Automated voxelization of 3D atom probe data through kernel density estimation

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Abstract

Identifying nanoscale chemical features from atom probe tomography (APT) data routinely involves adjustment of voxel size as an input parameter, through visual supervision, making the final outcome user dependent, reliant on heuristic knowledge and potentially prone to error. This work utilizes Kernel density estimators to select an optimal voxel size in an unsupervised manner to perform feature selection, in particular targeting resolution of interfacial features and chemistries. The capability of this approach is demonstrated through analysis of the γ / γ' interface in a Ni-Al-Cr superalloy.

Introduction

Atom probe tomography (APT) [1-3] allows 3 dimensional (3D) imaging at sub-nanometer spatial resolution by evaporating nanometer sized needles of sample materials under extremely high electric fields. The needles, typically comprising several million atoms, represent a 3D penetration into the sample making buried interfaces and other features easily accessible. In visualizing the acquired APT data, the high number of data points can easily obscure underlying structures. Therefore, information is extracted from the reconstructed APT data by first sectioning it into 3D boxes termed voxels [4-6], which encompass a collection of atoms [Fig. 1], and assigning a local density value to each voxel in terms of the chemical composition within the voxel. By tracking the variation in the density associated with voxels distributed throughout the sample, one can infer the presence of underlying features such as grain boundaries or precipitates.

Fig.1: Voxelization of random data points scattered in 3D, representative of atoms in a material. (a) Original data set within a 1 nm³ box. (b) The atoms are grouped into uniform voxels of edge length 0.2nm. The numbers of atoms contained within the different voxels represent the local density of that voxel volume.

Fig. 1 graphically denotes the process of voxelization for a data set of random points scattered in 3D [Fig. 1a], representative of atoms in a material. The volume encompassing the data is initially sectioned into voxels [Fig. 1b] of edge length of 0.2 nm (chosen arbitrarily for illustration). The data is then binned into the voxels, much like a 3D histogram. The voxels are then classified according to the number of data points they contain and assigned a density value. The density value of voxels is useful to pinpoint regions of high density, which may indicate the presence of precipitates, or to capture regions of different densities delineating different phases.

However meaningful feature identification requires appropriate selection of voxel size. The voxel size needs to be optimized to preserve features of interest [6, 7] because a very large voxel size could result in averaging of data and in loss of feature information, while a very small voxel size may result in final output being affected by statistical noise. Fig. 2 illustrates such a process where different voxel lengths are used to categorize the same dataset.

Fig.2: Voxelization and extraction of an arc shaped interface region inserted into the random data points from Fig. 1. Voxels with a density of greater than 20%, normalized to the voxel with the highest number of datapoints in it, are plotted. (a) Voxel edge length of 0.02nm: In this case voxels capture statistical noise in addition to the true interface feature (b) Voxel edge length of 0.1nm: here the statistical noise is minimized and a clearer image of the interface emerges. (c) Voxel edge length of 0.2nm: interface becomes diffuse due to averaging out over data points extraneous to the interface.

A set of data points randomly scattered in 1 nm^3 region enclosing a denser arc-shaped interface region is modeled by different voxel lengths. Once the voxels are constructed and their density content computed, we plot only those voxels with a density value greater than 20% compared to the voxel with the highest density, in hopes that the high density interface will be captured smoothly. In Fig 2(a) it can be seen that a very small voxel size of 0.02 nm^3 introduces a lot of statistical error. Several voxels throughout the sample report high density values due to statistical fluctuation of the data points. When the voxel edge length is increased to 0.1 nm , the statistical fluctuations get averaged out and a clearer image of the interface emerges [Fig. 2(b)]. On further increase of edge length to 0.2 nm , averaging takes place over data far from the interface and the interface becomes quite diffuse [Fig 2(c)]. While three choices of voxel size are shown here, in reality feature detection necessitates the variation of voxel edge length by the user, over a range of values, until a satisfactory image is obtained. Such selection typically involves heuristic decisions on part of user, which leads to ambiguity and bias based on prior knowledge. Thus, it is imperative to apply a technique that objectively performs feature selection through a data driven approach without user supervision. The main objective of this work is to minimize subjective user supervision in identifying nanoscale chemical features and instead to employ data driven quantitative analysis on APT data to navigate the specimen feature space. This is accomplished by utilizing Kernel density estimators to select an optimal voxel size conforming to error minimization [8], the details of which are elaborated in following section.

