Mater. Sci. Forum **15-18**, 529 (1987).
- <sup>41</sup>I. Chang and H. Sillescu, J. Phys. Chem. B **101**, 8794 (1997).
- <sup>42</sup>In liquid  $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$  the Stokes-Einstein relation fails to express Ni diffusivity in terms of shear viscosity. It appears, that even far above  $T_c$  the smaller atoms move in a relative immobile Zr matrix.
- <sup>43</sup>W. van Meegen, T. C. Mortensen, J. Müller, and S. R. Williams, Phys. Rev. E **58**, 6073 (1998).
- <sup>44</sup>V. Zöllmer, K. Rätzke, F. Faupel, A. Rehmert, and U. Geyer, Phys. Rev. B **65**, 220201 (2002).
- <sup>45</sup>F. Faupel, W. Franck, M.-P. Macht, H. Mehrer, V. Naundorf, K. Rätzke, H. R. Schober, S. K. Sharma, and H. Teichler, Rev. Mod. Phys. (to be published); A. Rehmert, K. Rätzke, F. Faupel, P. D. Eversheim, K. Freitag, U. Geyer, and S. Schneider, Appl. Phys. Lett. **79**, 2892 (2001) and references therein.
- <sup>46</sup>H. Mehrer, *Landolt-Börnstein New Series III* (Springer, Berlin, 1990), Vol. 26.
- <sup>47</sup>H. R. Schober, Solid State Commun. **119**, 73 (2001).
- <sup>48</sup>F. Faupel, H. Hüppe, and K. Rätzke, Phys. Rev. Lett. **65**, 1219 (1990).
- <sup>49</sup>H. Ehmler, A. Heesemann, K. Rätzke, and F. Faupel, Phys. Rev. Lett. **80**, 4919 (1998).