Published in final edited form as:

Soft Matter. 2013 January 28; 9(4): 1254–1265. doi:10.1039/C2SM26789F.

Glassy Interfacial Dynamics of Ni Nanoparticles: Part I Colored Noise, Dynamic Heterogeneity and Collective Atomic Motion

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Abstract

Most condensed materials exhibit a significant fraction of atoms, molecules or particles that are strongly interacting with each other, while being configured geometrically at any instant of time in an ‘amorphous’ state having a relatively uniform density. Recently, both simulations and experiments have revealed that the dynamics of diverse condensed amorphous materials is generally characterized by significant heterogeneity in the local mobility and by progressively increasing collective motion upon cooling that takes the form of string-like collective particle rearrangements. The direct experimental observation of this type of collective motion, which has been directly linked to the growing relaxation times of glass-forming materials, and its quantification under different thermodynamic conditions, has so far been restricted to colloidal and driven granular fluids. The present work addresses the fundamental problem of how to determine the scale of this type of collective motion in materials composed of molecules or atoms. The basic premise of our work is that large scale dynamic particle clustering in amorphous materials must give rise to large fluctuations in particle mobility so that transport properties, especially those related to particle mobility, should naturally exhibit *noise* related to the cooperative motion scale. In our initial exploratory study seeking a relationship of this kind, we find $1/f^\alpha$ or ‘colored noise’, in both potential energy and particle displacements fluctuations of the atoms within the glassy interfacial layer of Ni nanoparticles (NPs). A direct relation between the particle displacement (mobility) noise exponent α and the average polymerization index of the string-like collective motion L is observed for a range of NP sizes, temperatures and for surface doping of the NPs with other metal atoms (Ag, Au, Pt) to change of fragility of the glassy interfacial layer at the surface of the Ni NPs. We also introduce a successful analytic model to understand this relationship between α and L .

Simulation studies of the molecular dynamics of glass-forming (GF) liquids^{1–3}, the grain boundaries⁴ (GBs) of model polycrystalline materials, and the interfacial layers of nanoparticles (NPs)^{5, 6} have revealed remarkably similar patterns of transport dynamics involving large fluctuations in local atomic and molecular mobility and a distinctive type of collective molecular motion. Evidently, the molecular dynamics of strongly interacting

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amorphous materials has a *universal* character so that the physics of glass formation seems to have relevance to the transport properties of condensed materials rather generally.

One of the striking features of the dynamics of these strongly interacting, but amorphous, particle systems is the emergence of collective particle motion taking the form of string-like particle exchange events that has some resemblance to the local permutational ‘stirring’ atomic motions suggested by Feynman to describe the collective atomic motions underlying the superfluid state of He.^{4, 7–9} These ‘strings’ generally exhibit an exponential size distribution and have been directly observed experimentally through direct particle tracking in concentrated colloidal fluids^{10–15}, granular fluids^{16, 17} and the grain boundaries of colloidal materials.^{18, 19} Simulations for model GF polymer melts with NPs to tune the fragility of glass formation [essentially the ‘strength’ of the temperature (T) dependence of the structural relaxation time τ in comparison to Arrhenius temperature dependence^{20–22}] have also shown that the activation energy E_a for the structural relaxation time τ grows in proportion to the average length of these strings L .²² We thus have a well-defined structural quantity whose growing size can be directly associated with the slowing of the dynamics of GF liquids and with the slowing of structural relaxation and diffusion in many other forms of strongly interacting amorphous matter.

The present paper explores the possible relation between this apparently *universal* form of collective particle motion in ‘amorphous’ materials and another hitherto rather poorly understood property of condensed disordered materials, ‘colored’ or ‘flicker’ noise. It is natural that these phenomena might be related since the existence of dynamic heterogeneity in the dynamics of condensed disordered materials means that there must be mobility (i.e., diffusivity) fluctuations in the transporting species. Although there is not much agreement about the molecular mechanism of the colored noise observed in the conductivity of a significant fraction of all condensed materials,^{23–29} there is strong evidence that this phenomenon often has its origin in mobility fluctuations of the transported species.^{24, 29–31} The range of materials exhibiting this behavior is truly amazing and includes organic and inorganic semi-conductors, insulating materials, metals, electrolyte solutions and diverse types of devices including essentially all solid state devices-transistors, infrared detectors, microphones, amplifiers, electrolyte solutions, etc.²⁸ At the outset, we note that the apparent universality of the string-like collective motion found in former simulations^{1–6}, and confirmed by measurement^{10–15, 18, 19}, has the potential generality to explain the wide occurrence of colored noise in diverse condensed materials at or near *equilibrium*.^{23, 25, 26} We emphasize that we make no attempt to connect our modeling of colored noise in systems driven far from equilibrium where the concept of self-organized criticality serves as a model of this type of ‘driven noise’.³¹ We also emphasize at the outset that the present work is an exploratory study so that our findings for the interfacial dynamics of NPs will need to be confirmed of other model materials before any general relation between colored noise and the extent of collective particle motion can be claimed.

