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Strings and interstitials in liquids, glasses and crystals

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Abstract. – Recent work has shown that atom motion in liquids is not completely homogeneous, but that stringlike cooperative motion can be used to explain several properties of liquids. We now show that with increasing concentration the properties of interstitial atoms in crystalline materials smoothly approach and eventually completely match the properties of the string atoms in liquids. In terms of the interstitialcy theory of liquids and solids, the strings are direct manifestations of interstitials.

Introduction. – The structure and dynamics of liquids and amorphous solids are among the oldest and most important outstanding questions in condensed-matter physics. In the past several years, new findings have emerged from molecular-dynamics computer simulations concerning heterogeneities in the dynamics of supercooled liquids. These simulations have shown that small groups of atoms move cooperatively, in string-like fashion, while neighboring atoms are relatively unaffected [1–6]. The special interest in these strings derives from the potential they offer in connecting directly to existing theories and observations, such as the collective motion described by the mode-coupling theory [7], the cooperatively rearranging regions of Adam-Gibbs [8], and the dynamics of interstitial atoms in the interstitialcy theory [9]. We will show here that the properties of strings provide strong support for the interstitialcy theory of liquids.

The two key features of the interstitialcy theory are a reduction in the formation energy E^f of an interstitial with increasing concentration c_i and a large entropy per interstitial. These features lead to a multi-valued equilibrium concentration, corresponding to the crystalline and liquid states. The large entropy per interstitial is a physical property arising from the string-like structure of the interstitial, as shown previously [10], and the energy softening derives from the decreasing shear modulus with c_i , as is illustrated below. While many properties of liquids and amorphous materials are well described by the interstitialcy theory [9,11] such as the large entropy of liquids and the low-frequency resonance modes and high-frequency local modes in the vibrational density of states in glasses, a fundamental difficulty in the interstitialcy theory has been the identification of the interstitial within the liquid structure. The primary point of the present work is to illustrate that strings provide this link, which we do by showing that the properties of strings in liquids are virtually identical to those of interstitials in crystalline and amorphous solids.

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The techniques for illustrating the strings and their motions were developed by Schober *et al.* [1, 2] and Glotzer *et al.* [3–6], who found the following properties. There are low-frequency resonance modes as well as high-frequency local modes. The length scale is ≈ 2 nm involving 10 or more atoms. The modes have a quasi-one-dimensional character. The atoms are compressed along the string direction, but have an overall volume expansion. During a jump, no atoms move as much as a jump distance, it is the configuration that moves an atomic distance. The characteristic length of the string decreases with increasing temperature and the distribution of lengths is random. The existence of these strings has now been supported by simulations and experiments in a number of different systems [12–15]. These many properties, in fact, prompted Oligschleger and Schober to note that the behavior of strings bears the signature of an interstitialcy defect in crystalline metals [2]. We now show this quantitatively.

Method. – The present work employs the same statistical methods utilized on liquids by Glotzer, to show that interstitials in crystalline metals share many of the same characteristics as the strings. We chose to study Cu since the interstitial properties are well known in this metal [16], and potentials exist that describe well both liquid and crystalline Cu as well as interstitials in Cu [10, 17]. We simulated crystalline, liquid and supercooled liquid Cu at temperatures around the melting point of the potential (1295 K). We used periodic boundary conditions to prevent surface effects, well-established simulation methods to control the temperature and pressure in the cell [18] and the Sabochick-Lam interatomic potential [19], which we have previously demonstrated describes well all the Cu properties of interest here [10]. Simulations at widely different (500–55000 atoms) cell sizes were employed to ensure that our conclusions are not affected by finite-size effects. In the crystals we were able to simulate interstitial concentrations up to 0.03 before the crystal became mechanically unstable.

The basic approach used by Glotzer *et al.* to identify cooperatively moving “string” atoms is to label atoms which have moved farther than a distance r^* within a time t^* . t^* is determined either from the maximum in the non-Gaussian parameter α_2 [3] as a function of time, or the time when the distinct part of the van Hove correlation function for mobile particles G_d^m [3] reaches a maximum at $r = 0$. Both methods give similar values for t^* , which is interpreted as a characteristic time scale for correlated atom motion. When t^* has been obtained, a characteristic length scale r^* of a string is determined either as the distance where the deviation from a purely Gaussian displacement function becomes significant [3], or simply as a distance for which a pre-determined fraction of the atoms (*e.g.* 5%) have moved farther than r^* in a time t^* [5].