Data and Methods

APT on Ni-Al-Cr: For atom probe studies, needle shaped samples were prepared from the arc melted bulk alloy using a Electro discharge machine (EDM) to obtain thin rods of cross section $0.5 \times 0.5 \text{ mm}^2$, which were then electropolished (5% perchloric acid in acetic acid) into sharp needles. Finally these needles were further thinned to tip diameters $\sim 50\text{-}70 \text{ nm}$ using dual-beam focused ion beam technique (FEI Helios Nanolab 650). The needle samples were studied using Local Electrode Atom Probe (LEAP 3000X Si). The pulsed laser experiment was performed using a laser energy of 0.6 nJ at tip at pulse repetition rate of 200 kHz and tip temperature of 55 K .

Reconstructed Data: Consider the raw data obtained from APT based reconstruction of a Ni-Al-Cr specimen [Fig. 3]. The data is obtained as a table of $n \times 4$ where n is the number of rows, each representing an atom. The first three columns provide the geometric location of the evaporated atoms on the sample tip and the forth column gives the mass to charge ratio of the corresponding atoms, denoting the atomic species. The recovered sample contains 8.72 million atoms categorized into Ni, Al, Cr, O, H and other trace elements/ impurities. For ease of visualization, only the Al (blue dots) and Cr (red dots)

atoms are shown in Fig. 3. The microstructure consists of a fcc γ phase and precipitates of L1₂ ordered fcc γ' phase. These two phases are clearly visible and the atomic percentages of the different elements are shown for each phase. The γ phase is marked by an enrichment of Cr and depletion of Al, as expected [9], while the Ni concentration is consistent throughout.

Fig. 3: Raw data from APT based reconstruction of a Ni-Al-Cr specimen representing 8.72 million atoms. For ease of visualization, only the Al (blue dots) and Cr (red dots) atoms are shown. Two phases are clearly visible. The γ phase is marked by an enrichment of Cr and depletion of Al, as is already well known. The relative contributions of different elements in each phase is shown in the adjacent table. The last column represents the combined contribution of elements such as O, H and background noise.

Feature Extraction through non-parametric density estimation: Although the two phases in the Ni-Al-Cr sample are superficially visible here, the precise information about where the interface exactly lies or other features that may be buried inside the sample requires quantitative analysis of the material. Usually such information can be derived from the density information. For example, those regions where $Cr > Al$ could denote the γ' phase while those regions where $Cr < Al$ could denote the γ phase. The interface can be interpreted as the region where the two concentrations cross over, i.e., $Cr = Al$. In order to obtain such density information the APT data is divided into voxels and the density of each voxel is computed. This approach is called non-parametric density estimation which means that no assumption is made about the statistical distribution of the original data. Rather the density information is obtained from the raw data itself, such as through voxelization, and then isoconcentration surfaces can be drawn to capture features possessing similarity based on density information. In the simplest case the voxels can play the role of 3D histograms, with each voxel denoting the number of atoms it contains. However, the

discontinuity of density of neighboring voxels can make it difficult to model the gradient of concentration over the 3D space.

To overcome this problem kernel density estimation (KDE) is used to capture the contribution of each atom towards the voxel and to obtain a smooth overall density function representing the voxel. Each atom is represented by a kernel; a symmetric but not necessarily positive function that integrates to one as below

$$\int_{-\infty}^{\infty} K(x)dx = 1 \quad (1)$$

which contributes some value to the center of the voxel, with the center being representative of the region encompassed by the voxel. The contribution of the atoms within the voxel to the voxel center is a function of the atom's location and is determined by some sampling formula [10]. In the simplest case the contribution of each atom, located at position ' x ', towards a voxel of unit length centered around the origin can be represented by a Parzen window [11] given by

$$\begin{aligned} K(x) &= \frac{1}{2}, & |x| \leq 1 \\ &= 0, & |x| > 1 \end{aligned} \quad (2)$$

which indicates that all atoms within the voxel contribute equally independent of their location within the voxel. There are several other sampling functions and merits of each are discussed in [12, 13]. In this work we make use of Gaussian kernels as shown in Fig. 4.

Fig. 4 – KDE using Gaussian kernels. h is the edge length of the voxel. x_i denotes the location of atom ' i '. X denotes the center of the voxel at which the density is calculated.

If ' x ' is the atom position and X is the center of the voxel of edge length ' h ' where the individual kernel contribution is measured, the contribution of the Gaussian kernel is defined by the weighting function

$$w_G(x - X, h_d) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-X)^2}{2\sigma^2}} = \frac{1}{h_d} K\left(\frac{x-X}{h_d}\right) \quad (3)$$

where the value (h_d) is known as the bandwidth of the kernel and in the case of the Gaussian kernel: $h_d = \sigma$ where σ is the standard deviation. The standard Gaussian kernel (with zero mean and unit variance) is given by $K(t) = \frac{1}{\sqrt{2\pi}} e^{-\frac{1}{2}t^2}$.