Apart from the theoretical and tremendous practical interest of understanding the origin of colored noise in materials, our primary goal is to find a relationship between colored noise and collective motion in amorphous materials since it is generally difficult to observe string-like collective motion experimentally in atomic and molecular systems, as is possible for

colloidal^{10–15} and granular¹⁶ fluids. Since we are convinced of the fundamental nature of the string-like collective motion for understanding transport in diverse condensed materials, we are strongly motivated to find some experimental means to determine the length of these strings in molecular fluids. Our goal then is to somehow turn noise observations into measurements of the extent of string-like collective motion. To achieve this desired metrology of the strings, we need to establish quantitative relationships between the properties of the strings and colored noise measurements. This task is the focus of the present work, where we explore this relation in the particular context of the interfacial dynamics of Ni NPs. We choose this system as the starting point for our more general investigations of the colored noise-string relation because colored noise is a ubiquitous phenomenon in NPs that often limits their applications in sensing applications utilizing these particles^{32, 33} and because of the more manageable computational scale of simulating these particles in comparison to bulk materials. Our previous computations have shown that the collective dynamics of these particles is remarkably similar to the GB regions of polycrystalline materials and the collective dynamics of bulk GF materials so we do not think that confining ourselves to NPs is overly restrictive for the phenomena that we hope to uncover through our simulations (This expectation remains to be confirmed, however). Another attractive aspect of simulation of NPs is the physically natural way in which we can tune the collective interfacial dynamics by ‘doping’ the surface of the NP with other atomic species,^{5,6} varying NP size and shape, or simply placing the NPs on the boundaries of other materials, etc. All these changes should affect the collective interfacial dynamics and we then anticipate corresponding changes in the noise properties of the NP if our general reasoning about the relation between noise and collective motion is correct. Of course, all such changes have technological and scientific interest.

Before we begin our analysis, we note that it is a commonly asked whether colored noise is a *bulk* or an *interfacial* phenomenon. While we find collective motion to be characteristic of bulk GF liquids, this phenomenon also arises in ultra-thin films, GBs and the interfacial dynamics of NPs. A relation between colored noise and collective motion would then imply that colored noise should arise both as bulk and interfacial phenomenon, depending on the type of material and measurement. We next turn to our attention to colored noise and atomic interfacial collective dynamics in the interfacial region of Ni NPs.

Molecular dynamics (MD) simulations were performed to analyze fluctuations in potential energy and mobility and to characterize the string-like collective atom motions on the interfacial region of Ni NPs. The atomic interactions were described using the Voter-Chen form³⁴ of an Embedded Atom Method (EAM) potential³⁵ for pure Ni simulations. Our studies of Ag, Au, and Pt additives effects on fluctuations of interfacial properties of the NPs utilized the Sutton-Chen form³⁶ of EAM potential because all the potentials were available for the Ni, Ag, Au and Pt atoms as well as appropriate potentials for their mutual interaction (potential parameters for these models for the metals considered in the present work are given in Supplementary Material.) Free boundary conditions (free surfaces with vacuum) were applied for all simulations, which were performed within the canonical ensemble (NVT) where a constant temperature was maintained using the Nose-Hoover method.^{37, 38} Three different sizes of NP having $N = 369$, 2899 and 5473 Ni atoms were investigated

correspond to NPs having a radius r of 1 nm, 2 nm and 2.5 nm, respectively. The Ni NPs were initiated from an approximately spherical shape and a perfect local face-centered cubic structure. The NPs were subsequently relaxed at room T for 1.5 ns with zero angular and linear momentum values. The MD simulations utilized LAMMPS.³⁹

Cooperative Atomic Motion in the Interfacial Dynamics of Ni Nanoparticles

Cooperative particle dynamics is a characteristic feature of the dynamics of GF liquids fluids and recently we applied methods for characterizing this type of collective motion to interfacial atomic dynamics of Ni NPs under equilibrium conditions⁵ and even under the nonequilibrium conditions of NP melting and freezing following a T jump.⁶ Next, we briefly summarize our former results pertaining to the present investigation of noise fluctuations in our simulations of these same NPs. As a first step in identifying collective particle motion, we must identify the ‘mobile’ atoms in our system. As explained in detail elsewhere, the ‘mobile’ atoms are essentially those particles that move a distance $r(t)$ that is larger than the typical amplitude of an atomic vibration after a diffusive decorrelation time t^* , but this distance is smaller than the second nearest-neighbor atomic distance. Specifically, we identify these particles by a threshold atomic displacement condition, $0.35r_0 < |\mathbf{r}_i(t^*) - \mathbf{r}_i(0)| < 1.2r_0$, involving the bulk material interatomic spacing, r_0 . Notably, all the ‘mobile’ atoms are all located within the NP interfacial region since the NP cores are essentially defect-free. The diffusive decorrelation time t^* is not equal the structural relaxation time τ_s from the intermediate scattering function, but t^* scales inversely with D / T [See Fig. S1 in Supplementary Material]. In GF liquids, D / T scales inversely to an inverse power of τ_s , a phenomenon termed ‘decoupling’^{40–43} so that these characteristic diffusive and structural relaxation times are generally interrelated.

The identification of correlated atom motion requires a consideration of the *relative* displacement of particles. Collective atomic motion means that the spatial relation between the atoms must be preserved to some degree as the atoms move as a unit. Reference mobile atoms i and j are considered to be within a collective atom displacement ‘string’ if they remain in each other’s neighborhood and we specify this proximity relationship by, $\min[|\mathbf{r}_i(t^*) - \mathbf{r}_j(0)|, |\mathbf{r}_i(0) - \mathbf{r}_j(t^*)|] < 0.43r_0$, the same criterion used in past studies of collective motion of GF liquids and the dynamics of GB.^{1, 4} Application of this criterion reveals that the collective particle motion in the NP interfacial region at equilibrium takes the form of string-like collective motion⁵, as illustrated in Fig. 1a. The lines in the figure denote Ni atoms that belong to the same collective atomic movement, arrows indicate direction of atom movement, and the colors are introduced to help discriminate between distinct strings where $T = 1450$ K, $N = 2899$ and the nanoparticle radius equals 2 nm. An examination of the scaling relation between the radius of gyration R_g of the strings versus L indicates that their shape becomes more persistent with cooling, reflecting the progressively shrinking thickness of the interfacial layer thickness of the NP (See Figure S2 in Supplementary Material). In contrast, the string geometry in simulated GF polymer melts has been found to be more like self-avoiding walks, apart from an approach random walk scaling at low T as the strings become long and start to interact strongly as in concentrated polymer solutions of flexible polymers.⁴⁴

