Reply to comment on "The properties of free polymer surfaces and their effect upon the glass transition temperature of thin polystyrene films" by S.A. Hutcheson and G.B. McKenna

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Abstract. In this reply we address the comment by Hutcheson and McKenna regarding our recent manuscript [EPJE **15**, 473 (2004)] which studies the embedding of gold (Au) nanoparticles into Polystyrene (PS) surfaces. In particular, we clarify comments concerning the force used to model the embedding process. We also repeat our simulations using correct values for the creep compliance $J(t)$. We show that these new simulations more accurately describe the data presented in our original paper and reinforce our main conclusions regarding the nature of the properties of free polymer surfaces. Finally, we address their inability to reproduce our simulation results by showing that the use of their force [Phys. Rev. Lett. **94**, 076103 (2005)] in our embedding simulations enables us to mimic their own simulation results.

PACS. 64.70.Pf Glass transitions – 65.60.+a Thermal properties of amorphous solids and glasses: heat capacity, thermal expansion, etc. – 68.15.+e Liquid thin films – 68.35.Ja Surface and interface dynamics and vibrations

Hutcheson and McKenna's (HM) comment [1] regarding our manuscript introduces a series of questions about our simulation results. In this reply we discuss the differences between the force used in our original simulations [2] and those used in the simulations of HM [3]. We address the main concerns expressed in the comment and conclude by showing that in addition to being able to produce the simulations presented in reference [2] we are also able to reproduce (to within 1–2 K) the results of the HM simulations [3], with the residual discrepancies most likely being related to a difference in the way the Poisson ratio is treated.

Embedding mechanism

We begin by considering the form of the force used to describe the embedding process. There is a fundamental physical difference between the force we used in reference [2] and that used in reference [3]. In particular, we

assume a rapid initial coverage of the nanoparticle and that the embedding is driven by PS surface tension, while HM assume the embedding is driven by the gold-PS work of adhesion. HM state that the discrepancies in the magnitude of the forces that are used in the two studies leads to behavior that is consistent with differences in embedding temperatures of 3–5 K and that these differences are not significant. We contest this view as for temperatures near T_g a difference of 3–5 K would give rise to a significant difference in the material properties of the polymer. Moreover, the lowest experimental temperature studied is only 7 K below the measured glass transition temperature, and the entire temperature range studied in the original experiments (and thus the range used for simulations) is 15 K. Our assertion (supported by simulations both in Ref. [2] and below) is that it is these differences in the driving force that account for the different conclusions of the HM and STF (Sharp, Teichroeb, Forrest) studies.

In our calculations, the magnitude of the force used is comparable to the surface tension of PS and is a factor of ∼25 smaller than the corresponding gold-PS work of adhesion that was used in reference [3]. Our reason for

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choosing a mechanism where the surface tension of PS provides the driving force is that it gives the magnitude of the embedding force that best describes the embedding data at temperatures, $T > T_g$. We expect that the surface of the PS would have the same properties as the bulk polymer for $T > T_g$ and take the view that *any* model of the embedding process *should* be able to accurately predict the embedding behavior at $T > T_g$. No such condition was imposed in the simulations performed by HM [3] and their simulation temperatures differ from the experimental temperature by ~ 6 K for the above T_g embedding data.

