Gelation in an amorphous polymer: a discussion of its relation to membrane formation

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The phase equilibrium behaviour of polysulphone (PSF) in mixtures of *N,N*-dimethylacetamide (DMA) with added non-solvent, water, has been examined. The effect of solvent–non-solvent mixtures on the glass transition temperature depression was studied using differential scanning calorimetry while gel melting/gelation behaviour was examined using the falling-ball method. Analysis showed that a non-crystallizable membrane system may form a gel in the absence of a glass transition. The position of the thermoreversible sol–gel transition on the ternary phase diagram for PSF–DMA–water was determined to be invariant with respect to the time allowed for the gel to form. It is suggested that the gel melting temperature for PSF–DMA determined in the falling-ball experiments is simply that at which the viscous drag of the solution is sufficiently reduced to allow significant motion of the ball. An adequate description of both the motion of the falling ball and the gel melting temperature behaviour is provided through use of a Stokes' law calculation in which the solution viscosity is expressed as a function of temperature using the WLF equation with the glass transition temperature as the reference temperature. The implications of describing gelation in terms of a viscosity mechanism with regard to the structure formation processes associated with asymmetric membrane production are discussed in a semiquantitative manner.

(Keywords: membranes; gelation; sol–gel; glass transition; polysulphone)

INTRODUCTION

The majority of commercially available membranes are prepared by phase inversion, which involves casting a thin film of a homogeneous polymer solution onto a suitable substrate followed by immersion in a non-solvent bath. It is clear that the solvent/non-solvent flux ratio during the initial quench period strongly influences which phase transition processes will occur for a given system and ultimately, therefore, the resulting membrane morphology. Either symmetric or asymmetric ultra- or hyperfiltration membranes can be produced depending on the quench conditions. The latter type are characterized by a very dense, thin skin supported by a porous sublayer.

The role of thermoreversible gelation in the structuring process has been a question of concern in a number of studies; however, its role has been difficult to analyse theoretically since a number of mechanisms can be involved. Both crystallizable and non-crystallizable polymer solutions may undergo thermoreversible gelation directly, or, if a liquid–liquid phase separation occurs in the same temperature region as the sol–gel transition, gelation may be preceded by phase separation. Gelation may also be induced by conformational changes of the polymer molecules in solution[1].

Tan and coworkers[2,3] have examined thermoreversible gelation in a series of chlorinated polyethylene solutions and atactic polystyrene solutions. They observed that while non-crystallizable polymer solutions have equivalent gelation and gel melting temperatures, they differ for crystalline systems. Given that gelation of both the non-crystallizable and crystallizable polymer solutions exhibit the same dependence on concentration, it was suggested that a common mechanism leads to gel formation and that for crystallizable systems further stabilization of the network can be achieved through formation of microcrystallites.

Both Yang and Geil[4] and Kawanishi *et al.*[5] have reported that gelation in poly(vinyl chloride) solutions results from hydrogen-bonding interactions, with crystallization occurring subsequent to gelation. For the system poly(vinyl chloride)/γ-butyrolactone[5], it was concluded that, while spinodal decomposition may precede gelation, it is not a necessary condition.

On the other hand, several authors[6–9] have argued that gelation is a direct consequence of crystalline tie points and they offer evidence in support of this view. For example, Domszy *et al.*[6] have studied gelation in a series of homopolymers and copolymers of ethylene. They concluded that crystallization is responsible for gel formation provided a minimum polymer concentration is maintained, above which gelation can occur.

According to Wolf and coworkers[10,11], a sufficient number of intersegmental contacts between the individual polymer molecules and a minimum average lifetime of these temporary crosslinks must be achieved before thermoreversible gelation in polymer solutions can occur. The physical crosslinks can be the result of amorphous aggregates or through crystalline tie points.

Wellinghoff *et al.*[12], in studying the thermoreversible gelation of atactic polystyrene solutions, postulated that gelation in these systems occurs by liquid–liquid phase separation followed by glass transition in the concentrated

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phase, the glassy domains serving as the crosslinks. According to Arnauts and Berghmans[13], the initial polymer concentration determines whether these glassy microdomains will be dispersed in a solvated matrix of low polymer concentration or as a continuous polymer-rich glass with dispersed solvated phase. Experimental evidence is presented in the form of SEM photographs to support Berghmans' claim as well as the existence of a bicontinuous interpenetrating network structure for polymer concentrations between these two extremes[14]. It is believed that this bicontinuous network is associated with the passing from the metastable to the unstable region of the phase diagram.

