

Revised Ehrenfest Relations for the Glass Transition

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The derivation of the Ehrenfest relations for a second-order phase transition is generalized to include the case of glass transitions, where the lower temperature phase is out of equilibrium. The revised relations are shown to predict the variation of the glass transition pressure, measured in a computer simulation study, over a wide range of temperature. They reduce to the original Ehrenfest relations when the lower temperature phase is equilibrated.

1. Introduction

It is not obvious that thermodynamic rules should apply at a kinetic glass transition, but for many years¹ the applicability of the Ehrenfest² relations and the Prigogine Defay³ relation, at the glass transition, have been tested and discussed and explanations have been sought for their failure.⁴ The Ehrenfest relations were derived for a second-order transition,² where the first derivatives of the free energy vary continuously and second derivatives change sharply. A glass transition is similar to a second-order transition in that sense, but the phases involved in a second order transition are equilibrated, whereas a glass is not.¹ The properties of an equilibrated (stable or metastable) phase are determined by its composition and the imposed external variables,⁴ temperature T and pressure P . This paper generalizes the derivation of the Ehrenfest relations to include the case where the lower temperature phase is a nonequilibrated glass, whose properties depend on one or more internal parameters^{1,5} as well as on the external variables. The generalized relations reduce to the original Ehrenfest relations when both phases are equilibrated.

If the glass transition was a second order phase transition between two equilibrated phases then the slope of the line $T_g(P)$ of glass transitions would obey the two Ehrenfest relations

$$\frac{dT_g}{dP} = \frac{\Delta\kappa}{\Delta\alpha} \quad (1)$$

and

$$\frac{dT_g}{dP} = \frac{TV\Delta\alpha}{\Delta C_p} \quad (2)$$

In these equations V is the volume, $\kappa = -(\partial \ln V / \partial P)_T$ is the isothermal compressibility, $\alpha = (\partial \ln V / \partial T)_P$ is the isobaric expansivity, the isobaric heat capacity is $C_p = (\partial H / \partial T)_P$, where H is the enthalpy, and for any property $x = \kappa, \alpha$, etc., $\Delta x = x(\text{liquid}) - x(\text{glass})$ at the glass transition.

The derivation^{2,4} of eqs 1 and 2 assumes that, for a sample of fixed composition, the volume $V(T, P)$ and the enthalpy $H(T, P)$ of both the phases depend only on the external variables T and P . For a glass this assumption is invalid because the

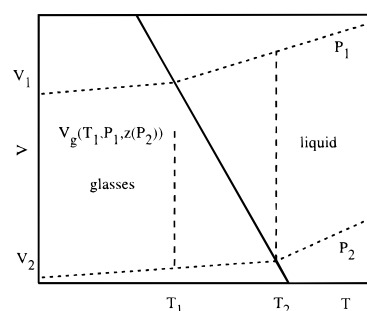


Figure 1. Dotted lines show volume versus temperature for an equilibrated (stable or metastable) liquid at two pressures $P_1 < P_2$ and for the glasses of kind $z(P_1)$ and $z(P_2)$ that it becomes trapped in at (T_1, V_1) and (T_2, V_2) , respectively. The solid line shows the locus of the glass transition. Vertical dashed lines show the increase in volume when the liquid or glass is decompressed isothermally from P_2 to P_1 .

properties of a glass also depend on one or more internal parameters,^{1,5} z , to reflect the dependence of its volume $V_g(T, P, z)$ and enthalpy $H_g(T, P, z)$ on its history. When this is taken into account the generalization of eqs 1 and 2 to the glass transition is straightforward.

