

# Calculation of the volume fraction crystallised in nonisothermal transformations

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Two approaches were employed to calculate the nonisothermal crystallisation of undercooled liquids on both heating and cooling, the first using the concept of additivity and the second using a rigorous expression. It is indicated that the additivity approximation is strictly valid in two limiting cases, (i) site saturation and (ii) complete overlap of nucleation and growth curves. Numerical calculations were performed for  $\text{SiO}_2$  glass, which has well separated nucleation and growth curves, and significant (orders of magnitude) differences were found between the two methods for the prediction of the volume fraction crystallised. Despite this discrepancy, the calculated critical cooling rates differ by less than an order of magnitude. It is also demonstrated that the overall crystallisation produced on heating is many orders of magnitude higher than that on cooling (for equal  $dT/dt$ ) due to the fact that the maximum nucleation rate occurs at a much lower temperature than the maximum crystal growth rate.

During the past several decades the quantitative evaluation of glass forming ability of materials has become possible as a result of the kinetic viewpoint of glass formation adopted by Turnbull<sup>(1)</sup> and Uhlmann.<sup>(2)</sup> The crucial element in this approach is the calculation of the volume fraction crystallised,  $x_t$ , as a function of cooling rate. If for a given cooling path the volume fraction crystallised does not exceed a critical value, then one considers glass formation to be in evidence via this thermal path.

The calculation of the volume fraction of glass crystallised as a function of thermal history is also a central issue in the fabrication of glass ceramics.<sup>(3)</sup> In this case, however, glass formation is usually not problematic because the issue is the computation of volume fraction of crystals produced during the heating of the glass.

The feasibility of the kinetic method hinges upon the knowledge of certain kinetic and thermodynamic parameters (e.g. the crystal nucleation and growth rates, temperature dependence of the viscosity, etc.),

and the functional relationship between  $x_t$  and these parameters. Herein, only the latter aspect of this method will be considered.

The simplest approach to the evaluation of glass forming ability is by the use of time-temperature-transformation (T-T-T) diagrams.<sup>(2)</sup> Such diagrams relate the times required to produce a given volume fraction of crystals for a variety of isothermal heatings. The critical cooling rate for glass formation is taken as that cooling curve which is tangent to the T-T-T diagram corresponding to a critical volume fraction of crystals transformed. It is known that this critical cooling rate is a conservative upper limit to the actual required rate.

Recently, more sophisticated techniques have been employed for the assessment of glass forming capability and the computation of volume fraction crystallised. Notably, these techniques include continuous cooling diagrams<sup>(4)</sup> and the method of additivity.<sup>(5)</sup> Although a precise expression for the volume fraction transformed has been derived,<sup>(6)</sup> its use is limited due to its complexity. Hence, there has been strong incentive to derive simple, yet accurate, methods for calculating the volume fraction crystallised for nonisothermal transformations.

The principle of additivity is a particularly attractive method for the calculation of  $x_t$  due to its simplicity. For example, MacFarlane has employed this method to calculate critical cooling rates for glass formation in  $\text{SiO}_2$  and two metal alloy compositions.<sup>(5)</sup>

This paper presents an examination of the areas in which the additivity assumption is valid, giving comparisons of the predicted values of  $x_t$  (for both cooling and heating) for the crystallisation of  $\text{SiO}_2$  employing both the concept of additivity and also the exact expression given by Hopper *et al.*<sup>(6)</sup> In addition, a discussion is presented on the different formulae which result for  $x_t$  depending upon whether additivity is a result of site saturation or of the similarity of the temperature dependence of the nucleation and growth rates. Finally, the sensitivity of the predicted critical cooling rate for glass formation to the method of computation of  $x_t$  is examined.