It has been suggested that gelation during membrane formation by phase inversion occurs through the crossing of a viscosity boundary by non-crystallizable systems[15] or through a crystallization mechanism for crystallizable polymers[16]. Burghardt *et al.*[17] suggest, on the other hand, that liquid–liquid phase separation during quenching is a necessary prerequisite for the formation of microporous skins in ultrafiltration membranes. They also argue that, since skin formation occurs generally on the millisecond timescale, the much slower crystallization process would be kinetically excluded as a mechanism in crystallizable membrane-forming systems.

Given the apparent importance of gelation to the asymmetric membrane formation process, it would seem desirable to represent it quantitatively. By studying a non-crystallizable membrane-forming system, it is hoped that the gelation behaviour can be more clearly understood, since any difficulties associated with crystallization effects are eliminated. Polysulphone (PSF) is important in commercial membrane manufacturing and is also an amorphous polymer. For these reasons we have undertaken a study of its glass transition and thermoreversible gelation behaviour in solvent, *N,N*-dimethylacetamide (DMA), and mixtures with non-solvent, water. A complete ternary phase diagram, showing both sol–gel transition and glassy region boundaries, is constructed. The objective in this paper is to present a discussion of the resulting features of our study which we believe have application to the asymmetric membrane formation process.

EXPERIMENTAL

Materials

The polysulphone (PSF) used (supplied by Amoco Performance Products Inc., as P3500 Polysulfone) was characterized by a weight-average molecular weight of 46 000. A d.s.c. trace of the pure polymer exhibited a discontinuity in heat capacity indicative of a glass transition at 184°C. The DMA (more than 99% pure) was purchased from Aldrich Chemical Co. and used as received. Pure-component glass transition temperatures for the two diluents were taken from the literature: DMA, 146 K[18] and water, 135 K[19]. Removal of a crystallizable oligomer fraction from the as-received PSF was carried out using the method suggested elsewhere[20]. The oligomer-free PSF was determined to be totally amorphous by two separate methods (optical microscopy and d.s.c.).

Apparatus

Glass transition experiments were carried out using two calorimeters: a Perkin–Elmer DSC-4 and a DuPont 910 DSC. Both instruments were equipped with cooling accessories for subambient operation. Standards for temperature calibration were indium ($T_m = 156.6$°C), n-decane ($T_m = -29.66$°C) and *p*-nitrotoluene ($T_m = 51.64$°C). All samples were placed in volatile sample pans and sealed with a specially designed crimping tool.

Gelation experiments were carried out using an apparatus and technique similar to that described by Burghardt *et al.*[17]. Gel melting temperatures were determined using the falling-ball technique, with a 1/16 inch ball-bearing. Ball height was monitored using a cathetomer accurate to 0.005 cm. Gel setting experiments (sol–gel transition) were also performed using sealed n.m.r. tubes and the same steel balls used in the gel melting experiments.

Glass transition measurements

Samples were prepared by one of two methods. For PSF in DMA, concentrated samples were obtained by evaporating DMA from homogeneous solutions. For PSF in water, samples were prepared by soaking films in water for various periods of time. In either case, the resulting materials were placed in d.s.c. pans and weighed prior to sealing. The exact composition of the samples was determined subsequent to thermal analysis. Pans were punctured, heated in a vacuum oven for one day at a temperature in excess of the diluent boiling point, and weighed to determine the weight loss. All d.s.c. scans were made using a heating rate of 10°C min^{-1} and samples were tested at least twice to ensure reproducibility.

Gel melting/setting measurements

Appropriate amounts of PSF and DMA were weighed and sealed with the steel ball in glass tubes and then heated for 48 h in an oil bath to form a homogeneous solution. Tubes were then transferred to a second oil bath maintained at 25°C and held for 24 h to form a gel, with the ball being held near the interface by a magnet. The set gels were then transferred to a third oil bath and heated at a rate of 0.5°C min^{-1}. The ball height was recorded as a function of bath temperature for determination of the gel melting temperature in the usual manner. Gel setting times at a given temperature ranged from 1 h to 24 h and were determined by inverting a tube after a specified time period and observing whether the ball remained stationary for at least 1 h.