The estimated *density function* at any point x within the voxel [Fig. 5] is defined by the average of the various kernel contributions (eq. 3) as

$$\hat{f}(x) = \frac{1}{nh_d} \sum_{j=1}^n K\left(\frac{x - X_j}{h_d}\right) \quad (4)$$

where $h_d > 0$ is the window width, also called the smoothing parameter or bandwidth.

Fig. 5: Illustration of density estimation through kernel density function (red lines) representing atom positions (yellow circles) in different voxels. The blue line is the estimated density of atoms in each voxel obtained by summing up the contributions of the various kernels within the voxel.

It is important to choose an appropriate bandwidth that will not lead to either oversmoothing or undersmoothing of the density estimate. When using a Gaussian kernel to represent the contribution of an atom to the voxel, one must consider the fact that by definition there is no spatial limit to which the Gaussian extends. However, in practice, one is interested in atoms within and around the vicinity of the voxel when computing the voxel density, and not about atoms located far away and contributing infinitesimally. Therefore, for practical purposes of numerical modeling an artificial cut is made to truncate the extent of the Gaussian function. The heuristic selection used in this work is to truncate at the full width at half maximum (FWHM) value of the Gaussian function and to set this width equal to the edge length ' h ' of the voxel using the formula $2\sqrt{2\ln 2}\sigma = h/2$. This selection logically allows an atom at the boundary of two voxels to contribute 50% of its maximum value to the voxel on either side of it,

while an atom located at the center of the voxel will contribute solely to that voxel since the spread of its distribution is truncated at the boundary of the voxel. Since the bandwidth selection has been tied to the voxel edge length, we now have one free parameter, i.e. voxel length ' h ', that requires to be optimized to minimize error. By varying h the bandwidth is correspondingly varied accounting for its optimal choice on the process of error minimization.

To automate the voxel size an error function is defined to compute the difference between the kernel estimated density of the data $\hat{f}(x)$ and its true density $f(x)$. A typical measure of the accuracy over the entire voxel is obtained by integrating the square of the error computed given by:

$$MISE(\hat{f}) = E \left[\int_{-\infty}^{\infty} (\hat{f}(x) - f(x))^2 dx \right] \quad (5)$$

where $MISE$ is the mean integrated square error.

Since the distribution of atoms does not follow any known pattern, especially at the region of interest such as the interface, the true density $f(x)$ is not known. The approach followed here to approximate the true density as closely as possible to the estimated density consists of the following sequence: $f(x)$ is first assumed to be a Gaussian distribution, assumed to represent the actual distribution of atoms within the voxel, although the atoms may very well be non-normally distributed. The mean and variance of this assumed Gaussian spread is calculated for the atoms within and on the boundary of the voxel of interest. Next, depending on the real distribution of the atoms, the Gaussian function may peak either at or off center in the voxel and in the latter case it is translated to the center of the voxel. The difference of this Gaussian distribution with $\hat{f}(x)$ is used for computation of $MISE$. For the cases where the initial assumption of $f(x)$ is a poor one, it will results in a high $MISE$. By gradually varying the voxel size the validity of this assumption reaches a most probable value corresponding to minimized $MISE$. The total squared error (E_{tot}) is then computed for the entire dataset given by the following equation

$$E_{tot} = \sum_{j=1}^V (MISE)_j \quad (6)$$

Where V is the total number of voxels. E_{tot} is then minimized with respect to varying voxel size.

Results and Discussion

The kernel density estimation was carried out on the Ni-Al-Cr dataset comprising ~ 8.72 million atoms. For each atom in a voxel, a Gaussian kernel was fit at the atom location and its amplitude was set at 1 with full width at half maximum set to the voxel edge length. The kernel contributions of atoms to the

voxel were calculated at the voxel center for all atoms within and on the boundary of a particular voxel. These values were then added giving the amplitude of density at the voxel center. The error was then calculated between the actual density and estimated density using the procedure explained in the previous section. This procedure is repeated for the voxel size varied from 0.5 nm to 2.5 nm in steps of 0.1 nm. A minimum error was obtained for 1.6 nm voxel size (Fig. 6) providing a tradeoff between the noise and data averaging. This voxel size of 1.6 nm reduces the atomic data set into a representation of 83,754 voxels at 1.6nm^3 each, and was used towards density estimation.