2. Derivation

The volume and enthalpy of a liquid and the glasses that it samples are the same at the glass transition.¹ The liquid samples glasses of the kind $z(T, P)$ that minimize its free energy, so z varies in the liquid, but it is fixed in a glass, and this is why the derivatives of V and H change at the glass transition.^{1,5}

Figure 1 plots the volume of a liquid and two of its glasses against temperature. When the liquid is cooled along an isobar it becomes kinetically trapped in one of the glasses that it samples⁵ at a glass transition temperature $T_g(P)$. $T_g(P)$ varies with the cooling rate, so the temperature and pressure at which a glass is trapped can be varied independently and two internal parameters (e.g. the T and P at which it became trapped) are required to characterize the glass.^{1,5} For a specified cooling rate, a line $T_g(P)$ can be defined as the locus of points where the volume versus temperature lines for the liquid and glass intersect, as shown in Figure 1. Because fixing the cooling rate defines a line $T_g(P)$, the temperature and pressure at which a glass is trapped are no longer independent and a single internal parameter (e.g., the P at which it was cooled) should suffice,

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for the present purpose, to characterize the glasses that a form along the line $T_g(P)$.

The volume of the liquid, $V_l(T, P)$, depends on T and P alone so the volume $V_1 = V(T_1, P_1)$, where $T_1 = T_g(P_1)$, can be calculated by following a path through the liquid from the volume $V_2 = V(T_2, P_2)$, where $T_2 = T_g(P_2)$, as

$$V_1 - V_2 = (\partial V_l / \partial P)_T (P_1 - P_2) + (\partial V_l / \partial T)_P (T_1 - T_2) \quad (3)$$

The first term on the right side gives the volume change, shown by the vertical dashed line at T_2 in Figure 1, when the liquid is decompressed from P_2 to P_1 , and the second term is the volume change on cooling along the P_1 isobar from T_2 to T_1 .

The volume of a glass $V_g(T, P, z)$ depends on T , P , and z , where $z(P)$ varies with the pressure at which the glass was formed, so following a path through the glasses leads to

$$V_1 - V_2 = (\partial V_g / \partial T)_{P,z} (T_1 - T_2) + (\partial V_g / \partial P)_{T,z} (P_1 - P_2) + (\partial V_g / \partial z)_{T,P} (dz/dP) (P_1 - P_2) \quad (4)$$

The first term on the right side gives the volume change when the glass of kind $z(P_2)$ is cooled along the P_2 isobar to T_1 . The second term gives the volume change, shown as the vertical dashed line at T_1 in Figure 1, when this glass is decompressed to P_1 . At the top of the dashed line the volume $V_g(T_1, P_1, z(P_2))$, is less than the volume $V_1 = V_g(T_1, P_1, z(P_1))$ of the glass formed at P_1 . This is the main point of the present paper. To get from the top of the dashed line to V_1 , the glass of kind $z(P_2)$ must be changed to a glass of kind $z(P_1)$, and the last term in eq 4 represents the volume change associated with this transformation. The importance of the last term is clear from Davies and Jones¹ discussion, it is emphasized by Goldstein,⁶ Jäckle,⁷ and Nieuwenhuizen,⁸ but it is overlooked in many other discussions of the Ehrenfest relations at the glass transition.

Equations 3 and 4 give the slope $dT_g/dP = (T_1 - T_2)/(P_1 - P_2)$,

$$\frac{dT_g}{dP} = \frac{\Delta\kappa + \delta V_P/V}{\Delta\alpha} \quad (5)$$

where the operational definition of $\delta V_P = (\partial V_g / \partial z)_{T,P} (dz/dP)$ is

$$\delta V_P = \frac{V_g(T, P, z(P_1)) - V_g(T, P, z(P_2))}{P_1 - P_2} \quad (6)$$

To measure δV_P , a glass of kind $z(P_1)$ is made by cooling the liquid at pressure P_1 , a second glass of kind $z(P_2)$ is made by cooling the liquid at pressure P_2 , and the numerator in eq 6 is the volume difference between the two glasses when they are compared at the same T and P . Equation 5 is correct⁸ because eq 6 defines δV_P to make it correct. If the low temperature phase is equilibrated its volume does not depend on z , so $\delta V_P = 0$ and eq 5 reduces to eq 1.