RESULTS

The complete phase diagram for the ternary PSF–DMA–water system at 25°C is represented in *Figure 1*. The liquid binodal and spinodal curves were obtained using the algorithm discussed by Yilmaz and McHugh[21]. The non-solvent–polymer interaction parameter, g_{13}, was determined using the technique described by Mulder and Smolders[22]. Vapour–liquid equilibrium data, taken from the literature[23], were used to generate a polynomial expression for the non-solvent–solvent interaction parameter, g_{12}, as a function of the polymer-free volume fraction of solvent, u_2. The solvent–polymer interaction parameter, g_{23}, expressed as a linear function of the polymer volume fraction, ϕ_3, was determined from a least-squares fit of the phase equilibrium equations to the experimentally determined tie line compositions and the previously determined g_{12} and g_{13} values[24].

The glassy region boundary, representing the locus of

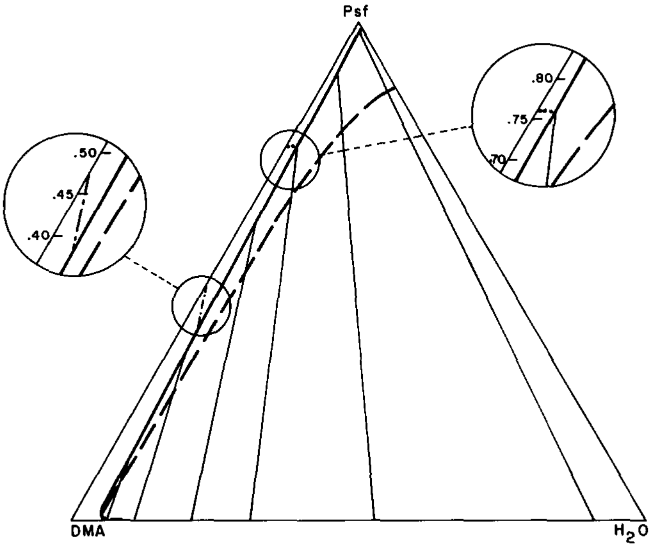

Figure 1 Liquid–liquid phase diagram for PSF–DMA–water at 25°C. Also shown are spinodal curve (– – –), glassy region boundary (· · ·) and sol–gel transition (—·—). Interaction parameters are:

$$g_{12}=0.164+1.54u_2-16.50u_2^2+90.24u_2^3-283.75u_2^4+530.74u_2^5 -583.36u_2^6+347.72u_2^7-86.75u_2^8,$$

$g_{13}=3.53$ and $g_{23}=-1.14+0.04\phi_3$, where u_2 is the polymer-free volume fraction of solvent and ϕ_3 is polymer volume fraction

compositions within the single-phase region of the phase diagram for which $T_g=25°C$, was generated using the Kelley–Bueche glass temperature depression equation generalized for ternary polymer systems containing two diluents as previously described by Burghardt *et al.*[17]. For the single-phase region of the phase diagram, any composition lying above the transition curve will become a glass at 25°C. Within the two-phase region, any overall composition in which the polymer composition in the concentrated phase is greater than or equal to that corresponding to the intersection of the glassy region curve and the binodal curve should result in the formation of a glass. Likewise, equilibrium concentrated phases outside this region should eventually become a glass as more solvent diffuses out of the cast film during the quench step.

Also represented in *Figure 1* is the sol–gel transition curve for the locus of compositions within the one-phase region of the ternary phase diagram for which $T_{gel}=25°C$. The position of this curve on the phase diagram was determined to be invariant with respect to the time allowed for gel formation. From the relationship between the sol–gel and glass transition curves shown in *Figure 1*, we conclude that a non-crystalline membrane-forming system may form a gel in the absence of a glass transition.

Insight on a simple explanation for gel formation can be gained from the comparison shown in *Figure 2* of data for the gel melting/gelation temperature with the glass transition temperature data for the binary PSF–DMA system. The temperature at which these gels both set and melt are nearly equivalent over the concentration range investigated here. While the gel melting temperature closely parallels the glass transition temperature, there is a consistent shift of approximately 90° at a given composition. Tan *et al.*[3] also determined that gel formation in atactic polystyrene solutions does not coincide with its glass transition temperature. The calculated glass transition temperature of solutions in their investigated range was at least 100°C lower than the observed gelation temperature.

The similarity in the gel melting and glass transition temperature behaviour for the binary PSF–DMA system suggests that the gel melting temperature determined in the falling-ball experiment may simply be that at which the viscous drag of the solution is sufficiently reduced to allow significant motion of the ball. Such an effect can be modelled in terms of a simple Stokes' law calculation in which the solution viscosity is expressed as a function of temperature using the WLF equation with T_g as the reference temperature. Details of the derivation are given in the Appendix.