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**Theory**
*General expression for volume fraction transformed*

A general expression for the volume fraction of material crystallised as a function of time for nonisothermal heating paths has been given by Hopper *et al.*<sup>(6)</sup> If one assumes that (1) the volume fraction transformed is small, (2) the cooling (heating) rate is constant, (3) the nucleation rate,  $I$ , and the growth rate,  $g$ , have no intrinsic time dependence (i.e. the time (or temperature) variation of these rates occurs only via the temperature change), (4) the growth is spherical, then the volume fraction transformed in cooling from  $T_m$  (the liquidus temperature) to  $T$  at a rate  $Q$  is given by

$$X(T) = \frac{4\pi}{3Q^4} \int_{T_m}^T I(\bar{T}) d\bar{T} \left( \int_T^{\bar{T}} dT' g(T') \right)^3; \quad (1)$$

this may be utilised in conjunction with any appropriate choices of  $g$  and  $I$  to compute  $X(T)$ . In the present work, specific selections of  $g$  and  $I$  will be made in order to give correspondence with those used in previous calculations of  $X(T)$  by other methods: they do not necessarily represent the best (or even good) choices for these rates but this is irrelevant since the basic intent is to evaluate the validity of certain methods of computing  $X(T)$ . Hence, any consistent selections of  $I$  and  $g$  will suffice and the following expressions will be used:<sup>(5)</sup>

$$I = \frac{N^0 k T_r T_m}{3\pi a_0^3 \eta} \exp\left(\frac{-1.024}{T_r^3 (\Delta T_r)^2}\right) \quad (2)$$

and

$$g = \frac{k T_m T_r}{3\pi a_0^2 \eta} \left[ 1 - \exp\left(\frac{-\beta \Delta T_r}{T_r}\right) \right] \quad (3)$$

where  $N^0$  is the number of atoms per unit volume,  $k$  is Boltzmann's constant,  $\eta$  is viscosity,  $T_r$  is the temperature divided by  $T_m$  (i.e. the reduced temperature),  $a_0$  is the average atomic diameter, and  $\beta$  is a dimensionless parameter equal to the molar entropy of fusion in units of  $R$  (the gas constant). If Equations (2) and (3) are used in Equation (1), then the following expression is found for  $X(T)$ :

$$X(T_r) = K' N^0 \int_1^{T_r} \frac{d\bar{T}_r \bar{T}_r}{\eta} \exp\left(\frac{-1.024}{\bar{T}_r^3 (\Delta \bar{T}_r)^2}\right) \times \left\{ \int_{T_r}^{\bar{T}_r} \frac{dT'_r T'_r}{\eta} \left[ 1 - \exp\left(\frac{-\beta \Delta T'_r}{T'_r}\right) \right] \right\}^3 \quad (4a)$$

where

$$K' \equiv \frac{4\pi}{3} \left( \frac{k T_m^2}{3\pi Q a_0^{9/4}} \right)^4. \quad (4b)$$

In the general case Equation (4a) may be evaluated numerically. However, if the viscosity exhibits an Arrhenius temperature dependence, then the growth integral can be expressed in terms of a standard form.

Hence, if

$$\eta^{-1} = A \exp\left(\frac{-C}{T_r}\right), \quad (5)$$

where  $A$  and  $C$  are constants, then it is convenient to define

$$G(T_r; \bar{T}_r) \equiv A \int_{T_r}^{\bar{T}_r} dT'_r T'_r \exp\left(\frac{-C}{T'_r}\right) \times \left[ 1 - \exp\left(\frac{-\beta \Delta T'_r}{T'_r}\right) \right]. \quad (6)$$

Thus Equation (4) may be expressed

$$X(T_r) = K' N^0 \int_{T_r}^1 d\bar{T}_r \bar{T}_r A \exp\left[-\left(\frac{C}{\bar{T}_r} + \frac{1.024}{\bar{T}_r^3 (\Delta \bar{T}_r)^2}\right)\right] \times G^3(T_r; \bar{T}_r). \quad (7)$$