A glass formed at high pressure is likely to remain more dense⁶ than one formed at low pressure, when they are compared at the same pressure, so that δV_P is negative. This explains why experiments^{4,9} usually find that the right side of eq 1 is greater than dT_g/dP .

Equation 5 is not new, it is implicit in Goldstein's paper,⁶ it was stated explicitly by Jäckle⁷ (with the terminology $\partial \ln V_g / \partial P_f = \delta V_P/V$, where P_f is the pressure at which a glass is formed) and restated by Nieuwenhuizen⁸ (who redefines $\Delta\kappa$ to absorb $\delta V_P/V$).

The second Ehrenfest relation is commonly derived in the same way with entropy in place of volume,⁴ but this may be

confusing when glasses are involved because there is an ambiguity^{8,10,11} about the entropy of a glass. To avoid this confusion, the second relation is derived in terms of the enthalpy H , which is clearly defined because its measurement does not depend on a reversible path. Replacing V in Figure 1 by H , and following the same reasoning, gives eqs 3 and 4 with H in place of V . The thermodynamic relation

$$(\partial H / \partial P)_T = V(1 - T\alpha) \quad (7)$$

and the definition of C_p then lead to

$$\frac{dT_g}{dP} = \frac{VT\Delta\alpha + \delta H_P}{\Delta C_p} \quad (8)$$

The term δH_P is defined by eq 6 with H in place of V , but there is an important difference between the two operational definitions. When two glasses are compared, their volume difference is a mechanical property than can be measured directly, but to measure the enthalpy difference requires calorimetric measurements along a path in which one of the glasses is converted to the other. Recent calorimetric studies of the kind needed to estimate δH_P are described by Samwer et al.¹² The results shown in their¹² Figure 1 suggest that δH_P may be negligibly small, which is consistent with the experimental finding^{4,13} that eq 2 is usually obeyed at glass transitions.

Nieuwenhuizen⁸ states that thermodynamics (e.g., eq 7) cannot apply in a glass, which is true when the glasses relax irreversibly with time. But a glass can be regarded as a constrained system in which the constraints^{14,15} prevent any irreversible relaxation, so that thermodynamics applies. His modification⁸ of the Prigogine Defay relation seems to require that the number of glasses that a liquid samples decrease with temperature, which is clearly¹⁶ wrong.

Equations 5 and 8 are appropriate for glasses made by cooling a liquid at constant pressure, but I have not found any experimental measurements which allow them to be tested. Glasses can be made by compressing a liquid along isotherms^{17,18} and in this case there is a systematic simulation study¹⁸ that provides a test.

When a liquid is compressed along an isotherm at temperature T it may form a glass at a pressure $P_g(T)$, and the above reasoning leads to

$$\frac{dP_g}{dT} = \frac{\Delta\alpha - \delta V_T/V}{\Delta\kappa} \quad (9)$$

where δV_T is defined by substituting T_1 for P_1 and T_2 for P_2 in eq 6. Similarly

$$\frac{dP_g}{dT} = \frac{\Delta C_p - \delta H_T}{VT\Delta\alpha} \quad (10)$$

where δH_T is defined by substituting H for V , T_1 for P_1 and T_2 for P_2 in eq 6.

Equations 9 and 10 have essentially the same content as eqs 5 and 8, respectively, and the cooling and compression rates could no doubt be chosen to make $dT_g/dP = (dP_g/dT)^{-1}$. Before testing eq 9 and 10 in section 4, special circumstances that simplify the analysis are described.