A fourth-order polynomial expression was fitted to the gel melting data of five representative falling-ball experiments for the purpose of mathematically describing the motion of the ball as a function of solution temperature. *Figure 3* represents the corresponding evaluation of these data in a manner consistent with equation (A.5), using a value of $c_2=51.6\,K$. An average value of $c_1=14.7$ (compared with the universal value of $c_1=17.4$) and an average glass viscosity of $\eta_{glass}=1.2\times10^{17}$ cP were determined for the PSF–DMA binary system. The glass viscosity of many polymer systems is of the order of $\eta_{glass}=10^{15}$ cP (ref. 25).

Data for the gel melting behaviour of a representative PSF–DMA sample and its predicted gel melting curve using equation (A.6) with $c_1=14.7$, $c_2=51.6\,K$ and $\eta_{glass}=1.2\times10^{17}$ cP are shown in *Figure 4*. The full curve in *Figure 5* represents the predicted gel melting temperature curve for PSF–DMA using equation (A.6) with these same parameters. Also shown in *Figure 5* is the PSF–DMA gel melting temperature data. From the fit shown, we conclude that an adequate description for both the motion of the falling ball and the gel melting temperature behaviour is provided through the use of equation (A.6). For these reasons we believe that the observed thermoreversible gelation behaviour in the

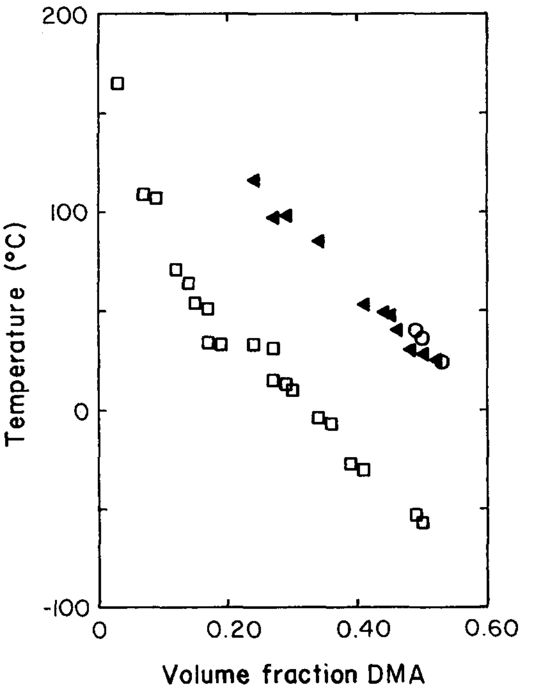

Figure 2 Gel melting temperature from falling ball (◀) and gel setting temperature (○) vs. volume fraction of DMA. Also shown are glass transition temperature data for binary PSF–DMA system (□)

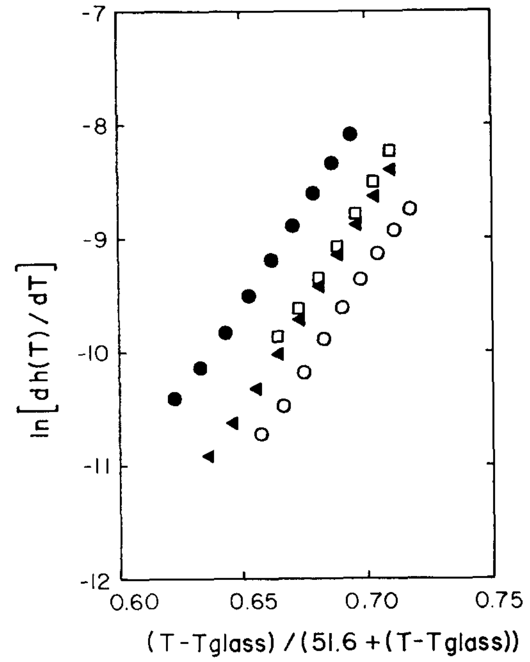

Figure 3 Evaluation of PSF–DMA gel melting data in a manner consistent with equation (A.5). The volume fractions of the polymer in solution are 0.48 (●), 0.56 (◀), 0.59 (□) and 0.76 (○)