Atomistic simulations of GF liquids and GBs indicate that the distribution of string lengths $P(n)$ is generally an exponential function of the number of particles n moving collectively, $P(n) \approx \exp(-n/\langle n \rangle)$, to an excellent approximation. Figure 1(b) shows the distribution of string lengths for the interfacial dynamics⁵ of our $N = 2899$ Ni NP and the average string length $\langle n \rangle$ is then simply determined from the slopes in this figure. At a fixed T , we previously found that the strings are larger in the smaller NPs and the temperature dependence of $\langle n \rangle$ becomes more rapidly varying with T . In the language of GF fluids, this means that the molecular dynamics of the NP interfacial layer is increasingly ‘fragile’ or the glass transition is becoming more cooperative as the NPs become smaller. This makes perfect sense since increasing fragility has been associated with increasing packing frustration (decreasing packing efficiency)⁵ and the higher curvature of the smaller NP can naturally be expected to diminish packing efficiency in the interfacial layer of the NP, thus leading to a glassy dynamics exhibiting a higher relative cooperativity.

Alloying offers the promise of creating less expensive, chemically stable and more efficient catalysts for diverse energy related applications and it is a matter of some importance to understand how the alloying effect can be optimized to create the greatest efficiency of catalytic behavior.^{45–51} There is particular interest in alloying Ni NP with Pt,⁴⁵ Ag,⁴⁶ Au^{47–49} and Pt/Ru^{50, 51} to reduce catalyst cost. These metals are rather immiscible with Ni so that these metals should segregate to the outer surface layer of the Ni NP. MD simulations were performed for Ni NPs with Pt, Au and Ag atoms initially uniformly distributed on the interface of the NP and the results of these simulations⁵ are summarized in Fig. 2, where we see that the Ag and Au atoms reduce the average string length, while the Pt atoms progressively increase the string length for NP that otherwise have the same T and radius. Below we consider the amplitude of mobility fluctuations in these same simulations of Ni NPs with and without interfacial additives of other metal species. It is important for our present purposes that the scale of collective atomic motion is highly tunable with T and surface composition.

Noise in the Interfacial Dynamics of Ni Nanoparticles

The highly cooperative string-like atomic motion in the interfacial region of NPs can be expected to influence many of the properties of these particles, including noise properties that are naturally associated with the dynamic heterogeneity phenomenon described above (See Conclusion). This intrinsic ‘flicker noise’ is a limiting factor in the use of NPs in sensing applications,^{32, 33} and is also crucial in the electronic properties of organic thin film resistors⁵² and other electronic devices, where the GB analog of the NP interfacial dynamics is apparently involved.

There has been much interest recently in the propensity of glass-forming materials to exhibit $1/f$ noise (or more generally colored noise $1/f^\alpha$ where α is variable) in their transport properties such as conductivity and their polarizability upon approaching the glass transition.^{53–60} There is also a large body of data^{27, 32, 33, 52, 61–63} indicating that $1/f$ noise is strongly associated with GBs of polycrystalline materials and the interfaces of NPs. The common occurrence of colored noise in all these systems is natural given the similar collective molecular dynamics seen in simulations of representative materials of these kinds.

Much phenomenological evidence can then be compiled which is consistent with the hypothesis that colored noise is somehow connected to the growing collective motion in GF materials, the amorphous interfacial regions of NPs, GBs, and the interfaces of crystals generally. What then is the quantitative relation between these phenomena?

We obtain our first clue into this type of relationship by considering the nature of one of the basic measures of dynamic heterogeneity, the so-called non-Gaussian parameter, δ :

$$\delta(t) = \frac{3\langle r^4(t) \rangle}{5\langle r^2(t) \rangle^2} - 1 \quad (1)$$

where $r(t)$ is the displacement of an atom in the time interval t . The non-Gaussian parameter δ has a long history in the transport theory of interacting gases where it is known as the ‘Burnett coefficient’.^{30, 64, 65} It arises in connection with investigations of the origin of the long time tail in the velocity autocorrelation function of dense fluids.^{66–69} Mathematically, δ is defined by a 4-point velocity autocorrelation function that generalizes the standard two-point velocity correlation function defining the mass diffusion coefficient, D .^{30, 64} At a basic level, δ describes ‘mobility’ (i.e., mass diffusivity) fluctuations in the fluid³⁰ so it should come as no surprise that this parameter also figures prominently in modeling $1/f$ noise in the conductivity of condensed materials at equilibrium. In particular, the amplitude of this type of noise has been predicted to be proportional to δ in a simple model introduced by Nieuwenhuisen and Ernst.³⁰ Below, we find that the nature of mobility noise found in our simulations is colored, but we do not find $1/f$ noise specifically. Thus, it is not possible to make a quantitative comparison with the predictions of Nieuwenhuisen and Ernst.³⁰ Nonetheless, their work greatly stimulated us to investigate how the dynamic heterogeneity of GF liquids might be related to colored noise.