In the Appendix it is shown that  $G(T_r; \bar{T}_r)$  can be expressed as

$$G(x; x_f) = \frac{A}{2} [C^2 Q(cx) - \exp(\beta)(C + \beta)^2 Q[(C + \beta)x] - \{c^2 Q(cx_f) - \exp(\beta)(C + \beta)^2 Q[(C + \beta)x_f]\}], \quad (8)$$

with

$$Q(y) \equiv \frac{\exp(-y)}{y} \left( \frac{1-y}{y} + y \exp(y) E_1(y) \right). \quad (9)$$

In Equations (8) and (9),  $x = \bar{T}_r^{-1}$ ,  $x_f = T_r^{-1}$ , and  $E_1(y)$  is the first exponential integral<sup>(7)</sup> and the final expression for the reduced volume fraction transformed during cooling at a constant rate,  $\bar{x} \equiv x(T_r)/K'$ , is therefore

$$\bar{x}^4 = AN^0 \int_1^{x_f} \frac{dx'}{(x')^3} \exp\left[-\left(\frac{1.024(x')^5}{(x'-1)^2} + Cx'\right)\right] \times G^3(x'; x_f). \quad (10)$$

*Volume fraction transformed assuming additivity*

In general both  $x(t)$  and  $dx(t)/dt$ , the transformation rate, are path dependent. However, when the principle of additivity is valid, then the transformation rate is solely a function of state.<sup>(5,8)</sup> In other words, the transformation rate can be expressed by

$$\frac{dx}{dt} = h(T)/j(x) \quad (11)$$

where  $h(T)$  is solely a function of temperature and  $j(x)$  is only a function of the instantaneous value of the volume fraction transformed.<sup>(5)</sup>

Equation (11) is much less formidable than Equation (1), and thus the assumption of additivity leads to a greatly simplified effort for the computation of the volume fraction transformed. However, an important question, which is addressed in a preliminary fashion herein, is the following: in which cases can the principle of additivity be invoked? This question has been

examined to some extent in the past<sup>(9)</sup> and it is known that this assumption provides exact results in two cases, but, as discussed below, the expressions for the volume fraction transformed are quite different in each of these two cases. Thus, for the computation of  $x(t)$  it is not sufficient merely to invoke the principle of additivity, but one must also examine how it comes about.

First, it has been demonstrated that if the nucleation rate is proportional to the growth rate (i.e.  $I$  and  $g$  have the same temperature dependence), then additivity is precise and for a constant cooling rate,

$$X(T) = \left( \frac{1}{Q} \int_{T_m}^T \frac{dT'}{K(T')} \right)^4 \quad (12a)$$

$$\frac{1}{K(T)} = \frac{kT}{9 \cdot 32 \eta} \left\{ \frac{N^0}{a_0^9} \exp \left( \frac{-1 \cdot 024 T_m^5}{T^3 (T_m - T)^2} \right) \times \left[ 1 - \exp \left( \frac{-\beta (T_m - T)}{T} \right) \right]^3 \right\}^{1/4} \quad (12b)$$

It should be stressed, however, that in general  $I$  and  $g$  have distinct temperature dependences and hence Equations (12a) and (12b) are not expected to be exact. In terms of the notation and transformations which have been employed here, Equations (12a) and (12b) can be written

$$\bar{x}^\dagger = \frac{X(T)}{K'} = 1/4 \left[ AN^0 \int_1^{x^r} \frac{\exp(-cx)}{x^3} \left\{ \exp \left[ \frac{-1 \cdot 024 x^5}{(x-1)^2} \right] \times [1 - \exp(\beta) \exp(-\beta x)]^3 \right\}^{1/4} dx \right]^4 \quad (13)$$

In the derivation of Equation (13) it has been assumed once again that the viscosity exhibits an Arrhenius form of temperature dependence.

