

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

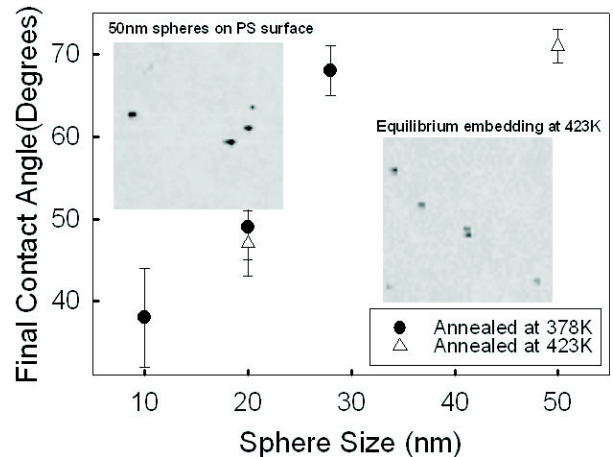


Fig. 1. Non-zero contact angle for PS on gold nanoparticles. The main panel shows the contact angle of PS on gold nanoparticles as a function of the nanoparticle diameter for particles that have been annealed on PS surfaces for 24 h. Annealing temperatures of 378 K (closed circles) and 423 K (open triangles) 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 $5 \mu\text{m} \times 5 \mu\text{m}$, and the max height is 50 nm.

1000 s of embedding. HM attribute this behaviour to the viscoelastic 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

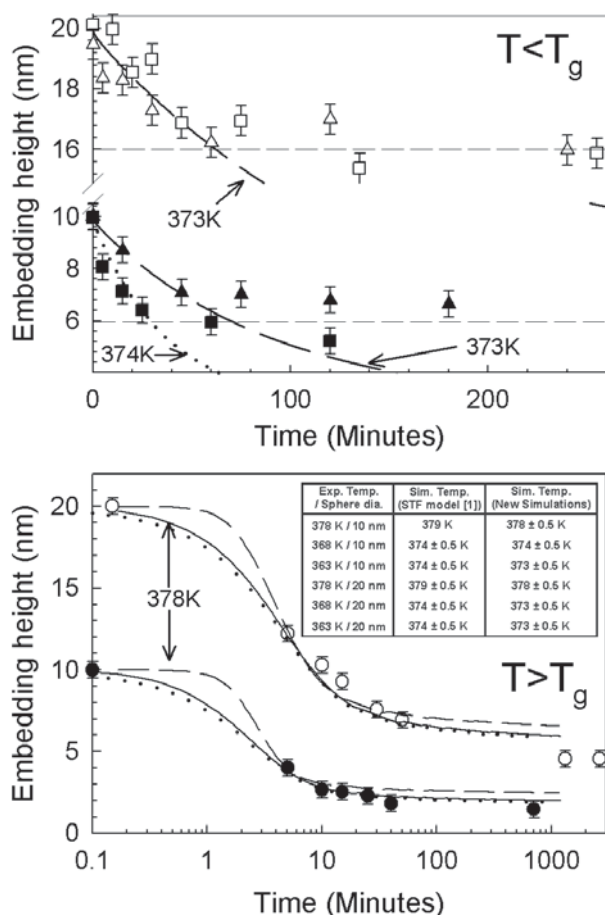


Fig. 2. Plots showing the predictions of the STF embedding model that were calculated using the correct values of the creep compliance, $J(t)$. Data points are shown for nanoparticle embedding at 378 K (circles), 368 K (squares) and 363 K (triangles). Data for 20 nm and 10 nm diameter nanoparticles are 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.