3. Prigogine Defay Ratio

Equations 1 and 2 imply that

$$\Delta C_p \Delta\kappa / VT(\Delta\alpha)^2 = 1 \quad (11)$$

The left side of eq 11 is called the Prigogine Defay³ ratio and experiments^{1,4,9} show that, for glass transitions in real materials, the ratio is usually about 2. However, for simple models like hard spheres or discs, in which the potential energy is fixed, eq 11 is exact at a glass transition. For hard spheres the energy $U = 3RT/2$ is all kinetic so $(\partial U/\partial V)_T = 0$, and the thermodynamic equation of state $P = T(\partial S/\partial V)_T - (\partial U/\partial V)_T$, together with the Maxwell relation $(\partial S/\partial V)_T = \alpha/\kappa$, yields

$$T\alpha = P\kappa \quad (12)$$

The isobaric heat capacity C_p is related to the isochoric heat capacity C_V by $C_p = C_V + TV\alpha^2/\kappa$, and $C_V = 3R/2$ when $U = 3RT/2$, so

$$T\alpha = T(C_p - 3R/2)/PV \quad (13)$$

Equations 12 and 13 apply to the fluid and to any of its glasses, so at a glass transition

$$T\Delta\alpha = P\Delta\kappa = T\Delta C_p/PV \quad (14)$$

which shows that eq 11 is exact when the potential energy is fixed.

The new ratio obtained from eq 5 and 8 is

$$R = \frac{\Delta C_p(\Delta\kappa + \delta V_P/V)}{\Delta\alpha(VT\Delta\alpha + \delta H_P)} = 1 \quad (15)$$

Equation 15 differs, by the inclusion of δH_P , from an alternative to eq 11 given by Jäckle⁷ (eq 10 of ref 7). When the potential energy is fixed $\delta H_P = P\delta V_P$, because $H = U + PV$, and eq 14 and 15 imply that $R = 1$, so eq 11 and 15 are both satisfied. Thus, there are special circumstances where eq 1 and 2 are both incorrect but eq 11 is correct.

4. Tests

The information about glasses formed with different histories that is required to test eq 5 and 8 may not be available for real materials, but a computer simulation study¹⁸ of a tetravalent network model provides the information needed to test eq 9 and 10. The tetravalent particles were modeled^{18,19} by a square well potential with the extra constraints that no particle may form more than four bonds and that a triangle of bonded particles is prohibited. The model simulates very efficiently,¹⁹ and its glass transition was studied over a wider range of temperatures and compression rates than have been reported for more realistic models or for real materials. The reduced temperature is kT/ϵ where k is the Boltzmann constant and ϵ is the depth of the square well. The density is expressed as $y = V_0/V$ where $V_0 = (64/27)^{1/2}N\sigma^3$ is the volume of the close packed diamond crystal that the model forms,¹⁹ N is the number of particles, and σ is the diameter of the repulsive core. The diameter of the square well is $(8/3)^{1/2}\sigma$.

A feature of the model that simplifies the following analysis is that at least 97% of the allowed bonds are already made below the glass transition density,¹⁸ so that the potential energy does not vary significantly in the vicinity of the glass transition. As a result, eq 14 can be applied without introducing significant error, the Prigogine Defay ratio is very close to unity, and $\delta H_T \approx P\delta V_T$. Equations 9 and 10 are therefore equivalent and only one of them needs to be tested.

The properties of 171 glasses, formed by independent compressions of the liquid at a wide range of temperatures and with 5 orders of magnitude variation in the compression rate,

TABLE 1: Properties of Glasses Formed by Compressing the Tetravalent Saturated Square Well¹⁸ Liquid along Isotherms with Compression Rate $d\sigma/dt = 10^{-3} (kT/m)^{1/2}$ from Table 4 of Reference 18^a

ϵ/kT	y_g	$P_g V/NkT$	y_o	C	$\Delta V/V_0$
0	0.693(4)	15.70(7)	0.817(3)	2.62(3)	0.009(7)
1	0.682(2)	14.80(7)	0.812(3)	2.65(2)	0.028(5)
2	0.651(7)	12.99(7)	0.795(3)	2.65(4)	0.032(7)
3	0.584(12)	9.11(8)	0.785(1)	2.80(1)	