Previous discussions of $1/f$ noise in diverse conductive materials have emphasized the importance of mobility fluctuations. Thermal conductivity is the transport property associated with energy fluctuations^{70, 71} and the Soret coefficient S_T , the ratio of the thermal diffusion coefficient to the mass diffusion coefficient, links thermal diffusion to mass diffusion.⁷² Recent measurements⁷² of S_T for concentrated polymer solutions approaching their glass transition temperature T_g have indicated that S_T varies slowly near T_g so that the thermal diffusion coefficient of these glassy materials evidently tracks the mass diffusion coefficient D , which means the thermal conductivity exhibits a very strong T dependence that follows a similar pattern to D and the shear viscosity η of GF fluids.⁷³ If the thermal conductivity tracks D , then intuitively we might expect the energy fluctuations in GF liquids to track mobility fluctuations. Even if there is not a one-to-one relationship, colored noise in the NP interfacial energy fluctuations are expected upon approaching T_g . There are indeed numerous simulation studies indicating colored potential energy fluctuation in cooled water, proteins and NPs and diverse other strongly interacting and amorphous systems,^{74–76} but the significance of this phenomenon to glass formation has never been explained before. We admit that the applicability of trends found in bulk GF fluids to NPs is somewhat questionable, but this simple reasoning serves as useful starting point for our discussion.

We initiate our investigation of noise in the interfacial dynamics of Ni NPs with a consideration of potential energy E noise. Previous studies of the collective dynamics of water^{74, 77} have been interpreted in terms of collective atomic motions within the hydrogen bond network in the case,^{70, 72} but only a qualitative relationship was inferred. We now seek a more quantitative and general relation.

Figure 3(a) shows the temporal evolution of the potential energy $E(t)$ of a NP with $N = 369$ Ni atoms at two T and Figure 3(b) illustrates the power spectrum of $E(t)$ fluctuations in the interfacial dynamics of our NPs over a range of T . The calculation of the power spectrum $P_E(f)$ of these fluctuations is defined by the transform,

$$P_E(f) = \left| \int E(t) e^{-2\pi i f t} dt \right|^2 \quad (2)$$

$P_E(f)$ reveals that the interfacial $E(t)$ fluctuations are colored, as expected. Encouragingly, we find a $1/f^\alpha$ scaling where the scaling exponent α varies with T and the size of the NP. Curiously, the exponent α_E characterizing the ‘color’ of this noise (an exponent of zero corresponds to white noise) increases at first upon heating towards the melting temperature T_m of the NP, but then the noise exponent drops suddenly near T_m . This drop becomes weaker as the NP becomes larger. The larger variation of the noise exponent with T in the smaller NPs parallels our previous finding of a weaker T dependence of the collective motion in these NPs as they become larger⁵, an effect interpreted before in terms of a variable fragility of the glassy NP interfacial layer.

Evidence for an Interfacial Roughening Transition in the NPs?

Recent simulations of fluctuations in the local coordination number of particles having a screened Coulomb interaction, another system for which string-like collective motion is exhibited, indicated colored noise ($1/f^\alpha$) with an α exponent that monotonically increased upon cooling.⁵³ Coordination fluctuations imply potential energy fluctuations so that maximum in the inset of Fig. 3(b) seems puzzling if the NP interface can simply be described as a GF liquid. Is this phenomenon somehow special to our NPs? This singular feature reminds us that we have been a little loose in describing the mobile interfacial layer as a ‘surface melted’ fluid.⁵ We might also expect a *surface roughening transition* of the crystalline NPs to lead to an enhanced interfacial mobility where a significant amount of local order is maintained. The surface roughening transition in bulk materials is thought to be described by a Kosterlitz-Thouless (KT) continuous phase transition (infinite order)⁷⁸ and a transition of this kind on the NP surface would naturally lead to local ordering and collective particle motion, as often observed in the ordering of near two dimensional fluids.⁷⁹ Roughening transitions have even been suggested for amorphous metal surfaces⁸⁰ so an interfacial order-disorder transition is possible.

Collective permutational particle motion is characteristic of near two-dimensional fluids both in simulations and experiment in the ‘hexatic’ regime between the ordered crystal and fluid states where periodic particle ordering only occurs locally.^{10, 11, 13–15, 81, 82} No quantitative study has been made of the collective motion in these systems, however. In bulk crystalline materials with a free interface, both simulation and experimental studies have

estimated the roughening transition to occur roughly a T around $0.8 T_m$ in bulk materials.^{83–87} Notably, a peak in the energy fluctuations occurs in our NP at a T around $0.9 T_m$, suggesting that collective interfacial motions in the surface melted NP are related to some vestige of a crystalline roughening transition. These observations together suggest that the peaking in the α exponent governing the $E(t)$ fluctuations in the interfacial dynamics of our NPs may be associated with the finite size of our NP system and that the collective dynamics of this glassy layer may actually be more accurately described as hexatic-like. These possibilities obviously require further consideration.

All this is interesting, but we must admit that our comparison of the T dependence of the noise exponent α_E in Fig. 3(b) to the scale of collective motion L in the inset of Fig. 1(b) does not reveal any evident correlation. Perhaps we are looking at the wrong fluctuating quantity?

Colored Noise Associated with Mobility Fluctuations

From the discussion in the introduction, it is desirable to probe some measure of mobility (diffusivity) fluctuations in the ‘glassy’ or ‘frustrated fluid’ interfacial region of the NP rather than $E(t)$ fluctuations to better assess how mobility fluctuations relate to the widely observed phenomenon of colored noise in the conductance of condensed materials. For this purpose, we need a mobility related property that can be defined after a short time and to consider fluctuations in this quantity. The Debye-Waller factor or mean square particle displacement $\langle u^2 \rangle$ after a caging time is evidently an attractive property for this purpose.^{88–91} A comparison of the exponent α_{DWF} describing the fluctuations in $\langle u^2 \rangle$ in Fig. 4 to the extent of collective motion L shown in Fig. 1(b) reveals a remarkable correlation between L and α_{DWF} for a $r = 2$ nm Ni NP over a range of T . Evidently, the noise exponent α_{DWF} equals $L - 1$ over a wide range of T to a remarkable approximation! The noise exponent α_{DWF} describing the mobility ($\langle u^2 \rangle$) fluctuation is then directly related to the extent of collective motion L in the NP interfacial dynamics.