The second instance which leads to additivity is when site saturation occurs; site saturation refers to the situation when all nucleation sites have been used up prior to growth. In other words, if nucleation and growth do not take place in a common temperature region, then the transformation rate is given by Equation (11). However, it is important to note that the reduced volume fraction transformed is not given by Equation (13). In fact, the volume fraction transformed will depend critically upon whether the nucleation occurs at higher or lower temperature than the growth, and whether one performs a cooling or heating experiment. These points are illustrated in the next section. However, here it is reemphasised that Equation (13) is inappropriate for the calculation of the volume fraction transformed if the principle of additivity holds in a given situation as a result of site saturation.

## Results

Figure 1 shows the reduced volume fractions which are transformed for both the heating and cooling paths,

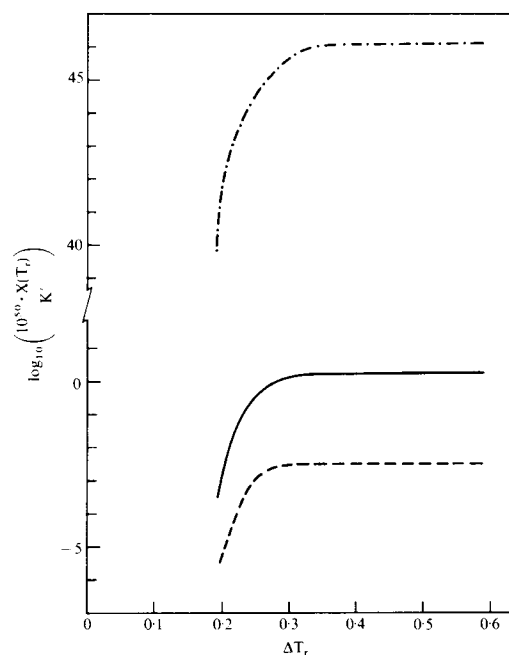


Figure 1. Logarithm of volume fraction transformed (arbitrarily normalised) as a function of reduced undercooling for constant cooling and heating rates

----- cooling, calculated using Equation (10)  
 ———— cooling, calculated using Equation (13)  
 - · - · - heating, calculated using Equations (15a) and (15b)

obtained by numerical computations of the general expressions obtained by Hopper *et al.*<sup>(6)</sup> as well as by the use of the approximate expression, Equation (13), using the additivity assumption. All curves were calculated for SiO<sub>2</sub> glass using the same physical parameters employed by MacFarlane.<sup>(5)</sup>

## Cooling path

First, the volume fraction crystallised for an arbitrary, but constant, cooling rate will be considered. Figure 1 shows that both Equation (10) and Equation (13) predict that crystallisation is essentially negligible until a reduced undercooling  $\Delta T_r$  of 0.15 is reached, increases rapidly for  $0.15 < \Delta T_r < 0.25$ , and then gradually slows down. A maximum value of crystallinity is attained at a reduced undercooling of approximately 0.35. Obviously, this behaviour is strongly dependent on the relative positions and magnitudes of the nucleation and growth rates. The important result, however, is that the values of  $X(T_r)$  predicted by using the additivity assumption are about three orders of magnitude larger than those obtained using the rigorous calculations. This large discrepancy has its origin in the inappropriateness of the use of Equation (13) for the present situation. This point is discussed in detail subsequently.

It should also be stressed that the temperature dependence of the reduced crystallinity computed by the two methods is different, as illustrated in Figure 2, where the values of the volume fraction crystallised found by Equations (10) and (13) were adjusted