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

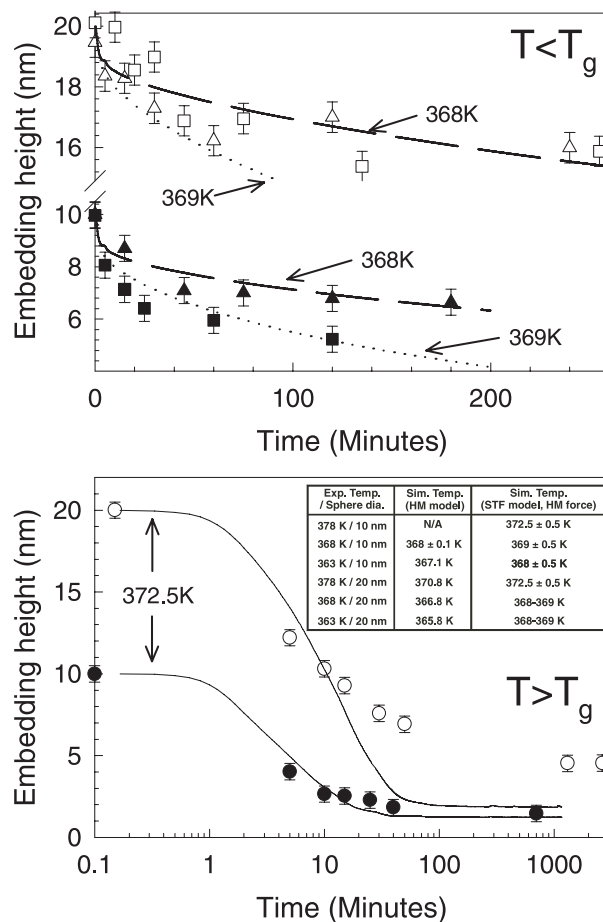


Fig. 3. Plots showing the results of simulations performed using the STF integration method with the force derived by Hutcheson and McKenna. Data points are shown for spheres embedding at 378 K (circles), 368 K (squares) and 363 K (triangles). Data for 20 nm and 10 nm diameter spheres is shown as the 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.

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 exaggerated 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 $T_{sim} \sim 373$ 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_g s of ~ 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_g s 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 ~ 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 ≈ 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 $T_g(\text{bulk})$ would result in vitrification of the bulk of the sample, but the surface would continue to behave as if it has a temperature near $T_g(\text{bulk})$. 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 (~ 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 $T \geq 371$ 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 ~ 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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Comment on “The properties of free polymer surfaces and their influence on the glass transition temperature of thin polystyrene films” by J.S. Sharp, J.H. Teichroeb and J.A. Forrest

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Abstract. Sharp, Teichroeb and Forrest [J.S. Sharp, J.H. Teichroeb, J.A. Forrest, Eur. Phys. J. E **15**, 473 (2004)] recently published a viscoelastic contact mechanics analysis of the embedment of gold nanospheres into a polystyrene (PS) surface. In the present comment, we investigate the viscoelastic response of the surface and conclude that the embedment experiments do not support the hypothesis of a liquid surface layer of sufficiently reduced “rheological temperature” to explain reports of very large reductions in the glass temperature of freely standing ultrathin polystyrene films. We also report some errors and discrepancies in the paper under comment that resulted in an inability to reproduce the reported calculations. We present our findings of error in a spirit of clarifying the problem of embedment of spheres into surfaces and in order that others can understand why they may not reproduce the results reported by Sharp, Teichroeb and Forrest. In the comment, we also examine the effects of the magnitude of the forces that result from the polymer surface-nanosphere particle interactions on the viscoelastic properties deduced from the embedment data and we provide a comparison of apparent surface or “rheological” temperature vs. experimental temperature that indicates further work needs to be performed to fully understand the surface embedment experiments. Finally, we comment that the nanosphere embedment measurements have potential as a powerful tool to determine surface viscoelastic properties.

