

One can certainly anticipate continuing refinements of such empirical potentials. So far, they have been mainly, though not exclusively, fitted to some experimental quantities relating to perfect or nearly perfect metallic crystals, e.g. equilibrium lattice spacing, cohesive energy, elastic moduli, plus some particular phonon characteristics. But one would envisage, in refinements (see also Heine, 1994) information about unusual bonding geometries (e.g. at reconstructed metal surfaces) or perhaps an interstitial atom at the maximum of its migration barrier, also being embodied.

1.9. *Pair Potentials*

Simulations using empirical interatomic potentials can often supply efficient and usually inexpensive routes for studying ionic structure and dynamics in metallic systems. For a long time, pair potentials were used very extensively in such simulation studies. They can reproduce usefully total energies for many systems. But when one turns to elastic properties, deficiencies begin to emerge (e.g. their inability to reproduce the so-called Cauchy discrepancy: see for instance Johnson, 1972). This situation can be remedied by the addition to the pair potential contribution of a volume-dependent, structure independent energy (the reasons being set out in Chaps. 6 and 7). But in specific examples, such as fracture of surfaces, where the volume is ambiguous, pair potential models need transcending. A further difficulty in the (simplest) pair potential scheme comes up in the determination to the vacancy formation energy E_v (compare Johnson, 1987). It is found empirically that this energy E_v is typically about 1/3 of the cohesive energy. In contrast, the straightforward pair potential models predict that, excluding the contribution from relaxation which is modest in close-packed metals, these two energies are equal. These limitations of the simple pair potential approximation have been addressed by the development of empirical many-body potentials which is the major theme of Chap. 8.

1.10. *Grain and Twin Boundaries*

Most solids do not occur as single crystals. Usually, they are assemblies of small crystallites randomly oriented with respect to one another. The boundaries between them are referred to as grain boundaries (Mclean, 1957; Kê, 1947, 1990). Rosenberg (1978) gives a figure (Fig. 3.7, p. 42) of crystallites and grain boundaries in α -brass: the specimen having been first cold-rolled and then annealed. Generally the structure of a grain boundary is complicated, but