the exponential must be less than about 100. This implies that the value for σ must not exceed about 20 ergs/cm². Values of the right hand side of Eq. (5.14) were therefore calculated for $\sigma = 20 \text{ ergs/cm}^2$. Values for the driving force G_{21} , which are given in multiples of A, were obtained from the two-phase equation of state for iron given in Appendix A. The value for $A = -8.33 \times 10^{-15}$ ergs/atoms is G_{21} at $P^{TL} = 130$ kbar, T = 338°K, which is the state for onset of transformation for the loading process. The value for G21(P=0,T=295°K) = 6.85 \times 10⁻¹⁴ ergs/atoms, which defines the initial distribution function shown in Fig. 5.5(a), was obtained using the approximation $G_{21} \simeq (V_2 - V_1)(P - P^T) - (S_2 - S_1)(T - 332^{\circ}K)$. (See Appendix A.) A constant value $V_2 = 1.045 \times 10^{-23} \text{ cm}^2/\text{atoms}$ for iron at P^{TL} = 130 kbar, T = 338°K was used since V₂ varies only from $1.045 \times 10^{-23} \text{ cm}^3/\text{atoms}$ to $1.021 \times 10^{-23} \text{ cm}^3/\text{atoms}$ over the stress range 130 kbar to 200 kbar. The number of iron atoms, N, in l cc is 8.48×10^{22} . The value for $(2/V_2)(dV_2/dG_{21})$ $\simeq 2K_{T}/(V_{2}-V_{1}) \simeq -150 \text{ gm/Mbar cm}^{3}$, where K_{T} is isothermal compressibility of phase 2 and the approximation $dG_{21} \simeq \Delta V dP$ was used. (See Appendix A.) Since $3/A = 3.4 \times 10^4$ gm/Mbar cm³, $(2/V_2)(dV_2/dG_{21})$ can be ignored.

Inspection of values given in the last column of Table 5.2 reveals that as the magnitude of G_{21} increases so does the magnitude of dN^*/dG_{21} . Since dN^*/dG_{21} for $G_{21} = A$ is so small compared to values at higher driving force, nucleation is initiated for values at a driving force between A and 2A. A smaller value for σ would force the initiation of 82

nucleation nearer A, but the adjustment appears unwarranted considering uncertainties in σ . Values of n^{*} become unphysically small for driving forces exceeding 2A. The value of this model and suggested ways to improve it are discussed in the next section.

If because of cold work, grain growth, or other energy concentrating processes, a number of permanent spherical embryos of phase 2 exist in the stable field of phase 1, then the energy required to reach critical size is less than for pure homogeneous nucleation. In fact, suppose that these pre-existing sites are of size n_0 and that normal statistical fluctuations create a distribution of sizes as in the homogeneous case; then Eqs. (5.4) and (5.5) are unchanged, except that $n + n_0$ is substituted for n. The important change comes in that N becomes the number of pre-existing sites N_0 of size n_0 . Substitution of N_0 for N in Eq. (5.14) results in an expression for dN^*/dG_{21} for the case of pre-existing sites.

5.4. The Quasistatic Hugoniot

Shock data described in Section 5.1 show that:

- 1. Initial transformation rate for close-in experiments exceeds 2×10^{7} /sec for mass fraction of phase 2.
- Any transformation taking place behind the plastic II shock is slow since there is no evidence of changes in stress behind the shock front.
- Hugoniot P-V states for 130 to 200 kbar are vastly different from those predicted by equilibrium hydrostatic thermodynamics and measured values of dP/dT.

83