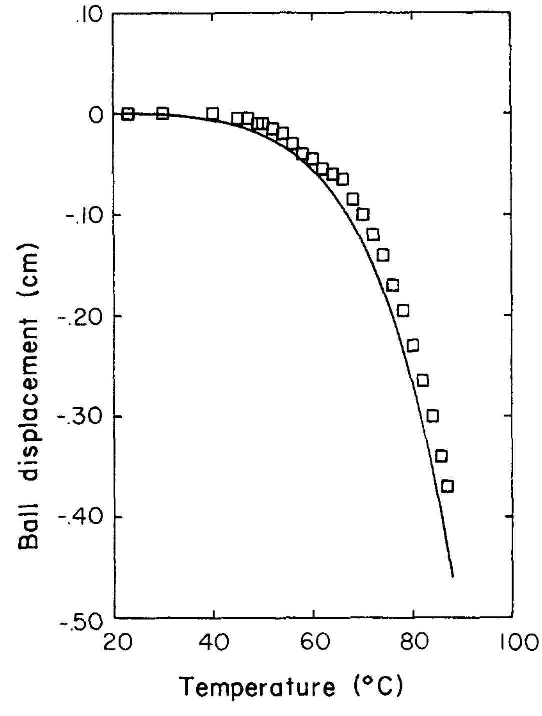

Figure 4 Gel melting data vs. temperature for PSF–DMA solution (0.56 volume fraction polymer) at a constant heating rate of 0.5°C min^{-1}. The full curve represents the predicted gel melting curve using equation (A.6) with $c_1 = 14.7$, $c_2 = 51.6$ K and $\eta_g = 1.2 \times 10^{17}$ cP

PSF–DMA binary system may be described in terms of the solution viscosity, in which a minimum viscosity must be reached before gelation can occur. For viscosities less than the threshold value the polymer chains possess sufficient mobility to move rather freely in solution. Having achieved the threshold viscosity, either through depletion of solvent or temperature quench, the polymer chains lose much of their mobility and become entangled in a complicated network structure which behaves as a gel.

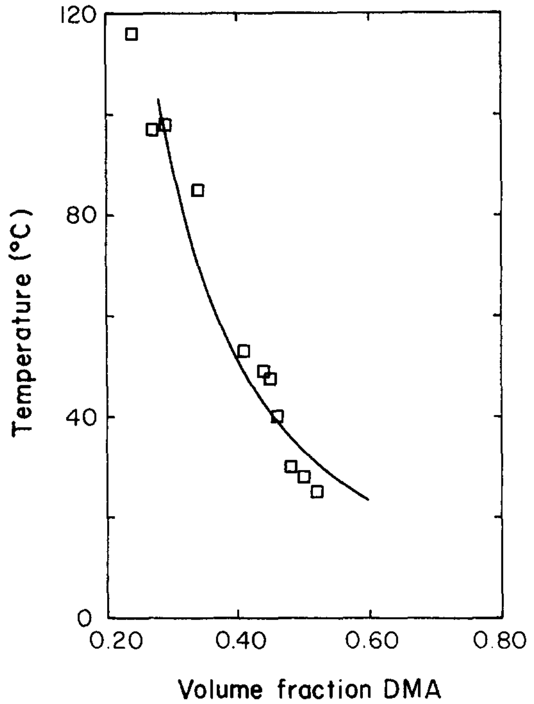

Figure 5 Predicted gel melting temperature curve for PSF–DMA using equation (A.6). Also represented are experimental gel melting temperatures from falling ball (□)

DISCUSSION

The results of our study demonstrate that a non-crystallizable membrane system may form a gel in the absence of a glass transition. Given the modelling results for the observed gelation behaviour in PSF–DMA solutions, it is suggested that the thermoreversible gelation behaviour of the PSF–DMA–water model membrane system can also be described in terms of the same viscosity mechanism. While gelation in membrane systems may be explained in terms of solution viscosity, it was not determined in this investigation whether gelation is a sufficient condition for providing structural rigidity to the resulting membrane. Since diffusion of both non-solvent and solvent does not cease with the onset of gelation, continued diffusion may lead the membrane system into the glass transition region, provided that such a region exists on the phase diagram. Solidification via crystallization may also occur subsequent to gelation in crystallizable membrane systems.

According to Smolders and coworkers[26,27], the gel region cannot be exactly located on the ternary phase diagram because of kinetic constraints. As previously discussed, the position of the sol–gel transition on the phase diagram for the ternary PSF–DMA–water system was determined to be invariant with respect to the time allowed for the gel to form. (The gel setting time ranged from 1 h to 24 h in this investigation.) Although this result appears to contradict the previous claim, the sol–gel transition may well shift to slightly higher polymer concentrations for gel setting times of the order of the timescale characteristic of membrane formation. Owing to limitations in the experiment, sol–gel transition measurements could not accurately be determined for gel setting times within this short timescale.