In a crystal, we cannot use all of the criteria used in a liquid to obtain t^* and r^* since the diffusion of atoms in a perfect crystal is negligible on short time scales. However, when vacancies or interstitials are present, some migration does occur. Accordingly, we first obtain t^* for a liquid at a given temperature, or detect the maximum at $r = 0$ in the distinct part of the van Hove correlation function for mobile particles, G_d^m , as in ref. [4], for a crystalline cell with interstitials (see fig. 1). Both methods were found to give similar values of t^* .

To obtain a reference value we also determine the maximum displacement of an atom in a perfect crystal with no defects over the time interval t^* , similar to the process used in ref. [5]. The r^* criterion for detecting mobile particles is then selected such that the probability that an atom in a perfect crystal is displaced more than r^* over a time interval of t^* is about 10^{-7} . This value was found to ensure that practically all atoms that are detected as mobile, in cells that contain interstitials, are associated with the defects.

Near the melting temperature, we obtained about the same value for r^* in the solid as the values of r^* determined in the liquid using Glotzer’s approach. Since the criteria in the liquid are somewhat arbitrary [5, 20], this allowed us to use the same value of r^* in simulations where

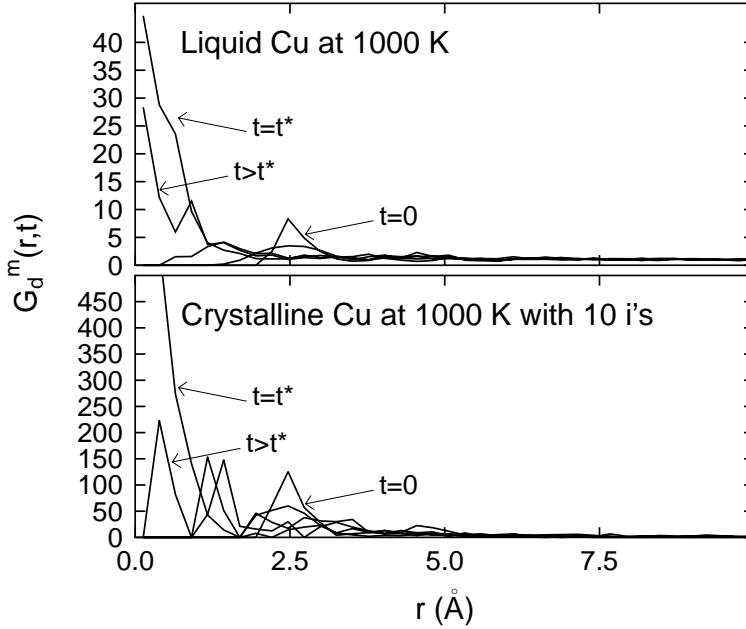


Fig. 1 – Distinct part of the van Hove correlation function $G_d^m(r, t)$ between mobile particles at various t , normalized with the density of mobile particles. Upper part: supercooled liquid Cu at 1000 K (other temperatures show the same effects). Lower part: crystalline Cu cell with 10 interstitials. For $t > t^*$ in the crystal there are peaks in G_d^m because the interstitial atoms are preferentially located in some high-symmetry lattice sites.

we compare the strings in the liquid with interstitials in the solid. In the final simulations ran at $T = T_{\text{melt}}$ we used $t^* = 600$ fs and $r^* = 1.8$ Å.

Results and discussion. – To verify that the strings observed in our liquid Cu indeed behave as those observed in LJ systems by Glotzer *et al.*, we reproduced all of the tests for detecting mobile atoms used in refs. [3–5]. Among the more stringent tests, we calculated the distinct part of the van Hove correlation function G_d . According to Kob *et al.* [3], G_d between mobile particles (G_d^m) should first have a peak at the nearest-neighbour distance, then one at $r = 0$ at $t = t^*$, which then should decrease for $t > t^*$. Figure 1 (upper part) shows that our mobile particles in the liquid behave exactly in this way. The magnitude of G_d^m is similar to that reported in ref. [3] for the mobile particles in the liquid, while it is larger in the solid because the atoms have less degrees of freedom to move, thus making the correlation stronger. We also checked that the correlation function $G_d^{m,i}$ between mobile and immobile particles does not have such a peak at $r = 0$, thus showing that the relative motion between mobile and immobile particles indeed behaves differently [5].