An important difference between the approaches that were used in the two different embedding models is that our calculations incorporate a non-zero contact angle between the gold and PS while HM's do not. This was motivated by observations that after long times, the spheres do not fully embed in to the PS surface at $T > T_g$. We have recently performed more detailed studies of nanoparticle embedding into PS at these temperatures and some of the results are shown in Figure 1. This graph shows the final embedding height of gold nanoparticles as a function of the nanoparticle diameter after thorough annealing at $T > T_g$. The atomic force microscope images in the inset of this figure show data for 50 nm Au nanoparticles that were taken (on different parts of the sample) before and after embedding into the surface of a PS sample at 423 K for 24 h. The situation shown in these images is expected to be extremely close to the equilibrium embedding condition for these nanoparticles. The image clearly shows that a non-zero equilibrium embedding height (or contact angle) is observed. This result is not surprising as the gold surface is not pure gold, but is likely to be covered with a salt coating. This coating is caused by the condensation of counter-ions on the surface of the particles during drying and occurs as a result of the charges on the gold surface that are used to stabilize the particle suspensions. We expect therefore that the final contact angle will also depend on the salt coating. This will result in sample to sample variations where the gold nanoparticles come from different batches. Differences in the surface chemistry of the particles are therefore likely to account for the observed differences in the embedding kinetics for what were nominally the same diameter nanoparticles. In our previous study [2], the embedding experiments were performed at $T > T_g$ and $T < T_g$ using the same batch of spheres. The $T > T_g$ studies were used to determine the equilibrium contact angle for each batch. This allowed us to calibrate the surface properties of each set of particles separately and enabled us to perform the $T < T_g$ studies with confidence. This addresses the concerns raised by HM relating to variations in the measured embedding kinetics in different experiments.

Embedding calculations

Hutcheson and McKenna show results of calculations that were performed using the Heaviside calculus in conjunction with our force function. These calculations predict that the particles should 'rebound' after approximately
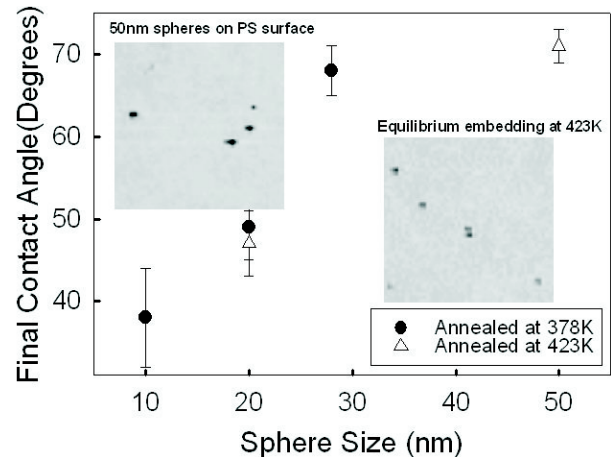

Fig. 1. Non-zero contact angle for PS on gold nanoparticles. The main panel shows the contact angle of PS on gold nanoparticles as a function of the nanoparticle diameter for particles that have been annealed on PS surfaces for 24 h. Annealing temperatures of 378 K (closed circles) and 423 K (open triangles) were used. The atomic force microscope images shown in the inset were collected from a set of 50 nm Au nanoparticles before and after embedding into a PS surface at 423 K. The image size is $5\,\mu$m $\times$ $5\,\mu$m, and the max height is 50 nm.

1000 s of embedding. HM attribute this behaviour to the visoelastic recovery of the polymer in response to the decreasing force in our model as the particles embed. Clearly, such a recovery does not occur in the experiments as the particles continue to embed at temperatures $T > T_g$ until an equilibrium embedding height is achieved. Similarly, our calculations do not show this rebound effect. We note that the integral used in all of the calculations is based on the original calculation of Lee and Radok [4]. As noted in the original reference and in many subsequent works, this integral is only valid as long as the contact boundary is monotonically increasing (i.e. when the particles are less than half way embedded). Solutions where the contact area has one or more maxima have been presented by Graham [5] and are given in many standard texts on viscoelasticity [6]. Since the HM simulations are taken to times beyond those for which the condition $h < R$ is first violated, HM are using the expression beyond its region of validity and any conclusions drawn from the calculations in this embedding region should be carefully scrutinized.