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

1 Introduction

In 2003 Teichroeb and Forrest [1] performed experiments in which the rate of embedment of colloidal gold nanoparticles placed onto the surface of a spin cast polystyrene film was measured at different temperatures from above to below the bulk glass transition temperature. Based on the raw embedment depth vs. time data, they interpreted their results as supporting the hypothesis that there is a liquid-like layer on the polystyrene surface [1]. In 2004 O’Connell et al. [2] and Sharp et al. [3] (STF) applied viscoelastic contact mechanics models to these data in order to provide a quantitative comparison between the surface properties and the bulk properties of polystyrene. The results of these and a subsequent work by Hutcheson and McKenna [4] (HM) in 2005 gave conflicting interpretations of the surface behavior. STF interpreted the results as implying that there is a liquid layer at the polystyrene surface and this can partially explain the large reductions observed in the glass transition temperature of ultrathin polystyrene films [5]. On the other hand, HM interpreted

the nanosphere embedment experiments to show little difference between surface and bulk viscoelastic properties of polystyrene. The purpose of the present article is to consider differences in interpretation and the significance of the experiments themselves as regards the determination of surface behavior of polymeric materials and to explore some of the reasons for quantitative differences between the STF and HM works.

The work is constructed so that we consider the meaning of the nanosphere measurements and where such measurements may be useful. We discuss the differences between the rheological temperature (T_{rheol}) or surface temperature that we define subsequently and the experimental temperature (T_{exp}) and show that, though they are different, the differences are insufficient to explain large changes in the glass transition temperature of ultrathin films as being due to high surface mobility or extremely low glass transition of the surface. We also argue that the nanosphere embedment measurements can be a useful tool to extract surface rheological properties.

Included in our discussion is a section that points out some errors in the STF reference [3]. These are provided

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for completeness for readers who may be interested in reproducing the results of either STF or HM. Importantly, these errors are not the cause of the differences in interpretation between HM and STF. We also point out that there is a difference in the force functions used by the two groups to “drive” the nanosphere into the sample. We show, with quantitative estimates, that the differing force functions are not the cause of significant differences in the estimates of surface properties.

2 Analysis

2.1 The viscoelastic contact mechanics problem

The problem of nanosphere embedment into a viscoelastic surface was early addressed by Lee and Radok [6] and by Ting [7]. These solutions are viscoelastic extensions of the Hertzian contact problem. Equation (1) shows the Lee and Radok model adapted for apparent sphere height, $h(t)$, as a function of time, t , on a viscoelastic surface:

$$h(t) = 2R - \left[\frac{3(1-\nu)}{8\sqrt{R}} \int_0^t J(t-\xi) \left[\frac{dP(\xi)}{d\xi} \right] d\xi \right]^{2/3} \quad (1)$$

where the applied load is $P(t)$ and $J(t)$ is the shear creep compliance. R is the sphere radius and ν is Poisson’s ratio. Both HM and STF used the Lee and Radok [6] solution, but HM further added to the problem by applying the ideas of Ting [7] to include a time-dependent Poisson’s ratio in their solution. The major differences in solutions between STF and HM were in the quantitative numbers used for the creep compliance in the analysis, the need by STF to use a “correction factor” of 7 to their force function to obtain agreement between their solution of equation (1) and the data, and the methods of numerical integration of equation (1) for the specified force $P(t)$ that pulls the sphere into the polystyrene surface. Importantly, as shown quantitatively in a subsequent section, because of the $2/3$ power dependence of the embedment depth on the integral of the force history in equation (1), the differences in the magnitudes of $P(t)$ do not have a significant effect on the results.

2.2 Embedment data

Figure 1 shows data for the embedment of 10 nm and 20 nm gold spheres into a polystyrene surface at 378 K. It is such data that can be used to test equation (1) or to use equation (1) to extract rheological properties, i.e., $J(t)$. We point out that the data are those reported by Teichroeb and Forrest [1] and by Sharp et al. [3]. Both sets of data are reproduced as there is a misstatement in the STF paper that “. . . most of this data has been reproduced from reference {current reference 1}”. As shown in Figure 1, the data reported in reference [1] for the embedment of both the 10 and the 20 nm spheres at 378 K do not