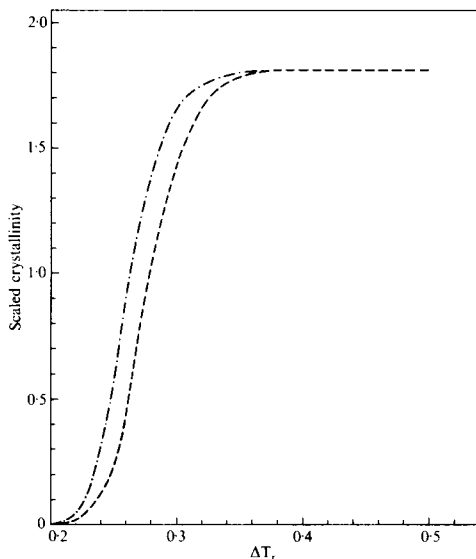


Figure 2. Temperature dependence of volume fraction transformed during cooling; predicted values using Equation (10) and (13) are normalised to give an identical value at large undercooling  
— Equation (10)  
- - - Equation (13)

(normalised) to give the same value at large undercooling, where the crystallisation is complete. Although one may observe that the predicted temperature dependences of  $X(T_r)$  are similar, they do not superimpose. Hence, the additivity method, as embodied by Equation (13), is not in error by merely a constant (temperature independent) scaling factor.

#### Heating paths

The volume fraction transformed when heating from  $T^-$  to  $T$  is given by an expression similar to that of Equation (1);

$$X(T) = \frac{4\pi}{3Q^4} \int_{T^-}^T I(\bar{T}) d\bar{T} \left( \int_{T^-}^T dT' g(T') \right)^3 \quad (14)$$

If one considers  $T = T_m$ , then following the procedure which led to Equation (10) one obtains

$$\bar{x}^\dagger = AN^0 \int_1^{x_1} \frac{dx'}{x'^3} \exp \left[ - \left( \frac{1.024(x')^5}{(x'-1)^2} + cx' \right) \right] G_u^3 \quad (15a)$$

where

$$G_u = -G(x'; 1). \quad (15b)$$

Figure 1, also, shows the reduced crystallinity computed from Equations 15(a) and 15(b) for heating from a given undercooling ( $\Delta T_r$ ) to  $T_m$ . The overall behaviour is similar to that observed for the cooling path although the final crystallinity (for  $\Delta T_r > 0.35$ ) is many orders of magnitude higher than that attained during cooling. In this case (heating) the additivity approximation is even worse than for the cooling path and gives estimates which are 46 orders of magnitude

smaller than the real crystallinity. It should be emphasised that the additivity approach predicts identical crystallinity values for both heating and cooling paths because a complete overlap of the nucleation and growth curves is intrinsically assumed.

Parenthetically, it should be remarked that often experiments do not reveal such a large difference between  $x_t$  in heating and cooling due, in part, to transient nucleation effects. At low temperatures (where the viscosity is large), the transient nucleation time is long and thus the effective nucleation rate is reduced. Hence, in a heating experiment, the low temperature portion of the nucleation curve (which does not overlap the growth curve) will not contribute to  $x_t$ .

It is interesting to compare the crystallinity curve shown in Figure 1 for heating with the values computed for the limiting case of site saturation. In this latter case, the first integral in the general expression, Equation (1), is equal to the total number of nuclei,  $N$ , and thus Equation (1) reduces to

$$x = \frac{4\pi N}{3Q^4} \left( \int_{T^-}^T g(T') dT' \right)^3 \quad (16)$$

The curve obtained by use of Equation (16) coincides with the 'heating' curve shown in Figure 1, which was computed using the precise equation for the volume fraction crystallised. This clearly demonstrates that site saturation is an excellent approximation in this case, and that the additivity approximation can be used to compute  $\bar{x}^\dagger$ , but one must employ Equation (16) and not Equation (13). In addition, it should be noted that the site saturation approximation would predict that  $\bar{x}^\dagger = 0$ . Thus, although the site saturation concept is useful in indicating that a small degree of crystallinity will result when cooling, it is not adequate to give a prediction of the small amount of crystals which will be formed. Thus, for cooling paths, one must resort to the use of Equation (10).

#### Overlap of nucleation and growth

As discussed above, the additivity approximation should only be strictly valid in two cases, either for site saturation or when there is a substantial overlap between the nucleation and growth curves. Below we discuss the extent of overlapping for  $\text{SiO}_2$  glass in both graphical and numerical representations.