Hutcheson and McKenna note a number of 'quantitative errors' in our original calculations. The first of these is related to the use of incorrect values of the creep compliance, $J(t)$, [8] in the STF simulations. As these authors state, the values were supplied in cm^2/dynes but were used as if they were given in Pa^{-1}. We have repeated our simulations using the correct $J(t)$. A consequence of this is that we no longer need the prefactor that was used in reference [2] to get good agreement with the $T > T_g$ data. Figure 2 shows experimental data that has been reproduced from reference [2] along with the results of these new simulations. This figure clearly shows that the conclusions of our original manuscript are supported by our
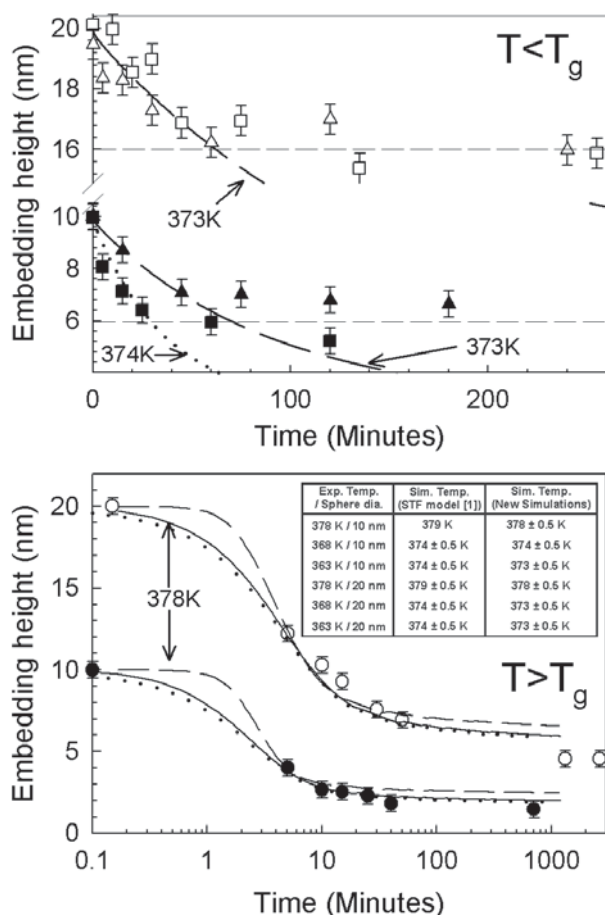
Fig. 2. Plots showing the predictions of the STF embedding model that were calculated using the correct values of the creep compliance, $J(t)$. Data points are shown for nanoparticle embedding at 378 K (circles), 368 K (squares) and 363 K (triangles). Data for 20 nm and 10 nm diameter nanoparticles are shown as the hollow and solid symbols respectively. Simulation results were calculated using a 1 s time step and are shown for the different sphere sizes using simulation temperatures of 378 K (solid lines), 373 K (dashed lines) and 374 K (dotted line) respectively. The dashed and dotted lines in the bottom panel are the results of calculations that were performed at 378 K using a 10 s and 0.1 s time step respectively. Horizontal dashed lines represent the mean maximum embedding observed for $T < T_g$. The inset shows a table summarising the main results of our previous simulations [2] and the results of our new simulations, for each nanoparticle diameter and each experimental temperature used.

Fig. 3. Plots showing the results of simulations performed using the STF integration method with the force derived by Hutcheson and McKenna. Data points are shown for spheres embedding at 378 K (circles), 368 K (squares) and 363 K (triangles). Data for 20 nm and 10 nm diameter spheres is shown as the hollow and solid symbols respectively. Simulation results are also shown for the different sphere sizes using simulation temperatures of 368 K (dashed lines), 369 K (dotted lines) and 372.5 K (solid lines). The inset shows a table summarising the main results of HM's simulations [3] and the results of our simulations using the HM form for the embedding force. Simulation results are summarised for each sphere diameter and for each set of experimental temperatures used.

new simulation results (i.e. the quantitative prediction of the embedding dynamics for $T > T_g$ and evidence for enhanced dynamics at $T < T_g$). We note however, that the embedding simulations do not follow the experimental data closely for embedding heights, $h < R$. This is not a cause for concern because the viscoelastic contact mechanics equations (and therefore the simulations) are not valid in this regime [6].