Fig. 6: Dependence of the normalized mean integrated square error (MISE) on the voxel size. The error is minimum for a voxel edge length of 1.6nm.

To provide a visual understanding of the error minimization process we provide snapshots [Fig. 7] of information representation in terms of voxels for varying voxel size. It should be noted that unlike Fig. 3, where each point is representative of an atom, each point in Fig. 7 is now representative of a voxel. This means that every point carries with it, information about the density of atoms of different species within the voxel it represents. Fig. 7 elucidates the effect of voxel edge length on capturing the precise interface between the γ / γ' region of the Ni-Al-Cr sample. As mentioned earlier a likely measure of the interface is where the concentrations of Al and Cr are approximately equal to each other. After voxelization of the data we plot out isosurfaces representing only voxels where $\text{Al} = \text{Cr}$.

The sequence of images with increasing voxel size shows the transition from the regime of statistical noise to oversmoothing of the final result with an intermediate value (1.6nm) capturing the features precisely. In the case of 1nm, the voxel size is too small to accurately estimate the density. Due to statistical fluctuation in the distribution of atoms there are many pockets of 1nm^3 throughout the sample where the concentration of Al and Cr are almost equal. As the voxel size is increased the increase in volume averages out the noise and a clear interface starts emerging. At 1.6nm most of the statistical noise

vanishes and a very sharp interface is obtained, with nanometer scale fluctuations visible on the isosurface representing the interface. As the voxel size is increased beyond this value, oversmoothing of data starts occurring. The interface starts becoming diffuse and the graininess in the image disappears. At this stage there is ideally no statistical noise and the residual clusters scattered throughout the volume could potentially be capturing the presence of nanoclusters, but this requires more detailed evaluation.

Fig. 7: Variation in feature topology with changing voxel sizes in units of nm. (a) 1, (b) 1.1, (c) 1.2, (d) 1.3, (e) 1.5, (f) 1.6, (g) 2, and (h) 2.5. Only those voxels where the Al = Cr concentrations are imaged, reflecting the γ / γ' interface. For images (a)-(d) we find that the voxel sizes are too small to capture the interface alone. Rather pockets of statistical fluctuation are captured throughout the sample. Images (e) and (f) show a high degree of clarity in interfacial features with minimal statistical noise in the sample. Finally images (g) and (h) show that although the statistical noise is almost entirely removed, the interface features themselves have become diffuse. The selection of voxel size could reasonably be selected between 1.5 and 2.5, as denoted by the labeling on the figure. From Fig. 6, we identify 1.6 nm as the optimal voxel size (ie. Minimum error), which also corresponds to Figure 7f, which appears with the sharpest interface.

To further emphasize the user bias typically inherent in selection of voxel size, the concentration profiles across the interface are shown in Fig. 8. While all of the profiles look reasonable, they result in greater than 2 nm difference in interfacial width. Through the approach described here, we can now identify the interfacial width for this system in a completely unbiased manner, with the width measured at 4.4 nm.

Fig. 8: Concentration profiles for voxel size of (a) 0.5, (b) 1.6, and (c) 2.0. Each element (Al, Cr and Ni) and variations in the interfacial width for each voxel size are shown. From our approach, we measure the interfacial width (4.4 nm) while removing the inherent bias in the process. This further emphasizes the benefit of the approach, as the resulting changes in the concentration profiles are subtle, as compared with the more obvious variations in the 3D spatial mapping.

It should be noted that when the automated voxelization procedure is applied to either the γ or the γ' phase alone a different value of optimum voxel size can result due to the homogeneity of those particular regions. The simultaneous inclusion of both regions allows the calculation of voxel size that would be optimal in capturing the interface region as well. The approach described in this study can in principle be expanded through the utilization of non-uniform voxel sizes, where large voxels can be used to model homogeneous regions while the voxels can be split around interfaces or nanoclusters. This is the subject of another investigation and reported subsequently.

Conclusions

This work has demonstrated utilization of kernel density estimators to select an optimal voxel size in an unsupervised manner to perform feature selection, in particular targeting sharpness of detail in recovering interfacial images. A case study of interfaces between the γ / γ' region in Ni-Al-Cr superalloy was presented. Using this example it was demonstrated that meaningful feature identification requires appropriate selection of voxel size, which is routinely carried out visually. In order to obtain an optimum value we incorporate error minimization to automate the selection of voxel size. The voxel size was optimized to preserve the feature of interest, while minimizing loss of feature information and noise.

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