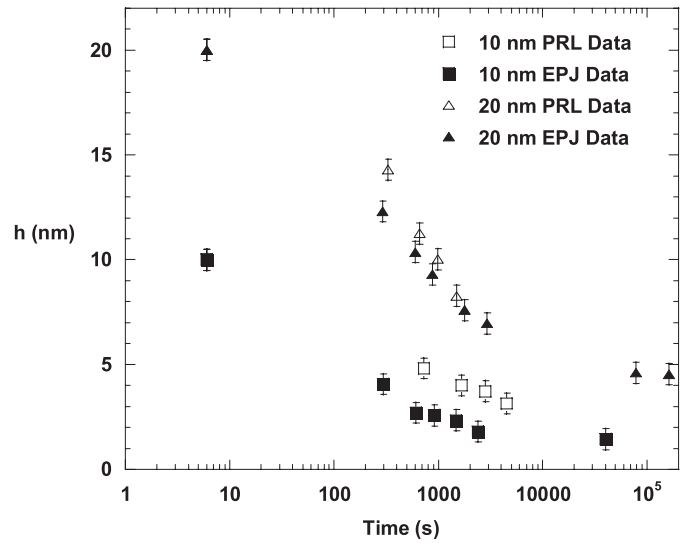


Fig. 1. Comparison of 10 and 20 nm embedment data at 378 K from reference [3] (solid symbols) and reference [1] (open symbols). Zero time data was offset by 0.1 min (6 s). This is the same offset used by Sharp et al. [3].

match those reported in reference [3] with the exception of the point at time $t = 0.1$ min (nominal initial point). This information is important if one tries to reproduce the results reported by STF. Next we examine the problem of integration of equation (1) and prediction of the data in Figure 1.

2.3 Integration of the viscoelastic equations

2.3.1 Integration by STF [3]

In order to reproduce the calculations reported by STF in reference [3] we set-up a program to solve equation (1) that is based on the Heaviside Calculus (commonly used to solve such convolution integrals) and using the trapezoidal rule [8,9]. To do this, one needs the force function from STF and this is reproduced here:

$$P = 2\pi R\gamma \sin(\phi) \sin(\theta + \phi) \quad (2)$$

where,

$$\cos(\phi) \approx \frac{h - R}{R} \quad (3)$$

P is the load (force), γ is the surface energy of polystyrene (~ 0.035 N/m) and θ is taken to be the equilibrium PS/Au contact angle of 46° for the 10 nm spheres and 59° for the 20 nm spheres [3], and the angle ϕ is estimated from the apparent sphere height versus time data for the HM calculation.

Figure 2 shows the results for both the 10 nm and 20 nm spheres embedded at 378 K. Also shown are the calculations reported by STF [3] and our calculations using their force function (Eq. (2)). In principle, the results should be the same. Clearly, they are not. Interestingly, our calculations using the STF force function predict that