How general is this phenomenon? We now consider simulations for a range of NP sizes and for NP doped with various other types of interfacial atoms to see if these fragility modifying perturbations preserve this relationship between α_{DWF} and L . Figure 5 shows a plot of α_{DWF} and L for NP having a radius, $r = (1 \text{ nm}, 2 \text{ nm}, \text{ and } 2.5 \text{ nm})$ and for NPs capped with Au, Ag and Pt. We then have an approximate equality of α_{DWF} and $L - 1$ and we find this relationship to be robust for all systems sizes, surface compositions, and T values that we simulate. Measurements on the colored conductance noise in metals⁹² have indicated that the magnitude of the noise exponent α increases upon cooling, in qualitative accord with Fig. 4 and an increase in α upon cooling has also been observed in the energy fluctuations of proteins.⁹³ Colored noise and collective motion are indeed phenomenologically related and we next develop a physical model that relates the mobility noise exponent α to L .

The relation between α_{DWF} and L shown in Fig. 5 implies a highly non-trivial relation between the diffusion coefficient D , structural relaxation time τ and noise color in bulk glassforming materials that could readily be tested experimentally. If L is identified with the size of the ‘cooperatively rearranging regions’ of Adams-Gibbs (AG)²² and α is

proportional to L , then both $\log D$ and $\log \tau$ should scale in proportionality to α . Exactly this type of scaling between D and α has been observed in recent simulations of water, silica and methanol^{94, 95} where α is the noise exponent for *potential energy* fluctuations. This suggests that the noise associated with potential energy and particle displacement fluctuations track each other in *bulk* materials and supports the wide applicability of the relation indicated in Fig. 5. This possibility will have to be checked by further simulations, of course. Part II of the paper extends the analysis of the present paper to consider the nature of energy and displacement fluctuations at an atomic scale with a view of better understanding the fundamental molecular processes underlying the generation of colored noise and collective atomic motion.

Model Relating Mobility Fluctuations to the Scale of Collective Motion in Glassy Materials

Recent modeling of collective transport in disordered materials,⁹⁶ and colored noise in the conductance fluctuations of doped semi-conducting materials, in particular,⁹⁷ and previous models of dielectric and stress relaxation in disordered materials^{98–100} together provide a good starting point for our consideration of a relation between L and α_{DWF} . In particular, Vinokur et al.⁹⁶ indicate that $1/f$ conductance noise commonly arises in the transport properties of disordered materials because of the inherently rugged, hierarchically structured, potential energy landscape that characterizes these materials. They discuss this noise based on a widely studied model of involving the movement of string-like defect structures within a background random media in which the strings become intermittently pinned in their motion. An analysis of the potential energy landscape of their ‘string defect’ mediated activated transport model led them to the conclusion that the local energy barriers

E , associated correlated particle motion connecting metastable minima on the potential energy surface, are distributed according to an asymptotically exponential distribution, $p(E) \approx \exp(-E/E_0)$ with E_0 a minimal barrier height. While this defect mediated relaxation model seems to be rather attractive mathematical model for understanding the general origin of colored noise in disordered condensed materials, the molecular origin of these activated barriers is unclear so we need to think more physically about the NP transport processes to make sense of these formal arguments from a molecular perspective.

Vinokur et al.⁹⁶ further argued that the collective hopping motions of transporting species in condensed materials exhibiting colored noise can be described by energy jumps governed by an exponential E distribution, each cooperative relaxation event being described by an Arrhenius relaxation time,

$$\tau_c = \tau_0 \exp(\Delta E/kT) \quad (3)$$

with $1/\tau_0$ the attempt frequency of conventional transition state theory. This model is well known in condensed matter modeling and leads asymptotically to a power-law waiting time distribution,^{96,98,99}

$$\psi(t) \sim t^{-2+\alpha} \quad (4)$$

for the hopping events where the exponent $\alpha(T)$ equals, $\alpha = T/E_o$. We emphasize the existence of an upper *cut-off* on the energy distribution range makes the average waiting time have an Arrhenius temperature dependence, despite the apparent power law nature of $\psi(t)$.⁹⁶ Essentially the same exponential distribution of activation energy argument^{101–106} as Vinokur propose for colored noise in amorphous semiconducting materials has been offered to rationalize the universal occurrence of high frequency power-law relaxation in condensed matter at equilibrium^{98, 99, 107} and also in non-equilibrium ‘soft glassy matter’.^{108, 109} This is also the essential mathematical idea behind modeling the ‘fast’ or ‘excess wing’ relaxation in glassforming liquids based on the asymmetric double well potential model.^{106, 110, 111} Refinements of this exponential distribution of activation energy to explain high frequency condensed matter relaxation often consider a distribution of activation entropies that are linked to the distribution of activation energies (enthalpy) by a phenomenological entropy-enthalpy compensation relation^{103, 112, 113}, but we do not consider this refinement in the modeling of the T dependence of α in the present paper.