Figure 3 shows the logarithm of the reduced rates ( $I/I_{\max}$ ,  $g/g_{\max}$ ) as functions of reduced temperature; these curves were calculated by means of Equations (2) and (3), using the same constants and viscosity values employed in Reference 5. The maximum nucleation rate occurs at  $T_r \approx 0.69$  and the maximum growth rate at  $T_r \approx 0.97$ . Therefore, taking into account the exponential dependence of both  $I$  and  $g$  upon temperature and the large distance between the two maxima, it is clear that very little overlap exists between the two curves.

A more quantitative way of analysing the degree of overlap is shown below. Let us define the following

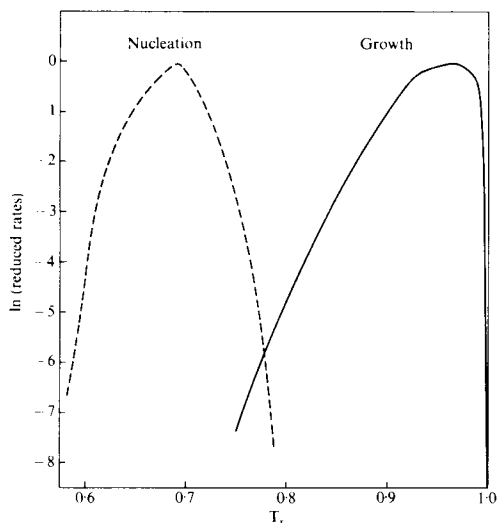


Figure 3. Logarithm of reduced nucleation ( $I/I_{\max}$ ) and growth ( $g/g_{\max}$ ) rates for  $\text{SiO}_2$  glass as a function of reduced temperature

ratio,  $\theta$ , by

$$\theta \equiv \frac{\int I(T)g(T)dT}{[\int I^2(T)dT \int g^2(T)dT]^{1/2}} \quad (17)$$

it is clear that both integrals are equal if  $I(T)$  and  $g(T)$  overlap completely, and thus  $\theta = 1$ , and if there is no overlap,  $\theta = 0$ . By using Equations (2) and (3) for  $I(T)$  and  $g(T)$  and integrating numerically between  $T_m$  and  $T_g$ ,  $\theta = 0.92 \times 10^{-4}$ . Therefore, there is only a marginal superposition between the nucleation and growth curves.

### Discussion

An assessment has been given of approximate means of computing the volume fraction of crystallites formed for continuous cooling and heating paths. As a typical example computations were performed for the crystallisation of  $\text{SiO}_2$  glass, and, in particular, the use of the concept of additivity was evaluated.

There are only two cases for which it is known that the additivity approximation is valid, (i) site saturation and (ii)  $I \sim g$ ; both imply a path independent crystallisation rate but they involve distinct expressions for  $X(T)$ .

For homogeneous crystal nucleation the maximum nucleation rate typically falls at larger undercoolings<sup>(10,11)</sup> while the maximum crystal growth rate occurs relatively close to  $T_m$ .<sup>(12)</sup> In this case the overlap between  $I$  and  $g$  will be small and hence site saturation will prove to be a good approximation in computing  $X(T)$  for heating but the additivity principle will be of limited utility for calculating  $X(T)$  in cooling. This was illustrated herein for the crystallisation of  $\text{SiO}_2$  glass.

On the other hand, for crystallisation via a heterogeneous mechanism, the peak nucleation rate may in principle occur at a temperature below, above, or near that of maximum crystal growth. In addition, the

degree of overlap between nucleation and growth curves can be small or large. Hence, the applicability of the additivity principle for the calculation of heterogeneous crystallisation depends upon the key parameters governing the relative positions of  $I_{\max}$  and  $g_{\max}$ , and the widths of the nucleation and growth curves. An investigation of such effects are reserved for a separate study.