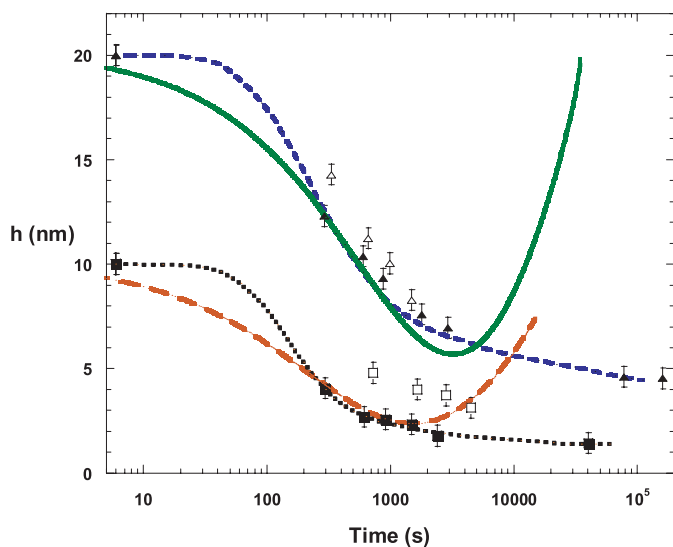


Fig. 2. Comparison of calculated and measured 10 and 20 nm sphere embedment into polystyrene surface using the STF model. Embedment data is for 378 K and is digitized and reproduced from reference [3] (solid symbols) and reference [1] (open symbols). Zero time data was offset by 6 s to fit on the log plot {procedure of STF}. The solid line is a plot of the HM solution to the Lee and Radok model (Eq. (1)) using the STF force function for 20 nm data supplied in reference [3]. The temperature used in the calculations is 378 K. The long dashed line is a plot of the HM solution to the Lee and Radok model (Eq. (1)) using the STF force function for 10 nm data supplied in reference [3]. The model reported by Sharp et al. [3] has also been digitized and reproduced from [3] (short and medium dashed lines). The temperature used in their calculations was 379 K [3].

the particle height will “rebound”, due to the viscoelastic recovery of the sphere due to the rapidly decreasing force in equation (2). It is noted that Ting [7] showed a similar viscoelastic recovery in certain decreasing load histories. The important point here is that the calculations of the sphere embedment reported by STF were not reproduced in our calculations. As a result we discovered several errors in the STF paper and the following section points those out.

2.3.2 Some quantitative errors

The quantitative errors at issue need to be understood simply for clarity for the community that would potentially try to reproduce the results of STF. First, STF assumed that the creep compliance data ($J(t)$ in Eq. (1)) given to them by Plazek [10] was in Pa^{-1} . This was not the case and the data were provided in the form of cm^2/dyne , which leads to a factor of 10 error in the numbers used in the STF paper for $J(t)$ in their numerical integrations. In the work of STF, this effect was partially offset by multiplying the forces between the polystyrene surface and the gold nano-particles by a factor of 7. This factor of 7 was deduced by determining the forces needed to embed

the spheres into the polystyrene at 378 K, a temperature which STF [3] assumed would exhibit bulk-like behavior because it was above the bulk glass transition temperature and they used Plazek [10] data shifted to a temperature of 379 K. Hence, in parlance developed later, $T_{rheol} = 379$ K for T_{exp} at $T = 378$ K [3].

The plots in Figure 2 take into account these errors, but we found that we were still unable to reproduce the STF results and Forrest and Sharp [11] graciously gave us a copy of the program they used for the integration of equation (1) using the force function of equation (2) for evaluation. We found two things that make their results differ from ours:

1. *Step size dependence*: step-size in numerical integration can be very important. Typically, there is a trade-off between accuracy and choice of step size (computational time). The program given to us by Forrest and Sharp [11] shows step size dependence and the value of the step size chosen by them was not small enough for the curves to converge to a limiting behavior. Figure 3 shows the step size dependence we obtained in running their program for both 10 and 20 nm spheres at a simulation temperature of 379 K (that used in Fig. 3 of Ref. [3]). The step sizes are in the range used in the STF paper as estimated from the initial data, discussed next. The step size issue is further magnified in the treatment of the STF force function. The derivative of their function (dP/dh) approaches negative infinity at $t = 0$. To bypass this problem, STF gave their sphere a little “nudge” into the surface at the first two steps in time. The “nudges” occur at a time related to the smallest step size and STF attempt to put an upper limit on the step size by choosing it “... such that it is well below the capillary wave roughness of a molten polymer surface and also below the roughness of a glassy polymer film (~ 1 nm as measured using AFM)” [11]. This procedure leads to a step size dependence of the short time response that is very visible in a double-logarithmic representation of sphere height vs. time of embedment (Fig. 3) and is, we think, another cause of the discrepancy between the STF and HM calculations shown in Figure 2. After the first two steps in time, the STF program uses the actual values for dP/dh . It is also noted that the program received from STF does not produce exactly the same response curve as reported in reference [3] even though we have accounted for the error in compliance and correction factor of 7. The curve of reference [3] has been digitized and reproduced in Figure 2 of this comment.
2. Another issue is that the STF program uses a modified explicit Euler method to evaluate the convolution integral in equation (1) to determine the $h(t)$ response at points past the first two steps in time. The explicit (forward) Euler method, while a valuable tool in understanding numerical techniques for evaluation of ordinary differential equations, is not recommended for practical use [12]. In addition, when this numerical technique is used, it is generally recommended that small step sizes be used and that it only be used for