^a The density at the glass transition is y_g and the compressibility factor at the glass transition is $P_g V/NkT$. C and y_o are the parameters in eq 16. The values listed are averaged over several independently formed glasses and the numbers in parentheses give the root mean square deviation in the last digit quoted. $\Delta V/V_0$ is the volume difference between a glass formed at ϵ/kT and one formed at $\epsilon/kT + 1$, calculated from eq 16, when they are compared at the same $P_g V_o/NkT$.

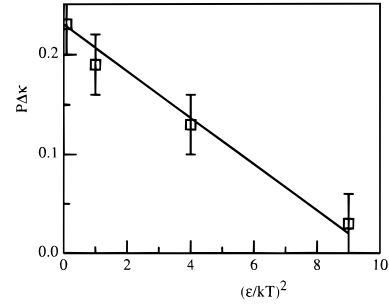


Figure 2. $P\Delta\kappa$ at the glass transition versus $(\epsilon/kT)^2$. The error bars show only the contribution from the uncertainty in $P\kappa$ for the liquid. The glass values were extrapolated to y_g using eq 16 and no attempt was made to estimate their uncertainty. The line shows the empirical eq 18.

are listed in Table 4 of ref 18. The pressure of each glass fits¹⁸ the empirical equation

$$PV/NkT = 1 + Cy/(y_o - y) \quad (16)$$

where the parameters y_o and C depend on the temperature and the rate at which the liquid was compressed to form the glass. Table 1 lists some properties of glasses formed by compressing the liquid along different isotherms at the same rate. The data set was selected because it shows the largest variation of P_g with T . The glass transition is located at the density where the pressure of the glass, extrapolated using eq 16, intersects the pressure of the liquid.

To keep the equations simple it is helpful to work with dimensionless quantities ($T\alpha$, $P\kappa$ and $T\delta V_T/V$ are dimensionless) and write eq 9 as

$$\begin{aligned} \frac{d \ln\{P_g^*\}}{d \ln\{T\}} &= \frac{T(\Delta\alpha - \delta V_T/V)}{P\Delta\kappa} \\ &= 1 - T\delta V_T/VP\Delta\kappa \end{aligned} \quad (17)$$

where the last step uses eq 14. The reduced pressure at the glass transition is defined by $P_g^* \equiv y_g(P_g V/NkT)kT/\epsilon = P_g V_o/N\epsilon$.

For the liquid, $P\kappa = 1/(1 + (\partial \ln\{PV/NkT\}/\partial \ln\{y\})_T)$ was estimated from plots of PV/NkT against density (the raw data from ref 19 are shown in Figures 1 and 2 of ref 18), near the glass transition density, and it has an uncertainty of about 10%. For the glasses $P\kappa$ was calculated from eq 16 with the constants in Table 1, which requires an extrapolation to y_g from lowest density at which the pressure of the glasses was measured,¹⁸ $y = 0.72$. The results are summarized in Figure 2, which shows

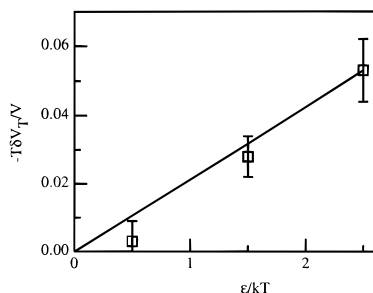


Figure 3. The correction term $-T\delta V_T/V$, from eq 19, plotted against ϵ/kT . The line shows the empirical eq 20.