An exponential distribution of relaxation times associated with hopping particle transport leads to a power spectrum $S(\omega)$ having power law form,^{96, 97}

$$S(\omega) \propto \int d\Delta E p(\Delta E) \tau(\Delta E) / (1 + [\omega \tau(\Delta E)]^2) \sim \omega^{-\alpha} \quad (5)$$

$$\alpha = 1 - T/E_o \quad (6)$$

where the exponent α , quantifying the ‘color’ of the noise, depends on T .

Simple models of relaxation on hierarchical Cayley tree lattices^{114–116}, which can be taken as cartoon models of the hierarchical potential energy surfaces of disordered condensed materials, provide a concrete mathematical realization of this type of hierarchical relaxation model. We then expect from Eq. (6) that α should increase upon cooling, but we must further consider the T dependence of the energy parameter E_o before we can firmly estimate the T variation of α . At this point, we attempt to put some physical meat on this formal mathematical argument. In particular, we argue for a connection between the distribution of activation energies E and the distribution function for the extent of collective motion, L .

First of all, the tendency for particle displacement events in cooled GF fluids to exhibit a power-law hopping time distribution is a well-documented fact.^{117–120} Based on our analysis of the string-like collective motion above, we then take the barrier height E with the particle hopping process to be proportional to the length n of the strings of collective atomic motion. Exactly this presumption was made before in modeling alpha structural relaxation in model polymer GF fluids where the strings were identified²² with the abstract ‘cooperatively rearranging regions’ of Adam and Gibbs (AG).¹²¹ Consistency would seem to demand this identification for high frequency relaxation as well. In particular, we take the hopping barrier E to be proportional to the string length n ,

$$\Delta E = \varepsilon_o n \quad (7)$$

with the constant of proportionality ε_0 as a reasonable model for the distribution of activation energies governing atomic mobility in the glassy interfacial regions of our NPs. Since strings are widely occurring in condensed matter systems, we expect this identification to be rather general. We then have the specific distribution of activation energies,

$$P(\Delta E) = \exp(-\Delta E / L\varepsilon_0). \quad (8)$$

where the functional form of the distribution is independent of T , but the decay constant depends on the scale of collective motion L times the energy ε_0 . This is apparently the first fluid structure based argument for an exponential distribution of activation energies in GF fluids. Recent calculations of the distribution of the potential energy¹²² and energy barriers associated with the inherent structure dynamics within meta-basins (of relevance to the fast beta relaxation rather than alpha structural relaxation)¹²³ have provided direct evidence for such an exponential energy barrier distribution. We now have a more concrete picture of where the barriers are coming from and we can now propose an explicit molecularly-based relation between α and L ,

$$\alpha = 1 - T / L\varepsilon_0. \quad (9)$$

Interestingly, the identification of L with the CRR of AG²² means that we can also relate α to the fluid configurational entropy s_c (entropy of fluid apart from the contribution from vibrational degrees of freedom). Within AG theory, L equals $s_c(T_A) / s_c(T)$ where $s_c(T_A)$ is the high T limiting constant value of s_c and α then equals the simple expression,

$$\alpha = 1 - (T / \varepsilon_0) [s_c(T) / s_c(T_A)] \quad (10)$$

The reference temperature¹²⁴ T_A is the ‘onset temperature’ for glass transition regime below which $s_c(T)$ starts to drop and the collective motion starts increasing so that $L(T_A) = 1$. Equation (10) is *exactly* the functional form deduced by Odagaki¹⁰⁵ for the waiting time distribution $\psi(t)$ governing particle displacements in GF liquids. We take this as encouraging for the plausibility of the current line of reasoning.

We can go further in our specification of α in terms of parameters governing the NP dynamics by taking T_A as a *boundary condition* that can be used to fix the energy ε_0 . This condition also prescribes an onset condition for colored noise accompanying the onset of collective motion in our physical picture of the origin of colored noise in materials at equilibrium. In particular, we take the noise to be white ($\alpha = 0$) above T_A , which means that we exactly identify ε_0 with T_A . This matching procedure for eliminating the energy scale ε_0 in favor of a reference temperature was argued for before by Glatz et al.⁹⁷ For substances that crystallize readily, such as Ni, there is evidence that onset temperature T_A can be identified with T_m .¹²⁵ We now have a simple and fully determined relationship between α and L ,

$$\alpha = 1 - (T / LT_A) \quad (11)$$

We see from Eq. (11) that α is predicted to approach 1 in the limit of vanishing T for a bounded L , while the noise becomes white ($\alpha = 0$) at the onset temperature for glass formation, T_A . To make comparisons between our α data at intermediate T , we must prescribe the functional dependence of L on T . The strength of this T dependence of L is basic for GF liquids because it determines the fragility²² of the GF liquid so that this T dependence can be highly variable depending on the particular material. The entropy theory of glass formation¹²⁴ in polymer materials, for example, predicts that $L - 1$ exhibits a simple power-law behavior in reduced temperature near T_A ,

$$L - 1 = C[(T - T_A)/T_A]^\kappa \quad (12)$$

where κ the exponent equals 2 and the ‘fragility constant’ of the high temperature regime of glass-formation C varies in a range between about 3 or 7, for strong and fragile polymer glass formers, respectively.¹²⁶ [These predicted values¹²⁶ are consistent with molecular dynamics simulation estimates of C for a model strong (antiplasticized) and fragile neat polymer melt, respectively.] However, it is apparent from the T variation of L shown in inset of Fig. 6 that the exponent describing the T dependence of L must be smaller for the interfacial dynamics of the Ni NPs than in the case of bulk glass forming materials. Accordingly, we fit the L data for $r = 2$ nm NP to Eq. (12), but fit to an empirical exponent value, $\kappa = 0.42$; the maximum deviation of this curve from the simulation data is 5 % over the T range investigated. This fitted expression for L is then inserted into Eq. (11), along with our estimates of T_A , and reasonable consistency between our simulated and estimated noise exponent α_{DWF} values (largest deviation is 15 %). While this agreement is encouraging, further checks of Eq. (11) are evidently warranted.

