Pair distribution function and its relation to the glass transition in an amorphous alloy

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Data for the pair distribution function $g(r)$ are presented as a function of temperature for amorphous $Nb_{0.4}Ni_{0.6}$. We show, based on a simple model, that $g(r)$ varies linearly with T over a wide temperature range in the glass as was found empirically by Wendt and Abraham. We also find that in our glass the behavior of $g(r)$ near the glass transition is, within experimental error, similar to what they found in their Monte Carlo calculation. We interpret the deviation from linearity at the glass transition as due to the onset of diffusive motion of the atoms.

In a recent paper,[1] Wendt and Abraham proposed a new empirical criterion for determining the liquid to glass transition. They calculated, using Monte Carlo methods, the pair distribution function $g(r)$ for a Lennard-Jones fluid in the super-cooled regime and introduced a new parameter $R = g_{min}/g_{max}$, where g_{min} and g_{max} are the values of $g(r)$ at its first minimum and first maximum, respectively. By plotting R as a function of T and/or P they found that over a large portion of the liquid state R was linear in both T and P and similarly that over a large portion of the glassy state R was again linear but with a different slope from that found in the liquid. The linear extrapolations of the liquid and glassy branches of $R(T, P)$ intersect at a value of $R \cong 0.14$. This value of R, where the liquid and glassy branches intersect, was independent of which variable, T or P, was varied. The authors proposed that this value of R, $R_a = 0.14$, was a criterion for the onset of the glassy state by quenching and/or compressing the liquid. Subsequently, Stillinger and Weber[2] have found similar behavior in a Gaussian core model.

In this paper, we present experimental data on $g(r)$ as a function of temperature for an amorphous metal, $Nb_{0.4}Ni_{0.6}$, below the glass transition. In this glass we find that R is an approximately linear function of T over a wide temperature range. It will be shown that this behavior in the glass is not dependent on the particular interatomic force law assumed but is a general consequence of the fact that in the glass each atom vibrates around an equilibrium position and that the self-diffusion constant is very low. We also find that the slope of R versus reduced temperature ($T_r \equiv T/T_M$ where T_M is the melting temperature) determined from our data is close to that found by Wendt and Abraham in their calculation of R vs $T*$.

We have reported elsewhere[3] the temperature dependence of the x-ray structure factor for this

$Nb_{0.4}Ni_{0.6}$ sample. In that study it was found that the experimental data were in excellent agreement with the theoretical prediction[4]:

$$S_T(k) = 1 + [S_0(k) - 1]e^{-2[W(T)-W(0)]} . \qquad (1)$$

Here $S_T(k)$ is the structure factor at temperature T and wave vector k and $e^{-2W(T)}$ is the Debye-Waller factor at temperature T. This prediction is based on a very simple model for the glass in which each atom was allowed to vibrate about its equilibrium position and no atomic diffusion was permitted.[4] The only adjustable parameter in this model is the Debye temperature that enters into $W(T)$:

$$\Delta W(T) \equiv W(T) - W(0) = \frac{3\hbar^2 k^2}{2Mk_B\Theta}\left(\frac{T}{\Theta}\right)^2 \int_0^{\Theta/T} \frac{z\,dz}{e^z - 1} . \qquad (2)$$

At high temperatures $\Delta W(T)$ is linearly proportional to T and even for temperatures only slightly larger than the Debye temperature Θ, the deviations from linearity are quite small.

From the data on $S_T(k)$ one can derive the pair distribution function, $g_T(r)$:

$$g_T(r) = 1 + \frac{1}{2\pi^2 r \rho_0} \int_0^{\infty} k\,dk\,[S_T(k) - 1]\sin\vec{k}\cdot\vec{r} . \qquad (3)$$

Here ρ_0 is the density of the sample which we have measured to be 8.72 ± 0.08 g/cm^3 in the case of the $Nb_{0.4}Ni_{0.6}$ glassy alloy. The experimentally determined $S(k)$ and the corresponding $g(r)$ are shown in Fig. 1 for the $Nb_{0.4}Ni_{0.6}$ glass at room temperature. A damping factor multiplying $[S(k) - 1]$, $e^{-k^2/150}$ (where k is in Å^{-1}), was used in order to counteract the effects of the finite cutoff of the integral in Eq. (3).

One can easily solve for the temperature dependence of $g(r)$ by substituting $S_T(k)$ from Eqs. (1) and (2) into Eq. (3). At temperatures greater than Θ, one obtains
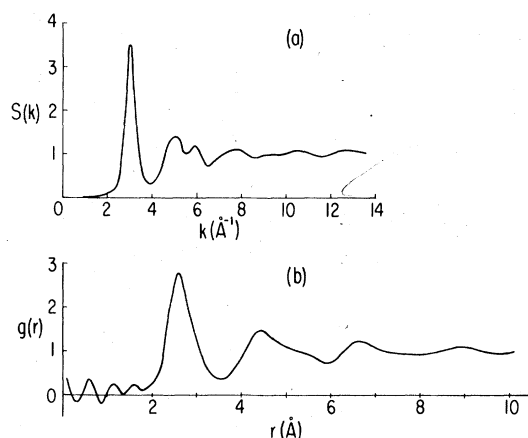
FIG. 1. (a) Room-temperature structure factor of amorphous $Nb_{0.4}$ $Ni_{0.6}$ determined from x-ray diffraction. (b) The room-temperature pair distribution function of the amorphous $Nb_{0.4}$ $Ni_{0.6}$ sample determined from the structure factor data using Eq. (3) in the text. The oscillations of low values of r are due to a finite cutoff of the integral in that equation.