Having shown that liquid Cu contains similar strings as the LJ liquids studied by other groups, we proceeded to test whether interstitials in crystalline Cu share similar characteristics. We first looked at the behavior of isolated interstitials in crystalline Cu. Since they are known to be highly mobile [10, 16] close to the melting point, we tested whether their motion occurs in a similar correlated manner as the string motion. We calculated the distinct part of the van Hove correlation function for mobile particles G_d^m in a cell with 10 isolated interstitials [21]. The behavior observed is exactly the same as for the strings in a liquid: at $t = 0$ G_d^m has a maximum at the nearest-neighbor distance, then at $t = t^*$ a strong maximum at $r = 0$ develops, which then recedes at longer times (see fig. 1 (lower part)). We also checked

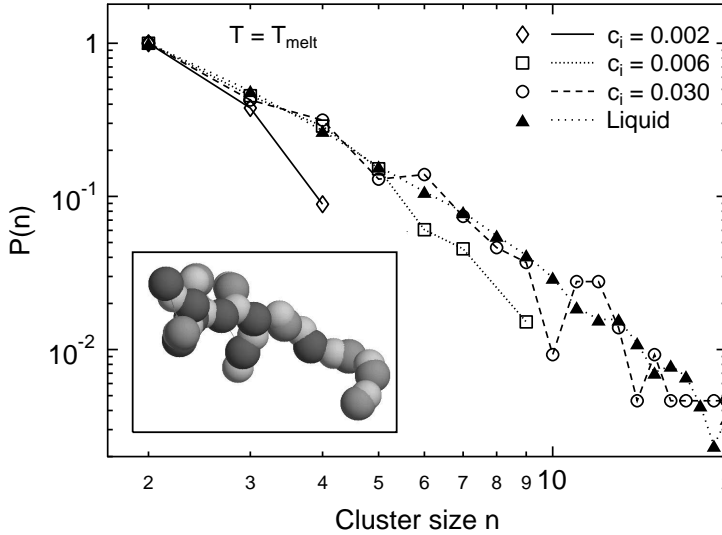


Fig. 2 – Probability of finding a cluster of size n of mobile particles in crystalline Cu with varying interstitial concentration (open symbols), and in liquid Cu (closed triangles). The distributions have been scaled to be $= 1$ for a cluster size of 2. The low concentration-distributions end abruptly because no larger clusters were observed during the simulation time. Inset: atom displacement following interstitial introduction in quenched amorphous Cu. Light (small) spheres represent pre-insertion position, and darker (larger) spheres indicate final relaxed positions. All plotted atoms moved more than 0.7 \AA and those with a darker shade of gray moved more than 1.2 \AA .

that the correlation function between mobile and immobile particles $G_d^{m,i}$ does not develop a peak at $r = 0$ at $t = t^*$, as expected [5].

Although the motions of single interstitials and strings are similar, some differences in the structures of the two are also observed, the details are discussed below. Within the interstitialcy theory [9], these differences are a consequence of the concentration of interstitials. According to that theory, the Gibbs free energy of the system should first increase with c_i , reach a maximum, and then decrease to a second minimum representing the liquid state. This led Granato to propose that a liquid can be understood as a solid with a high concentration ($\sim 9\%$) of interstitials with stringlike properties [9]. At concentrations above the maximum in the free energy, the properties of the material should smoothly approach that of the liquid state as c_i increased further.

Using our computer simulations we are able to test this prediction. We introduced increasingly higher concentrations of interstitials into the cells, calculated the properties of the mobile particles, and compared them with the properties of the mobile particles associated with the strings in a liquid.