Representation of sol–gel transition curves on the phase diagrams of crystallizable membrane systems for gel setting times much in excess of the timescale characteristic of membrane formation is probably of little value in describing the role of gelation in membrane formation for these systems. For timescales much larger than those characteristic of membrane formation it has been demonstrated that the processes of gelation and crystallization in PPO are highly related[17]. However, for the much shorter timescales characteristic of membrane formation, especially the millisecond timescale suggested for skin formation, the crossing of a gel region boundary (sol–gel transition) as described in terms of the kinetically much slower crystallization process probably does not occur. That minimal crystallinity is observed in PPO membranes strengthens this assertion. However, such a transition is possible during membrane formation if gelation in these crystallizable systems is also described in terms of solution viscosity.

SUMMARY

The purpose of this study has been to investigate the possible roles of various phase transition processes in the formation of asymmetric membrane structures. The glass transition and thermoreversible gelation behaviour in a non-crystallizable model membrane system (polysulphone (PSF) in dimethylacetamide (DMA) solvent with added non-solvent, water) were examined. It was concluded that a non-crystallizable membrane system may form a gel in the absence of a glass transition. In addition, it was determined that the gel melting temperature behaviour for PSF–DMA may be adequately represented in terms of a solution viscosity mechanism. A discussion is given of the role of gelation in both the ternary phase diagram for PSF and its relation to asymmetric membrane formation.

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APPENDIX

From a simple force balance on a falling ball of diameter D and density ρ_s under Stokes' law conditions in a fluid medium of viscosity η, it can be demonstrated that the transient term will go as:

$$\exp(-18\eta t/D^2\rho_s) \qquad (A.1)$$

For typical values of η, the time constant for the transient (i.e. $D^2\rho_s/\eta$) will be such that the instantaneous velocity of the falling ball may be set equal to its terminal velocity without the introduction of significant error into the calculation. Under these conditions the velocity of the ball through the solution is given by:

$$v(t)=\frac{\mathrm{d}h(t)}{\mathrm{d}t}=\frac{D^2(\rho_s-\rho)g}{18\eta} \qquad (A.2)$$

where g is the gravitational constant.

For a constant heating rate, λ, applied to the system, equation (A.2) may be rewritten as:

$$\frac{\mathrm{d}h(T)}{\mathrm{d}T}=\frac{D^2(\rho_s-\rho)g}{18\lambda\eta} \qquad (A.3)$$

The solution viscosity relative to its value at T_g may be represented in terms of the WLF equation:

$$\eta=\eta_g \exp\left(\frac{-2.303c_1(T-T_g)}{c_2+(T-T_g)}\right) \qquad (A.4)$$

Substitution of equation (A.4) into equation (A.3) and taking the logarithm of the resulting expression yields:

$$\ln\left(\frac{\mathrm{d}h(T)}{\mathrm{d}T}\right)=\ln\left(\frac{k}{\eta_g}\right)+\frac{2.303c_1(T-T_g)}{c_2+(T-T_g)} \qquad (A.5)$$

where $k=D^2(\rho_s-\rho)g/18\lambda$ and can be readily evaluated.

An expression describing the displacement of the falling ball in terms of the solution temperature may also be obtained upon substitution of equation (A.4) into equation (A.3). Doing so leads to the following:

$$\Delta h=\frac{kc_1c_2\exp(c_1)}{\eta_g}\left\{\ln\left(\frac{c_2+\beta_0}{c_2+\beta}\right)+\frac{1}{c_1c_2}\right.$$
$$\times\left[(c_2+\beta)\exp\left(\frac{-c_1c_2}{c_2+\beta}\right)-(c_2+\beta_0)\exp\left(\frac{-c_1c_2}{c_2+\beta_0}\right)\right]$$
$$\left.+\sum_{n=1}^{\infty}(-1)^n\frac{1}{n!\,n}\left[\left(\frac{c_1c_2}{c_2+\beta}\right)^n-\left(\frac{c_1c_2}{c_2+\beta_0}\right)^n\right]\right\} \quad \text{(A.6)}$$

where $\beta=T-T_g$. The series term converges, with no changes in Δh occurring within eight decimal places for $n>125$.