FIG. 2. Ratio R for amorphous $Nb_{0.4}$ $Ni_{0.6}$, as a function of reduced temperature, $T_r = T/T_M$, where the melting temperature T_M is 1443 K for this alloy.[5] Note that for $T_r > 0.1$, R varies approximately linearly with T_r. The dashed line is the extrapolation of R to temperatures higher than that where the sample started to crystallize.

$$g_T(r) \cong g_0(r) - T \frac{3\hbar^2}{M k_B \Theta^2} \frac{1}{2\pi^2 \rho_0 r}$$

$$\times \int_0^\infty dk \, [S_0(k) - 1] k^3 \sin \vec{k} \cdot \vec{r}$$

$$\cong g_0(r) - Tf(r) . \tag{4}$$

This demonstrates why $g_T(r)$ should have a linear temperature dependence. Also, since $f(r)$ is closely related to $[g_0(r) - 1]$ we can see that $f(r)$ will be positive when $g_0(r)$ has a maximum and it will be negative when $g_0(r)$ has a minimum. Thus a peak in $g_0(r)$ will decrease linearly and a minimum will increase linearly with temperature. Therefore R will increase linearly with temperature in the glassy state just as was found empirically by Wendt and Abraham.[1] Also this derivation shows that it is a general phenomenon and is not dependent on the particular interatomic potential. This result also makes it possible to interpret the deviation from linearity at the glass transition that was found in their Monte Carlo study. As long as the atoms are only allowed to vibrate around their equilibrium positions our calculation predicts a linear temperature dependence for R. A deviation from linearity implies, therefore, that the atoms are not all confined to their initial positions but are able to diffuse throughout the system. At higher temperatures, where diffusion is dominant, there may also be a linear variation of R. The transition defined by the change in slope of R, therefore, indicates the onset of diffusive motion in the glass.
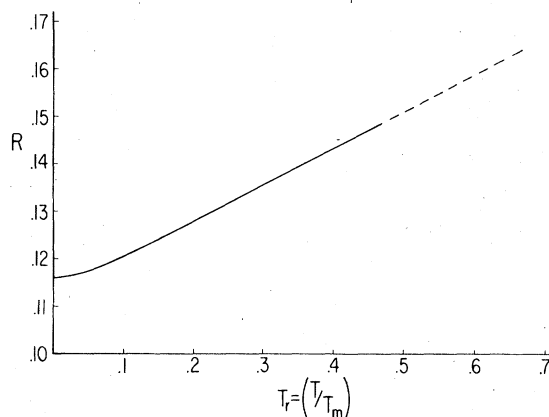
In Ref. 3 we reported the temperature depen-

dence of $S(k)$ and found excellent agreement with Eq. (1) for the variation of both temperature and wavevector. The value of the Debye temperature which was found was $\Theta = 370$ K. We can therefore compute numerically $g(r)$ and the value of R at the different temperatures spanned by our data. In Fig. 2, we show the results for R vs T_r ($T_m = 1443$ K for this alloy[5]). As we showed earlier, at high temperatures R increases linearly with T. At low temperatures, $T < \Theta$, R has a quadratic variation with temperature. The slope of the linear section of this curve is 0.09 ± 0.02. This is to be compared with the value of the slope obtained from the Monte Carlo calculation which is 0.12.

The absolute value of R at the temperature where the sample begins to crystallize is 0.15 ± 0.04. The estimated error on this number is large since significant errors are introduced into the pair distribution function when the Fourier transform of $S(k)$ is taken. The cutoff in the data of $S(k)$ at finite wave vector is the major source of these errors. However, this $Nb_{0.4}Ni_{0.6}$ sample, which has a close packed structure,[3] does seem to behave in a qualitatively similar manner to the Lennard-Jones glass studied by Wendt and Abraham.

In conclusion we have given experimental evidence that the ratio $R = g_{min}/g_{max}$ varies linearly over a large temperature range in a glass. We have also shown that this is to be expected generally in an amorphous close-packed solid where atoms are constrained to move in small vibrations around their equilibrium positions. The slope of our curve of R vs T_r, as well as the absolute value of R, is of comparable magnitude to that found from Wendt and Abraham's Monte Carlo calculation.

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[5]F. A. Shunk, *Constitution of Binary Alloys*, 2nd Suppl. (McGraw-Hill, New York, 1969), p. 192.