Ngai²⁸ has made some important observations relevant to the current discussion of the noise exponents in relation to collective relaxation and the phenomenon of ‘universal response’ in condensed matter described by universal power law scaling of storage and loss components of the response functions $[\chi'(\omega), \chi''(\omega)]$ for the dielectric constant. He likewise concludes that conductance fluctuations have an origin in mobility fluctuations and that universal response in the dielectric properties are linked to the origin of colored noise. Galeczki et al.¹²⁷ have rederived the results of Ngai²⁸ in a more transparent way where it is shown that the conductance noise exponent α equals $1 - \phi$ when the complex dielectric susceptibilities scale as, $\chi'(\omega) \sim \chi''(\omega) \sim (\omega)^\phi$ in the high frequency limit such that $0 < \phi < 1$ (See also Dyre¹⁰⁰). These arguments imply that the magnitudes of the relaxation exponent ϕ and the noise exponent α are related so that ‘universal dielectric response’ and the color of conductance noise are plausibly interrelated.

There also has been some speculation that collective motion has some relation to the stretched exponential relaxation of disordered condensed materials and this interesting hypothesis can be examined in our NP interfacial dynamics simulations. In particular, a number of authors^{128, 129} have suggested that the scale of collective motion in GF liquids, i.e., the number of particles in a cooperatively rearranging regions and the quantity we identify with L , should be inversely proportional to the stretching exponent β_s describing the decay of the intermediate scattering function $[I(q, t) \approx \exp[-(t/\tau)^{\beta_s}]]$; [See Supplementary Material for definition of $I(q, t)$ and some illustrative data] and other structural relaxation

processes of GF materials.^{130, 131} If this relation were true for our NPs, then it would link the variation of β_s to the noise exponent α_{DWF} and L . To test this possibility, we determined $I(q, t)$ for the NP interfacial dynamics and found the stretching exponent to be essentially *unchanged* ($\beta_s = 0.36 \pm 0.02$) for the entire T range we investigate, a similar β_s value being obtained in our previous simulations of Ni GBs.⁴ We thus find no support for a direct relation between the extent of cooperative motion L and a variation of the stretching exponent β_s . We note that molecular dynamics simulations of model GF liquids have indicated an appreciable T dependence of β_s ¹³² and it might be worthwhile in the future to examine how β_s varies in relation to L and α . The present observations make it clear, however, that no universal relation exists between β_s and the extent of collective motion L in the interfacial dynamics of our NPs. We have also examined collective atomic motion in the case of the bulk melting of Ni and again we unfortunately find no relation between the T variation of L and β_s .¹³³ The exponent β_s *cannot* be taken as a general measure of cooperativity.

Conclusions

Understanding the origin of colored noise and the nature of the collective atomic motions underlying the frequently strongly non-Arrhenius changes in the rates of relaxation and diffusion in glass-forming and polycrystalline materials have been long-standing challenges for theoretical modeling. Our molecular dynamics simulations focusing on the glassy interfacial layer of Ni nanoparticles indicate that these mysterious phenomena are intimately related. In particular, we find that the magnitude of the colored noise exponent α for mobility fluctuations, measured specifically by fluctuations in the Debye-Waller factor, essentially equals $L - 1$ where L is the extent of collective particle motion. Cooperative molecular motion and mobility fluctuations then go hand in hand with each other. Previous work on simulated polymer glass-forming liquids²² has shown that L also describes the growing activation energy in these glass-forming liquids and the large variations in the fragility of glass-formation, the strength of the temperature dependence of structural relaxation, that can be obtained by adding nanoparticles to these model polymer materials. Strikingly, the large observed variations in fragility with these additives can be explained by the change in the T dependence of L . In the present work, we find that the variation of L can also account for the T dependence of the colored noise associated with mobility fluctuations and a simple model, validated by simulation, is introduced to rationalize the observed relation between the extent of collective particle motion L and noise color α .

The quantification of the extent of collective motion and the physical variables that modulate the configurational entropy¹²⁴, and thus the scale of cooperative motion L , provides a new framework for engineering the relaxation and noise properties of diverse condensed materials. The measurement of noise also promises to provide a metrology for the extent of collective motion, a property normally difficult to observe experimentally in molecular fluids. In a technological context, noise is often an unwanted phenomenon and this relation between colored noise offers a strategy towards noise reduction through appropriately chosen molecular additives and interfacial treatments that alter molecular packing at the nanoparticle interface and the packing frustration that primarily underlies fragility variation in glass-forming liquids.¹²⁴ Modulation of noise color can also be

expected to enhance signal discrimination in technological applications¹³⁴ and this phenomenon is no doubt operative in the recognition processes and proper biological function in diverse biological systems.¹³⁵ Examples of such systems include proteins and cell membranes where we expect the same type of collective motions and thermal noise to arise.