In fig. 2 we compare the size of the clusters of mobile particles (detected by identifying clusters of nearest-neighbor mobile particles [5]) in a crystal and liquid. We see that at low interstitial concentrations the probability of finding a mobile cluster $P(n)$ of length n falls off rapidly with size. This is due to the dumbbell structure of the interstitials. However, as c_i increases, the length distribution approaches that of a liquid, and at a high concentration ($c_i \geq 0.03$) it is indistinguishable from it. The exponent for a power law fit $n^{-\tau}$ to the $P(n)$ data for the liquid is 2.0 ± 0.1 (using a fit range of $n \leq 20$), which compares well with the value of 1.86 reported in ref. [5] for a Lennard-Jones liquid.

We also monitored the average potential energy of mobile and immobile particles in Cu as a function of c_i . As shown in ref. [5], the mobile particles have, on average, a higher potential

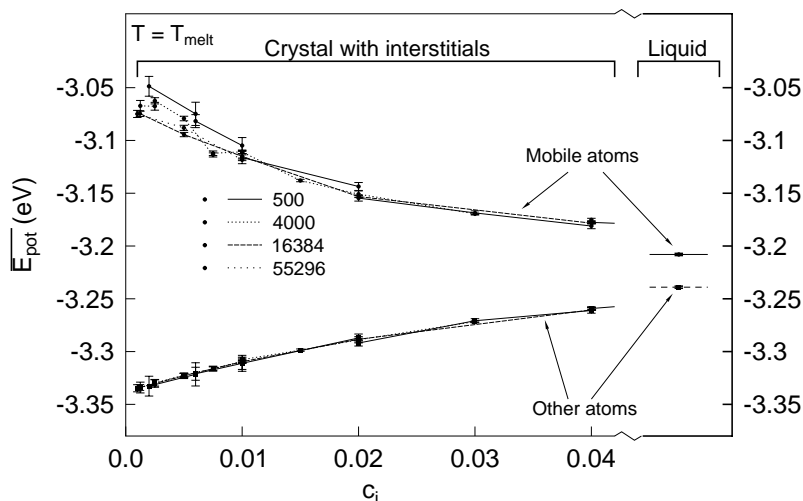


Fig. 3 – Average potential energy per atom for mobile and all other atoms in simulation cells with 500–55000 atoms. The good agreement between the curves of different sized cells rules out finite-size effects. The left part shows the average energy in a crystal as a function of the interstitial concentration. On the right end, the values in a liquid are shown. It is evident that on even higher interstitial concentrations the average potential energy of both the mobile and immobile atoms will eventually match the value in the liquid part.

energy than the immobile particles. Figure 3 shows that this is also the case in crystalline Cu. Moreover, the figure shows that, again, as c_i increases the properties of the crystalline system approaches that of a liquid [22].

Extrapolation of the potential energy in the crystalline phase to match the values in the liquid phase (see fig. 3) shows that at $c_i = 6 \pm 1\%$ the average potential energy of the mobile atoms in the solid is essentially the same as that in the liquid. This shows that the properties of the interstitial atoms in the solid approach continuously those of the string atoms in the liquid. The value of 6% is also in good agreement with the interstitialcy theory [9].

In the above discussion the mobile atoms in the liquid were identified explicitly through their van Hove correlation functions, and we showed similarity between those atoms and the interstitial in the solid. We continued this study by examining quenched amorphous Cu [23], where we can directly observe the relaxation behavior following the introduction of an interstitial into the system. This procedure provides a complementary means to elucidate the connection between point defect behavior in crystals and string-like relaxation in liquids.

We first determined whether it is possible to define an interstitial-like defect in amorphous Cu. To that end, we performed calculations of system evolution following the introduction of interstitial-like and vacancy-like defects. The vacancy-like defect was formed by simple removal of an atom, as discussed previously by Delaye and Limoge [24]. The interstitial-like defect was created by replacing a single atom with two atoms separated by the distance expected for a dumbbell interstitial in the crystal. Addition of both kinds of defects resulted in the same three types of system evolution: stable defect formation (with a positive formation energy and volume), localized defect annihilation and extended cooperative relaxation. The extended relaxation illustrates string-like behavior where a few chains of atoms, originating from the site of defect introduction, are displaced. The displacement is done in a strict sequential order as described for strings in ref. [25].

In the case of the interstitial, the displacement is away from the introduction site and opposite for the vacancy. These “chains” contained a total of less than 10 atoms for vacancies

TABLE I – Formation volume V^f and energy E^f for stable point defects in quenched amorphous Cu, as described by our EAM potential. The defect formation volumes for a single interstitial and vacancy in the crystalline states at a temperature of 10 K are 1.0 ± 0.05 and $0.75 \pm 0.05\Omega_0$, respectively.