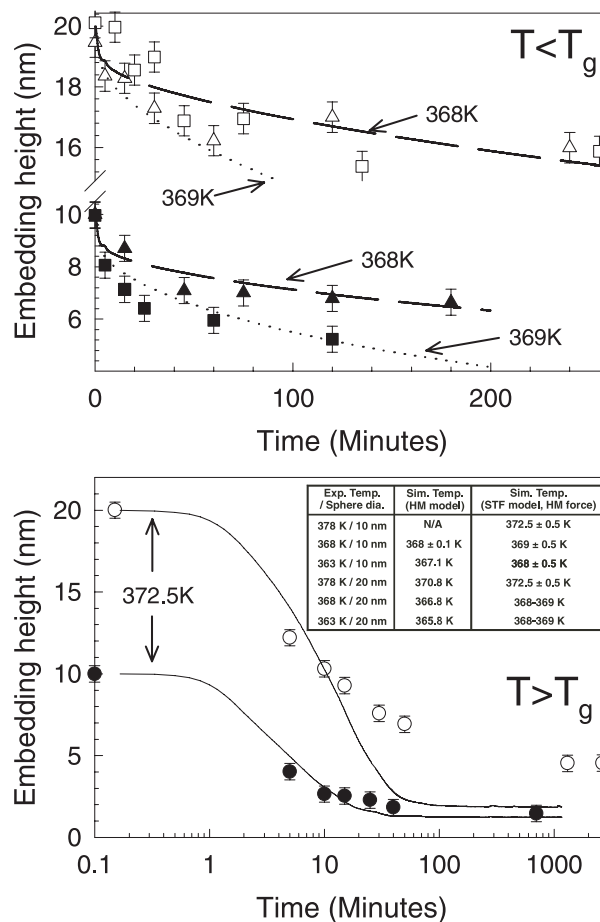The second quantitative error identified by Hutcheson and McKenna relates to the step size dependence of our

embedding calculations at early times. We acknowledge that our original calculations do have an intrinsic step size dependence when the embedding time is comparable to the step size used. This is to be expected and is exagerrated in semilogarithmic plots of the embedding kinetics of the particles similar to those shown in Figure 3 of HM's comment when the embedding time is comparable to the step size used in the calculations. The results of the calculations shown in both panels of Figure 2 were generated using a 1 s step size. The bottom panel of this figure also shows the results of embedding calculations that were performed using a step size of 0.1 s (dotted lines) and using a simulation temperature of 378 K. At this temperature we expect the step size dependence of

the simulations to have the greatest effect in our calculations. As can be seen from this figure, the calculations that are performed using step sizes of 0.1 and 1 s agree within the limits defined by the experimental error bars. This indicates that the calculations are convergent upon the true physical behavior of the model on the time scales studied in the embedding experiments. The dashed lines in the bottom panel also show the results of calculations that were performed using a 10 s step size for comparison. This figure shows that changing the step size that is used in the calculations does not alter the conclusions of our original paper i.e. that the embedding can be accurately described for $T > T_g$ using the experimentally determined temperatures and that for $T < T_g$ the embedding kinetics at all the temperatures studied are best described using a simulation temperature $T_{sim} \sim 373\,\mathrm{K}$ that is higher than the measured sample temperature.

We now turn to HM's claim that they are unable to reproduce the results of our simulations using the STF force in their calculations. While we cannot comment on why this is the case, we can perform a similar test. Clearly, if both models use the same integral equations to describe the embedding dynamics of the spheres, then simply changing the force should enable us to reproduce each others simulation results. The only difference in this case is that we have chosen to use a time independent Poisson ratio in our simulations. This will have a difference in simulation height values of at most a few 10's of percent, and does not change the conclusions of the paper. Figure 3 shows the results of simulations that were performed using our direct numerical integration method in conjunction with the force used by HM [3]. These results clearly show that we are able to reproduce the key results of the simulations performed by Hutcheson and McKenna to within 1–2 K in each case and indicate that simply changing the form of the force results in agreement between the two separate studies. This also addresses HM's concerns about the use of the explicit forward Euler method in our calculations.