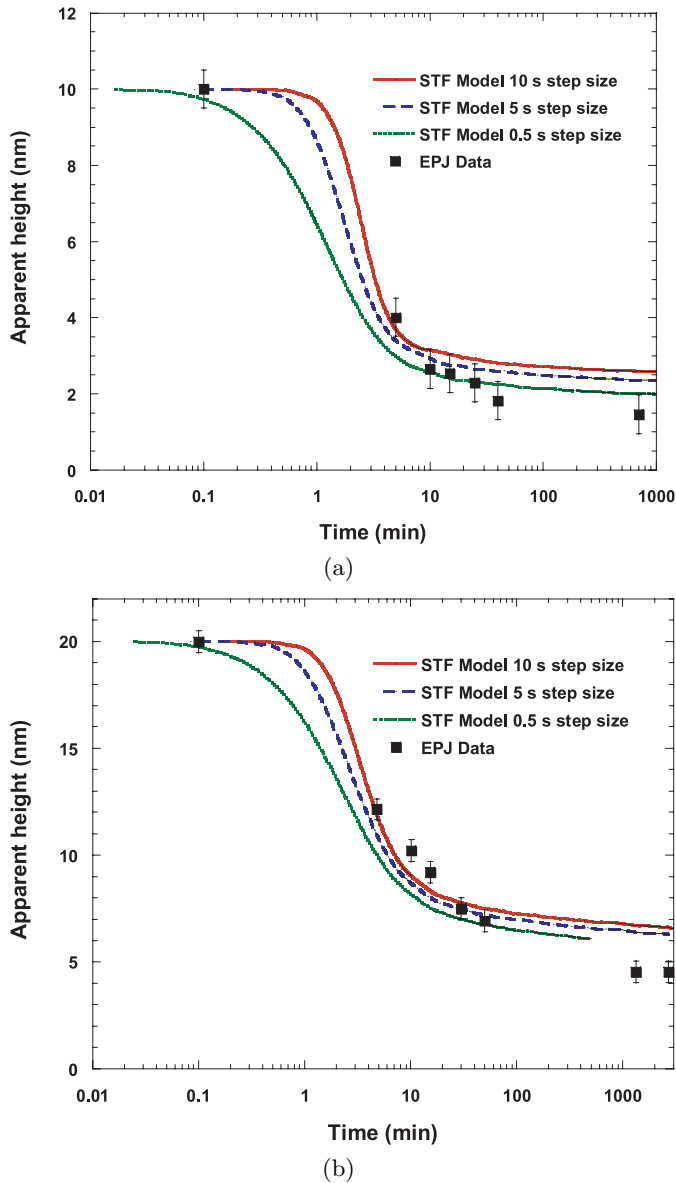


Fig. 3. (a) Step size comparison of STF Model for 10 nm spheres. The simulation temperature is 379 K. (b) Step size comparison of STF Model for 20 nm spheres. The simulation temperature is 379 K. The 10 and 20 nm simulations were performed using the program submitted to us by Forrest and Sharp [9] and modified by us to take into account the order of magnitude error in the compliance and the correction factor of 7 that occurred in reference [3].

small values away from the initial boundary condition — a condition not met here; also, the method is not recommended for stiff functions [13].