		Stable defect	Localized annihilation	Extended relaxation
Atom	V^f (Ω_0)	0.3 ± 0.15	0.0 ± 0.1	-0.7 ± 0.5
addition	E^f (eV)	0.5 ± 0.25	-0.1 ± 0.2	-1.0 ± 0.5
Atom	V^f (Ω_0)	0.5 ± 0.2	0.0 ± 0.1	-0.4 ± 0.3
removal	E^f (eV)	0.7 ± 0.3	0.1 ± 0.2	-0.7 ± 0.5

and about 30 atoms for interstitials. Figure 2 (inset) demonstrates the location of the displaced atoms following the introduction of an interstitial.

The results of formation volume and energies of the inserted defects are summarized in table I. The relation between the different defect relaxation mechanisms indicated in this table and the different types of strings identified in [25] is currently under study.

The formation volumes and energies of the stable defects in the amorphous Cu were considerably lower than the corresponding values for the crystalline case, which are 1.2 eV for a vacancy and 3.2 eV for an interstitial.

We can understand the values for interstitials by noting that the incremental formation energy E^f of the interstitial dumbbell is given by [9]

$$\frac{dE^f}{dc_i} = \alpha_1 G_1(c_i)\Omega + \alpha_2 B\Omega, \quad (1)$$

where B is the bulk modulus, Ω the atomic volume, and the shear modulus depends on c_i as

$$G_1(c_i) = G_0 e^{-\beta c_i}. \quad (2)$$

A fit to experimental data for Cu [26] yields $\alpha_1 = 0.9$ and $\alpha_2 = 0.03$. With the values of $G_0\Omega = 4$ eV and $B\Omega = 10$ eV, a formation enthalpy of 3.9 eV for $c_i = 0$ and 0.7 eV for $c_i = 0.09$ derives [27]. Equation (1) is the primary assumption in the interstitialcy theory. We find here by simulation that indeed the formation energy of the interstitial in crystalline Cu falls from 3.2 eV at low concentrations to 1.0 eV at our highest tested concentration, $c_i = 0.03$, which is in good agreement with eq. (1). We are unaware of a similar expression as eq. (1) for the vacancy, and do not discuss this defect further.

Finally, we examined the atomic diffusion and crystallisation in quenched Cu in the temperature range 100–400 K. Above 150 K the cells were found to crystallize completely within 10 ns. By tracking the motion of all atoms in the system, we determined the diffusion coefficient D as a function of temperature. It is well fit by a simple Arrhenius-like curve $D_0 \exp[-E^m/k_B T]$, with $H^m = 0.08 \pm 0.01$ eV. This value agrees well with the activation energy for interstitial migration in crystalline Cu in our model, 0.081 eV [10]. By contrast, the activation energy for vacancy motion in crystalline Cu is 0.7 eV [10].

Conclusions. – In summary, we have shown that the “string” atoms in liquids have many of the same properties as interstitials in a crystal, and that these properties become even closer as the interstitial concentration approaches a few percent. We also found that the properties of inserted interstitials in glassy Cu have the expected properties for interstitials in crystalline Cu at high concentrations. These various findings offer strong support for the interstitialcy theory of liquids and glasses.

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- [21] The only reason for using more than one interstitial in this case was simply that this is the easiest way to obtain statistically significant results.
- [22] In the simulations with high interstitial concentrations, we encountered the practical problem that in large cells the interstitials clustered into extra atom planes, which complicated the analysis. Hence for large interstitial concentrations and cells we introduced artificial constraints which prevented atom clustering but did not affect normal vibrations or the potential energy. In cases where clustering did not occur, the results of constrained and non-constrained simulations were in good agreement.
- [23] Amorphous Cu samples were made by quenching liquid Cu from 1600 K to 10 K at a rate of 100 K/ps and initial pressure of 1 kbar. This procedure and sample size (90000 atoms) was chosen in order to ensure that we indeed have a stable amorphous sample.
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- [27] Since our potential yields a lower formation enthalpy at low concentrations, a value somewhat less than 0.7 should be obtained in the amorphous phase.