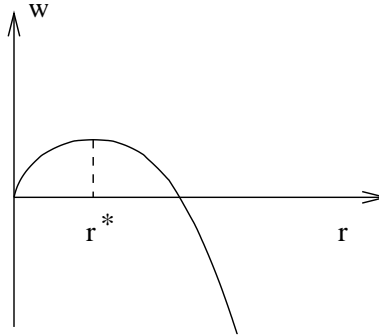


**Question B1 The driving force** for nucleation  $\Delta G_v$  is controlled by the temperature of annealing. It is low close to the transition temperature, high at lower temperatures where the transformation might however be inhibited by low diffusion rates. Producing a nuclei ‘costs’: interfacial energy between crystal and glass + elastic strain energy (low if glass is of same composition).

For a nuclei to be stable, its growth must be accompanied by a decrease in Gibbs free energy. Consider the work done to create a nuclei of radius  $r$ :

$$W = 4\pi r^2 \sigma + \frac{4}{3}\pi r^3 \Delta G_v$$



where  $\Delta G_v$  is negative if the transformation is to occur. The critical radius is given by  $\frac{\partial W}{\partial r} = 0$ , ie:

$$r^* = -\frac{2\sigma}{\Delta G_v}$$

**What is the critical radius ?** It is the radius above which a nuclei is stable and therefore able to grow. Any nuclei smaller than  $r^*$  will disappear. The critical radius depends on the temperature: the lower the temperature (with regard to the transformation one), the larger the driving force, therefore the smaller  $r^*$ . We can clarify the temperature dependency of  $\Delta G_v$ :

At equilibrium:

$$\begin{aligned} \Delta G_v(T_{eq}) = 0 &= \Delta H_v(T_{eq}) - T_{eq} \Delta S_v(T_{eq}) \\ \Rightarrow \Delta H_v(T_{eq}) &= T_{eq} \Delta S_v(T_{eq}) \\ \Rightarrow \Delta G_v(T) &= \Delta H_v(T_{eq}) \left(1 - \frac{T}{T_{eq}}\right) \end{aligned}$$

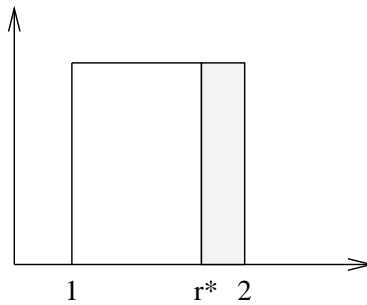
where in fact we assume that  $\Delta H_v$  and  $\Delta S_v$  are not changing with temperature. This is reasonable within a limited range of temperature.

**Obtaining a grain size of  $40\mu m$ :** this is a simple three step problem: (1) find the number of nuclei we need to grow to produce this grain size (2) express it as a percentage of the total number of nuclei formed and find the critical radius we want, (3) once we know what we want  $r^*$  to be, we calculate the temperature that will give it.

(1) We need to assume that a unit volume is filled up by cubic grains, each grain comes from one nuclei. These grains can be taken to have a side length of  $40\mu m$ , therefore each occupy a volume of  $(4 \cdot 10^{-5})^3$  and the number of nuclei (per unit volume) is the number of times we can fit this volume into a unit volume.

$$1/(4 \cdot 10^{-5})^3 = 0.1562 \cdot 10^{14}$$

(2) The graph shows that the nuclei are uniformly distributed by size between 1 and 2 nm, the total number of nuclei per unit volume being  $10^{14}$ . We need to find  $r^*$  which will lead to the growth of  $0.1562 \cdot 10^{14}$  nuclei. Nuclei which grow are located at radii larger than  $r^*$  as illustrated below:



That means the ratio  $\frac{2-r^*}{(2-1)}$  should be equal to  $\frac{0.1562 \cdot 10^{14}}{10^{14}}$ , which gives:

$$r^* = 1.84nm$$

(3) Using the expression for  $r^*$ , obtain the wanted driving force. Using the expression for the change of  $\Delta G_v$  with temperature, calculate the temperature giving the wanted driving force. We obtain:

$$T = 1161^\circ C$$