On the other hand, the HM [4] procedure to integrate the STF model takes a more classical approach widely used in solving convolution integrals in viscoelasticity. Equation (1) is evaluated using the Heaviside Calculus and the trapezoidal rule for integration [8,9]. The HM procedure uses a stretched exponential fit to the experimental em-

bedment data to produce a function for $h(t)$; this function is substituted into the STF $P(h)$ equation, thus giving a function $P(t)$ that is inserted into equation 1 and integrated numerically using the trapezoidal rule. Both computer programs are available on the World Wide Web for the interested reader as supplemental information [14].

2.4 Force functions: attraction between the PS surface and the gold particles

As indicated earlier, the force function does not have a huge effect on the results, at least in the early stages of the embedment because of the $2/3$ power on the right hand side of equation (1). For completeness, we present the HM force function and explain why the differences between the HM and STF force functions are not the cause for differences in interpretation. The HM [4] force function is based on particle adhesion to flat substrates and can be written as [4,15,16]

$$P(t) = 2\pi w_A \sqrt{R^2 - (R - \alpha(t) - h_m)^2} \quad (4)$$

where, $\alpha(t)$ is the embedment depth and h_m is the meniscus height. w_A is the thermodynamic work of adhesion and is defined as:

$$w_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \quad (5)$$

where, γ_{SV} is the surface energy of gold, γ_{LV} is the surface energy of the polymer and γ_{SL} is the interfacial energy between gold and polystyrene. The value of w_A for polystyrene and gold interaction used by HM was 1.091 N/m. It is possible that this is unrealistically high in actual situations [17] but the differences between the HM force model and the STF force model are not the cause of the different estimates in the “surface temperature” between the two studies. It is worth remarking that the differences in the HM and STF forces can be as high as a factor of 50 and we return to this shortly. It is also worth noting that the HM [4] and STF [3] force functions are arrived at by different approaches. However, there is a considerable literature on how to treat the problem of forces between particles and surfaces or particles and each other and the differences in approach are similar to those in the literature [18–27]. The reader is referred to this literature for further information.

The reasons that the force functions do not have a large effect on the estimate of the surface temperature comes from the following consideration. Since in equation (1) the particle height is expressed as the $2/3$ power of the load, the impact of the load on the embedment rate is greatly diminished. For example, the 50 fold difference mentioned for the STF and HM functions implies an embedment rate only 14 times different. This is 1.1 logarithmic decades in rate and, so, near to the glass temperature such a difference implies a 3 to 5 degree K difference in the apparent temperature relative to the glass temperature using conventional notions of the glass transition event [28,29]. This difference is similar to the uncertainties of the apparent surface temperatures obtained from the data analyses.

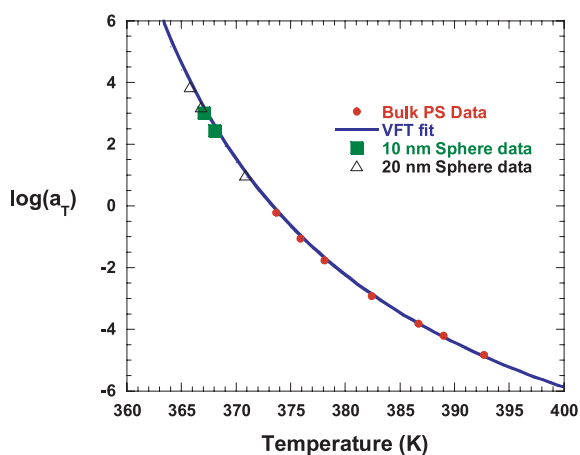


Fig. 4. VFT fit reported in reference [10] to shift factors from said reference. Small squares are shift factors for bulk polystyrene data. Also included are the shift factors for the surface rheology calculated in reference [4] for experimental data supplied in reference [1]. The large squares are for 10 nm diameter spheres. The open triangles are for 20 nm diameter spheres.