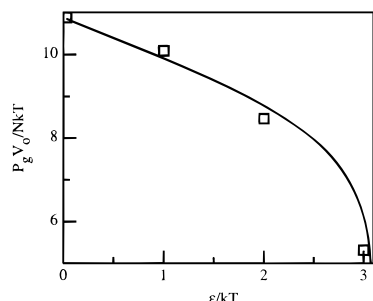


Figure 4. $P_g V_o / NkT$ at the glass transition versus ϵ/kT . Squares show values from Table 1. The line shows eq 21. The line would be horizontal if the Ehrenfest relation ($\delta V_T = 0$) applied.

that they can be approximated by

$$P\Delta\kappa = a - b(\epsilon/kT)^2 \quad \text{at} \quad y_g \quad (18)$$

with $a = 0.23$ and $b = 0.023$. The model liquid changes from fragile to strong¹³ as ϵ/kT increases¹⁹ so that $\Delta\kappa$ is very small and the uncertainty is about 100% when $\epsilon/kT = 3$.

To calculate δV_T , eq 16 was inverted to get the volume difference $\Delta V/V_o$ between glasses formed at ϵ/kT and $\epsilon/kT + 1$, when they are compared at the glass transition pressure, $P_g V_o / NkT$ of either glass. The results are listed in Table 1. (Equation 6 requires that the volumes of the two glasses be compared at the same $PV_o/N\epsilon$ and ϵ/kT , but once a glass has been made, P/T does not vary significantly when ϵ/kT is varied at constant density.) The quantity required in eq 17 is then

$$T\delta V_T/V = (V_o/V)(\Delta V/V_o)(Td(\epsilon/kT)/dT) \quad (19)$$

The value of V_o/V used in eq 19 is the average of the glass transition densities for the glasses formed at ϵ/kT and $\epsilon/kT + 1$. Figure 3 shows that the results are approximated by

$$T\delta V_T/V = -c\epsilon/kT \quad (20)$$

with $c = 0.020$.

Substituting the empirical forms, eqs 18 and 20, into eq 17, and integrating, yields

$$\frac{P_g V_o / NkT}{(P_g V_o / NkT)_{\epsilon/kT=0}} = \left(\frac{\sqrt{a/b} - \epsilon/kT}{\sqrt{a/b} + \epsilon/kT} \right)^d \quad (21)$$

where the constants are $(a/b)^{1/2} = 3.1$ and $c/2(ab)^{1/2} = 0.14$.

Equation 21 is compared with the measured values of $P_g V_o / NkT$, from Table 1, in Figure 4. The good agreement is fortuitous in view of the uncertainties emphasized in Figures 2 and 3. However, I agree with Nieuwenhuizen⁸ that eq 5 and 9 are correct (by definition) and any disagreement in Figure 4 should be attributed to the uncertainty in $T\delta V_T/VP\Delta\kappa$. Because the potential energy of the model is essentially constant near the glass transition, eq 10 is as good as eq 9 and on this point I disagree with Nieuwenhuizen.⁸

Experiments on real materials⁹ usually show that T_g varies linearly with P while eq 21 predicts a pronounced curvature. This is because the range over which T_g is varied in real experiments is negligible relative to the range studied in the simulation experiment. To emphasize this point, we may choose a typical bond strength $\epsilon = 10$ kJ/mol which makes $\epsilon/k = 840$ K, then $\epsilon/kT = 3$ corresponds to $T = 280$ K, while $\epsilon/kT = 0$ corresponds to infinite temperature and pressure. The divergence of kT/ϵ and $PV_o/N\epsilon$ when ϵ/kT is zero is disguised in Figure 4 by plotting their ratio, $P_g V_o / NkT$, against ϵ/kT .

5. Conclusions

The Ehrenfest² relations are generalized to the case where the lower temperature phase is a glass, with properties that depend on its history as well as on the external variables T and P . When the low temperature phase is equilibrated, the original Ehrenfest relations are regained.

The revised relations predict the variation in the glass transition pressure with temperature, measured in a simulation study,¹⁸ to within the precision of the measurements required to test them, over a wider range of temperature and pressure than those accessible in experiments on real materials.

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