Discussion

The difference in the 'apparent' T_g shifts that are reported by HM [3] define a range of T_gs of $\sim$10–11 K. This is comparable to the range of apparent T_g shifts that can be inferred from our simulations using the HM force and is also comparable in magnitude to the shifts that are implied in our below T_g simulations (i.e. simulation temperatures of 373 K for embedding experiments performed at 363 K). This implies that there is a significant amount of agreement between the two sets of calculations, but that the different conclusions are a result of the mechanism chosen to describe the embedding. In our simulations we use a force function that provides agreement between experiment and simulation for $T > T_g$. Within this framework, we get an initial embedding at $T < T_g$ that is characterized by a temperature greater than the sample temperature. In the simulations of HM, they get embedding for $T < T_g$ that is described by the experimental tempera-

ture, but for $T > T_g$ there is a large difference between sample and rheological temperature. In either case there is a temperature region where the sample and rheological temperatures are significantly different. The ability to choose between them becomes a matter of determining the correct physical mechanism. Given the nature of the problem, we believe agreement in the melt to be a minimal requirement of any model/mechanism.

Finally, we conclude by addressing HM's comment that the enhanced surface mobility observed in our original nanoparticle embedding studies does not account for the large reductions in the T_g of ultrathin free standing films of polystyrene. We agree that the embedding studies cannot account for the observed T_g reductions in free standing PS films directly, but when considered in combination with the results of other studies, the embedding studies help to provide a convincing argument for the existence of enhanced surface dynamics being responsible for the T_g reductions in thin polymer films. In previous experimental studies we have shown that it is possible to remove the thickness dependence of the T_g in thin supported films of polystyrene by carefully manipulating the polymer films to ensure that there are no free surfaces in the system [2,10]. These experiments have shown that correctly capping the free surface results in the measurement of bulk T_gs in PS films as thin as 7 nm and has provided extremely strong evidence that it is the near surface region that is responsible for the T_g reductions in thin PS films. One issue that is raised by HM is that in the embedding studies that were performed at temperatures $\sim$7 K below the bulk T_g, the surface layer has properties that are similar to a layer that is only 10 K above this temperature. Therefore this single observation can not account for large T_g reductions (such as those of $\approx$70 K that have been observed in free standing PS films [11]). However, the surface region does not necessarily need to have properties that differ from the bulk by 70 K at all temperatures for it to produce T_g reductions of 70 K in these samples. The observed T_g reductions could be accounted for by a decoupling of the temperature dependence of the properties of the surface layer and the bulk polymer. In such a scenario, cooling the sample below $T_g(bulk)$ would result in vitrification of the bulk of the sample, but the surface would continue to behave as if it has a temperature near $T_g(bulk)$. Preliminary evidence for the existence of such a decoupling of the temperature dependent properties of the surface and the bulk have been provided in similar embedding studies to the ones reported in our original manuscript [12]. These earlier experiments studied the embedding of 20 nm diameter colloidal gold nanoparticles into PS surfaces at sub T_g temperatures ($\sim$313 K) and showed that these particles embedded by a distance of 4 nm over a period of 8 h. Assuming that our force function is valid and that these spheres have similar surface properties to the ones used in the current study, a calculation of the resulting embedding kinetics (not shown) reveals that a simulation temperature $T \geq 371\,\mathrm{K}$ is needed to describe these embedding kinetics. This implies that the material properties of the surface have only changed by amount that corresponds to

a temperature shift of 1–2 K when the bulk properties of the polymer have changed by $\sim$50 K. This suggests that the temperature dependence of the properties of the near surface region is significantly different (and weaker) than that of bulk PS. These combined studies [2,10,12] could account for the magnitude of the T_g reductions that are observed in free standing PS films.

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