A key issue related to the prediction of  $x_t$  is the estimation of critical cooling rates for glass formation. The prediction of critical cooling rates depends both on the model used to relate the volume fraction transformed to the kinetic parameters ( $I$  and  $g$ ) and on the choice of the temperature dependent nucleation and crystal growth rates. In order to obtain meaningful values for the calculated critical cooling rates one should probably employ experimentally determined nucleation and growth rates since the theoretical rates can be in error by many orders of magnitude.<sup>(10)</sup> For the present analysis, however, it is merely desired to assess the sensitivity of the model chosen for computing  $x_t$  to the ultimate result for the critical cooling rate,  $Q_c$ . Hence, one can determine the error produced in  $Q_c$  due to the model. If one designates  $Q_{ce}$  and  $Q_{cA}$  as the critical rates for the exact and additivity calculations,

$$\frac{Q_{ce}}{Q_{cA}} = \left( \frac{x_e}{x_A} \right)^{1/4} \quad (18)$$

where  $x_e$  and  $x_A$  are the saturation values of crystallinity for  $\Delta T_r > 0.35$ . From Figure 1, it can be concluded that  $Q_{ce}/Q_{cA} \approx 0.2$ , and therefore, although the use of the additivity principle produces errors of several orders of magnitude in  $X(T)$ , it results in an error of more modest proportions for  $Q_c$ .

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### Appendix

An expression is derived below for the integral of the growth rate, i.e. of Equation (8).

Equation (6) gives the definition of  $G(T_r; \bar{T}_r)$

$$G(T_r; \bar{T}_r) = A \int_{T_r}^{\bar{T}_r} dT_r T_r \exp\left(\frac{-c}{T_r}\right) \left[ 1 - \exp\left(\frac{-\beta \Delta T_r}{T_r}\right) \right]; \quad (A1)$$

if one introduces new variables  $x' (\equiv 1/T_r)$ ,  $x_r (\equiv 1/\bar{T}_r)$ , and  $x (\equiv 1/T_r)$ , Equation (A1) it becomes

$$G(x; x_r) = A \left\{ \int_x^{x_r} \frac{dx'}{x'^3} \exp(-cx') - \exp \beta \times \int_x^{x_r} \frac{dx' \exp[-(c+\beta)x']}{x'^3} \right\}. \quad (A2)$$

Both integrals in Equation (A2) are of the same form, and either may be expressed in slightly different form after integration by parts. If  $\alpha$  denotes either  $c$  or  $c + \beta$ , then

$$\int_x^{x_f} y^{-3} \exp(-\alpha y) dy = 1/2 \left\{ \frac{\exp(-\alpha x)}{x^2} (1 - \alpha x) - \frac{\exp(-\alpha x_f)}{x_f^2} + \alpha^2 \left[ \int_z^\infty \frac{\exp(-z')}{z'} dz' - \int_{z_f}^\infty \frac{\exp(-z')}{z'} dz' \right] \right\} \quad (A3)$$

where  $z' = \alpha y$ ,  $z = \alpha x$ , and  $z_f = \alpha x_f$ . The last two integrals in Equation (A3) are  $E_1(z)$  and  $E_1(z_f)$ , the exponential integrals.<sup>(7)</sup> If we define  $F(z) = z \exp(z) E_1(z)$ , then

$$\int_x^{x_f} y^{-3} \exp(-\alpha y) dy =$$

$$= \frac{\alpha^2}{2} \left[ \frac{\exp(-\alpha x)}{\alpha x} \left( \frac{1 - \alpha x}{\alpha x} + F(\alpha x) \right) - \frac{\exp(-\alpha x_f)}{\alpha x_f} \left( \frac{1 - \alpha x_f}{\alpha x_f} + F(\alpha x_f) \right) \right] \quad (A4)$$

and the use of Equation (A4) in Equation (A2) yields Equation (8) in the main body of the text.

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