2.5 T_{rheol} vs. T_{exp}

The expression, equation (1), contains the creep compliance $J(t)$. In extracting $J(t)$ from the experimental embedment data, we found that the bulk compliance data of Plazek and O’Rourke [10] for a similar polystyrene to that used by Teichroeb and Forrest [1] gave consistency with the data with only a change in temperature from the experimental temperature, i.e., an apparent shift in the glass transition temperature. Figure 4 shows the shift factors calculated from the analysis in reference [4] for the different experiments run by Teichroeb and Forrest [1]. The Vogel-Fulcher-Tammann (VFT) [30] equation is fit using the shift factors reported by Plazek [10]. We have analyzed the data from reference [1] and determined the shifted temperature according to where the shift factors lay on the VFT fit, which we refer to as the rheological temperature or T_{rheol} . In Figure 5 we compare this rheological temperature with T_{exp} the temperature at which the experiments of Teichroeb and Forrest [1] were actually run and we observe that there is a close to linear relationship between T_{rheol} and T_{exp} and that the slope is lower than unity, i.e., the apparent surface (rheological) temperature differs from the experimental temperature and is greater than T_{exp} when the latter is below the glass temperature and lower than T_{exp} when T_{exp} is above the glass temperature. Interpretation of the result is unclear. One reasonable possibility for the differences in T_{rheol} and T_{exp} could be experimental uncertainty in these very difficult experiments, but this requires further investigation.

Figure 5 also shows that the difference between T_{rheol} and T_{exp} from the HM analysis is not greater than approximately 7 K. As discussed above, the differences in force magnitudes between the HM model (Eq. (4)) and the STF model (Eqs. (2) and (3)) do not significantly alter this finding (by no more than 3–5 K). Hence, while the STF

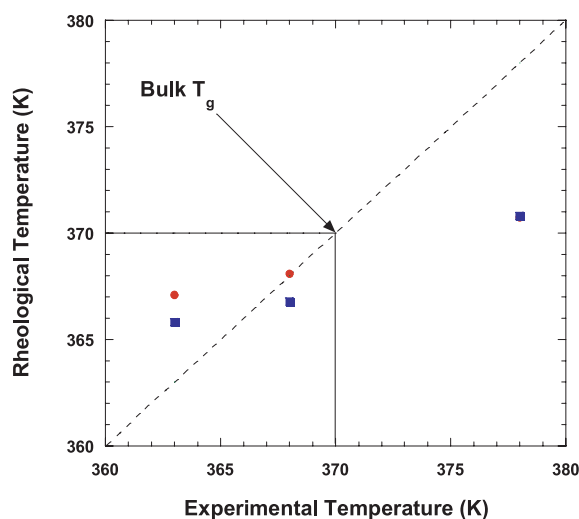


Fig. 5. Comparison of experimental temperature with the corresponding surface rheological temperature as determined by shift factor calculation from the viscoelastic contact model used in reference [4].

results do, in fact, indicate that the surface may behave somewhat differently from the bulk material, the magnitudes of mobility difference as estimated by $T_{rheol} - T_{exp}$ are insufficient to explain reported 65 K or greater reductions in the glass transition temperature of freely standing films of polystyrene [5].

3 Final comments

There is a significant controversy in the literature concerning the possible origins of the large reductions in the glass temperature seen in freely standing polystyrene films and the reader should look into this with the perspective that we know that not all materials undergo the same magnitude of reduction [31]. The information gained by the present type of work is very interesting because it does suggest that the surface exhibits greater mobility than does the bulk material, but not enough to explain the reduction of the T_g in polystyrene. At the same time, the set of analyses presented here show that it is possible to use the nanosphere embedment experiment to extract surface properties [32]. The properties can be elastic or viscoelastic. The major quantitative problem is to know the magnitude of the forces and this remains an unresolved question in surface science. Estimates of T_{rheol} are less affected by the actual force magnitudes.

4 Supplemental information

The reader who is interested can also go to <http://www.che.ttu.edu/McKennaGrp/EPJEProg.htm> to look at the computer programs and compare them. If readers do discover explicitly why the two calculational schemes seem to give different results, they are invited to let us know.

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