

2.1.1 Atomistic Local Strain

It is not too difficult to define local strain when the reference state is known: one may carry out a least-square fitting procedure outlined in (6.34) to get a best fit of the affine transformation matrix \mathbf{J} to the relative positions of atoms nearby. The problem is harder when there is no given reference system, for example a dislocation would cause lattice mis-registry that makes the original reference hard to keep track of. What we need is a *geometrical* characterization of the local atomic environments that works in much the same way as the coordination number, but provides strain information when the measure is applied to a piece of deformed yet perfect lattice. Because there is no reference frame, it can at best output the *matrix invariants* of the strain tensor, e.g., the dilatational component

$$\eta_m \equiv \frac{1}{3} \text{Tr} \eta, \quad (2.22)$$

and the shear component,

$$\eta_s \equiv \sqrt{\frac{1}{2} \text{Tr}(\eta - \eta_m \mathbf{I})^2}, \quad (2.23)$$

calibrated to the cases of hydrostatic dilatation $\eta_{xx} = \eta_{yy} = \eta_{zz} = \eta_m$, and pure shear $\eta_{xy} = \eta_{yx} = \eta_s$.

Consider 3×3 matrix,

$$\mathbf{M}_i \equiv \sum_{j \in N_i} \mathbf{q}_{ij} \mathbf{q}_{ij}^T, \quad (2.24)$$

defined at each atom i , where \mathbf{q}_{ij} is the relative position between atom j and i ,

$$\mathbf{q}_{ij} \equiv \mathbf{q}_j - \mathbf{q}_i, \quad (2.25)$$

and $j \in N_i$ is the set of i 's neighbors, whose definition is to be chosen. Two possible choices are,

$$N_i^R : \{j \in N_i^R \mid |\mathbf{q}_{ij}| \leq R\}, \quad (2.26)$$

where R is a cutoff distance, usually picked to be between the first and second nearest

neighbors at the material's perfect crystalline state; or,

$$N_i^C \equiv N_i^{R_i}, \text{ with } |N_i^{R_i}| = C, \quad (2.27)$$

i.e., we sort j according to $|\mathbf{q}_{ij}|$ and pick only the nearest C atoms, where C is the ordinary coordination number of the crystal, like 12 for fcc, etc. Anyway, N_i must be chosen such that,

$$\mathbf{M}_i^0 = d_0 \mathbf{I}, \quad (2.28)$$

at the material's perfect crystalline equilibrium. Satisfying (2.28) may seem quite impossible at the first glance, but actually materials with cubic or T_d symmetry automatically do, including fcc, bcc, hcp (perfect c/a ratio), diamond cubic, and NaCl, ZnS, CsCl binary structures.

Consider how local strain and rotation influences (2.24) of a perfect crystal. For a given local affine transformation \mathbf{J} ,

$$\mathbf{q}_{ij} \rightarrow \mathbf{q}'_{ij} = \mathbf{J} \mathbf{q}_{ij}. \quad (2.29)$$

Therefore, if *neighbors do not enter or leave* N_i ,

$$\mathbf{M}_i = \sum_{j \in N_i} \mathbf{q}'_{ij} \mathbf{q}'_{ij}{}^T = \mathbf{J} \left(\sum_{j \in N_i} \mathbf{q}_{ij} \mathbf{q}_{ij}{}^T \right) \mathbf{J}^T = \mathbf{J} \mathbf{M}_i^0 \mathbf{J}^T. \quad (2.30)$$

But if requirement (2.28) is satisfied, there would be

$$\mathbf{M}_i = \mathbf{J} (d_0 \mathbf{I}) \mathbf{J}^T = d_0 \mathbf{J} \mathbf{J}^T. \quad (2.31)$$

As the local Lagrangian strain at atom i is defined to be,

$$\eta = \frac{1}{2} (\mathbf{J}^T \mathbf{J} - \mathbf{I}), \quad (2.32)$$

the local strain hydrostatic invariant is,

$$\eta_m = \frac{1}{3}\text{Tr}\eta = \frac{1}{6}(\text{Tr}\mathbf{J}^T\mathbf{J} - 3) = \frac{1}{6}(\text{Tr}\mathbf{J}\mathbf{J}^T - 3) = \frac{1}{6}(d_0^{-1}\text{Tr}\mathbf{M}_i - 3), \quad (2.33)$$

and the local strain shear invariant is,

$$\begin{aligned} \eta_s &= \sqrt{\frac{1}{2}\text{Tr}(\eta - \eta_m\mathbf{I})^2} \\ &= \sqrt{\frac{1}{2}\text{Tr}\eta^2 - \frac{3}{2}\eta_m^2} \\ &= \sqrt{\frac{1}{8}\text{Tr}(\mathbf{J}^T\mathbf{J} - \mathbf{I})^2 - \frac{3}{2}\eta_m^2} \\ &= \sqrt{\frac{1}{8}\text{Tr}\mathbf{J}^T\mathbf{J}\mathbf{J}^T\mathbf{J} - \frac{1}{4}\text{Tr}\mathbf{J}^T\mathbf{J} + \frac{\text{Tr}\mathbf{I}}{8} - \frac{3}{2}\eta_m^2} \\ &= \sqrt{\frac{1}{8}\text{Tr}\mathbf{J}\mathbf{J}^T\mathbf{J}\mathbf{J}^T - \frac{1}{4}\text{Tr}\mathbf{J}\mathbf{J}^T + \frac{\text{Tr}\mathbf{I}}{8} - \frac{3}{2}\eta_m^2} \\ &= \sqrt{\frac{1}{8}\text{Tr}(\mathbf{J}\mathbf{J}^T - \mathbf{I})^2 - \frac{3}{2}\eta_m^2} \\ &= \sqrt{\frac{1}{8}\text{Tr}(d_0^{-1}\mathbf{M}_i - \mathbf{I})^2 - \frac{3}{2}\eta_m^2} \\ &= \sqrt{\frac{1}{8}\text{Tr}(d_0^{-1}\mathbf{M}_i - \mathbf{I})^2 - \frac{1}{24}(d_0^{-1}\text{Tr}\mathbf{M}_i - \text{Tr}\mathbf{I})^2} \\ &= d_0^{-1}\sqrt{\frac{1}{8}\text{Tr}(\mathbf{M}_i - \frac{\text{Tr}\mathbf{M}_i}{3}\mathbf{I})^2}. \end{aligned} \quad (2.34)$$

After obtaining $\{\mathbf{M}_i\}$ for all atoms, one may also compute system average $\langle\mathbf{M}\rangle$ and evaluate local deviations from $\langle\mathbf{M}\rangle$. The above scheme (2.24) to (2.34) works extremely well in practice, allowing one to directly visualize microstructures and their strain fields with color-encoding. Successful examples include point defects, dislocations, cracks, grain boundaries, stacking faults and even kinks.

2.2 Thermodynamic Ensembles and Fluctuations

This section deals with the thermodynamic state of an atomistic simulation which can either be molecular dynamics (MD) or Monte Carlo (MC) [7]. In MD, one numerically