Sensing applications using nanoparticles, in particular, is a huge application area where cooperative motion and noise can be expected to be of crucial significance. For instance, there has been tremendous interest in assembling nanoparticles such as Au into periodic arrays for a wide range of electrical and optical applications.³² In particular, these particles are being used as gas phase sensors based on monitoring the electrical resistance of these layers when exposed to changes in environmental exposure.³² These highly sensitive sensors are currently being developed for an extremely wide range of applications, including the detection of explosives, medical diagnostics and the monitoring of industrial emissions.³² Controlling colored noise is important for the performance of these devices and requires an understanding of how the interaction of the nanoparticles with each other and their environment modifies the colored thermal noise in these materials. Applications of magneto-resistive sensors are growing at an explosive rate to meet pressing demand in medical, military, information technology and industry communities.³³ As in the case of gas phase sensors, the sensitivity of these sensors is limited by colored noise and fundamental understanding of the origin of this type of noise could greatly enhance materials development in this area.³³

One of the recurrent materials issues found in applications of nanoparticles in sensing and other electronic/optical applications that guides our planning of future work is that interactions between the particles and between the particles and their environment can greatly influence the nanoparticle noise characteristics. For example, the colored noise fluorescence intensity fluctuations of clusters of CdSe quantum dots have been measured to be different from the isolated nanoparticles^{136, 137} (See Part II for further discussion of energy state blinking and its relation to collective motion) and synchronous photoluminescence has been observed in semiconducting quantum wires¹³⁸ that can be reasonably modeled as linear arrays of quantum dots. This noise coherence effect has evident significant implications for applications (solid state lighting sources, biomedical imaging, high efficiency solar cells, optical electronic components of quantum computers, etc.) that are under development.¹³⁹ Blinking is also sensitive to whether the particles are dispersed in solution or deposited on a substrate.¹⁴⁰ In response to these numerous observations that colored noise of nanoparticles depends on their environment, we plan to systematically study how the collective dynamics and noise of nanoparticles become *coupled* through interaction by simply allowing our Ni nanoparticles to come into contact or by placing the nanoparticles on supporting solid substrate of various kinds and roughness. Since the nanoparticles in arrays are often interrogated with laser radiation, we also plan to investigate how the noise and collective motion can be modulated by the rapid heating that normally accompanies irradiation. Emergent nanotechnology applications require some understanding of how nanoparticle interaction effects affect the noise characteristics of particles configured and supported in position in devices. The noise sensitivity is not entirely

a nuisance; this effect also offers opportunities for measurement if the coupling between the nanoparticles and their environment can be understood

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

HZ gratefully acknowledges the support of the Natural Sciences and Engineering Research Council of Canada. JFD acknowledges support of this work under the NIH grant (1 R01 EB006398-01A1).

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Figure 1.

(a) String-like collective atomic motion on the surface of a Ni nanoparticle at equilibrium. The lines denote Ni atoms that belong to the same collective atom movement and the colors are introduced to help discriminate between distinct strings. (b) The mean ‘string length’, $\langle n \rangle = \sum n P(n, t)$, provides a natural measure of the scale of cooperative particle motion in strongly interacting liquids, where $P(n, t)$ is the probability of finding a string of length n in time interval t . Atomistic simulations of glass-forming liquids indicate that the distribution of string lengths $P(n)$ is generally an exponential function of n , $P(n) \sim \exp(-n/\langle n \rangle)$, to an excellent approximation. The inset shows the average string length $\langle n \rangle$ as a function of reduced temperature for NPs of radius ($r = 1$ nm and 2 nm) at $t = t^*$, where the non-Gaussian parameter, δ (see text for definition) exhibits a maximum. The average ‘string length’ L is then defined as, $L = \langle n \rangle$. In our previous paper⁵, we calculated the average string length $\langle n \rangle$ at the time interval where the mean string length shows maximum, which led to a somewhat temperature dependence of $\langle n \rangle$ than in the present figure.

Figure 2. Change in string length in Ni NP ($N = 2899$; NP radius = 2 nm) interfacial region due to Ag, Au and Pt alloying at $T = 900$ K with up to an 18 % relative mass of additive metal. Dashed lines are added to guide the eye.

Figure 3.

(a) Potential energy of NP with $N = 369$ Ni atoms as a function of simulation time at $T = 1000\text{K}$ and 1200K . (b) Power spectra $P_E(f)$ of the fluctuation of the potential energy of interfacial region of NP (radius ≈ 1 nm).

Figure 4.

Power spectra $P_{DWF}(f) = |\int \langle u(t)^2 \rangle e^{-2\pi i f t} dt|^2$ of the fluctuation of the mean square particle displacement $\langle u^2 \rangle$ (Debye-Waller Factor) of atoms in the interfacial region of $N = 2899$ NP in the temperature range from 1000 K to 1500 K.

Figure 5.

Noise exponent of $\langle u^2 \rangle$ versus scale of collective motion, $L - 1$. MD simulations were performed for Ni NPs with 18 % Pt, Au and Ag (relative mass) for $N = 2899$ based upon the Sutton-Chen alloy potentials. The additive atoms were initially uniformly distributed on the interface of the NP.

Figure 6.

Comparison between α_{DWF} from simulation and exponent α from theoretical prediction of Eq. (11) for $N = 2899$ and $r = 2$ nm NP. The inset shows power law fitting of L [Eq. (12)] with $\kappa = 0.42$ and $C = 1$ (solid line) and dashed line indicates the prediction of α for a fragile polymer melt where $\kappa = 2$ and $C = 7$. Evidently, the strength of the T dependence of L of $r = 2$ nm Ni NP cannot be well described by Eq. (12) with $\kappa = 2$, which is appropriate for bulk GF liquids. A smaller exponent $\kappa = 0.42$ better describes the glassy NP interface. This difference between the interfacial dynamics of NP and bulk GF liquids is to be expected since the glassy NP interfacial layer ranges from being thick, or three dimensional, near T_m to atomically thin or a nearly two dimensional form at low T . Such a change in effective dimensionality does not arise in bulk GF liquids.