Role of Strain in Controlling the Orientation Distribution in Oscillatory Shear of Diblock Copolymers as Studied by SAXS[1]

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ABSTRACT

Small-angle X-ray scattering is used to quantitatively examine the distribution of lamellar orientation in shear aligned diblocks as a function of strain amplitude at constant shear duration, frequency, and temperature. At all strains, predominately perpendicular alignment is observed with some parallel alignment. Also, there is a small amount of transverse alignment. This suggests that alignment by shear occurs at the expense of intermediate alignments followed by reducing transverse alignment. Increased strain at constant time increases the sharpness of the distribution of perpendicular alignment.

1. INTRODUCTION

Diblock copolymers are interesting materials due to the microphase transition these materials undergo, forming a nanoscale patterns in the ordered state. Much recent work has been devoted to the microscopic nature of the order-disorder transition, concentrating on the structure of the ordered state as viewed within a single grain and in the absence of applied fields [1,2]. As the nature of the ordered state becomes better understood, there has been an increase in the attention given to the larger scale structure of these materials, that is to say the overall orientation of the domain structures in the bulk sample. An understanding of methods of manipulating the orientation of the bulk sample is important both as a means of producing orientated samples for practical use and understanding the ordering process of these materials. One established approach to controlling the orientation is the use of flow [3,4].

Recently, there has been much work done to explore the effect of shear on the orientation of lamellar domains in polystyrene-*block*-isoprene (SI) and polystyrene-*block*-poly(ethylene-alt-propylene) (SEP) diblock copolymers [5-15]. There are three defined directions for alignment: perpendicular alignment, where the lamellar normal is parallel to the vorticity direction; transverse alignment, where the lamellar normal is parallel to the flow direction; and parallel alignment, where the lamellar normal is parallel to the shear gradient direction. It has been reported that large amplitude oscillatory shear can bring about both "perpendicular" and "parallel" alignment in these materials depending on the maximum strain, shear frequency, and temperature [5-7]. By the use of in-situ birefringence measurements during shear, a route to final alignment has been proposed [5]. Real time

small-angle X-ray scattering (SAXS) has also been used to observe the orientation of styrene-SEP diblocks under large scale oscillatory shear [8].

Through the use of SAXS measurements, we can quantitatively observe the distribution of lamellar orientations in a sample. While such measurements cannot easily be done in-situ, and thus there is the concern of changing the sample during the sample preparation process (i.e., cutting from the shear tool, mounting in X-ray holder), they provide valuable information to extend the birefringence results reported by other groups, which measure the average orientation of the lamellar domains, but not the orientation distribution.

2. METHODS

2.1 Specimen

An SI diblock copolymer was synthesized by anionic polymerization. The polystyrene (PS) block has a number average molecular weight of 1.12×10^4 and the polyisoprene (PI) block, a molecular weight of 1.46×10^4. The heterogeneity index for the molecular weight distribution of the block copolymer, M_w/M_n, is less than 1.05. By SAXS measurements on the sample, the order-disorder transition (ODT) temperature was determined to be 172.5 ^{o}C. Details of the procedure for determining ODT are described elsewhere [16,17]. Samples were first cast from toluene solutions (ca. 5 wt. % polymer). Less than 1% antioxidant (Irganox 1010) was added to the polymer to prevent degradation. The samples were then annealed under vacuum to remove residual solvent. Finally, they were annealed above the ODT temperature and quickly cooled to insure random alignment of grains by erasing the effect of solvent casting on orientation.

2.2 Procedure

Shear experiments were performed with an oscillatory shear device at 153 ^{o}C with a sample thickness of 1 mm and under nitrogen flow to prevent degradation. The shear can be described by $\gamma=\gamma_0 \sin(\omega t)$ where γ is the strain experience by the sample, γ_0 is the strain amplitude, ω is the frequency, and t is time. The shear frequency was 0.1 Hz, giving an angular frequency of 0.2π (0.628) rad/s. The samples were sheared for the 1.5 hours each. They were then quenched with liquid nitrogen and carefully cut from the machine for further analysis by SAXS. We define the axes of our coordinate system as follows: x is the flow direction, y is the velocity gradient, and z is the vorticity (neutral) direction.

SAXS measurements were performed with an 18 kW rotating anode X-ray generator (Mac Science Co. Ltd., Japan) with a graphite crystal monochromater, a He gas filled scattering path, and a two dimensional imaging plate detector. The sample center to detector distance was 800 mm. Beam collimation was achieved by two 0.5 mm pinholes in series. Results were corrected for background scattering and sample absorption. The edge view is the view obtained with the beam parallel to the z axis (neutral direction) and the through view is that obtained by making a measurement with the X-ray beam parallel to the y axis (velocity gradient direction).

3. RESULTS AND DISCUSSION

In Figures 1a, and 1b, we show the 2-D scattering patterns from the through and edge views of this diblock after shearing at 153 ^{o}C for 1.5 hours with a frequency of 0.1 Hz and a strain of 1.50. The inset of each figure shows the alignment of the sample with respect to the X-ray beam. The first order peak, clearly shows orientation of the sample, and from

Figure 1a, the through view, we see that the sample shows predominately perpendicular alignment, that is lamellar normals parallel to the voricity direction. In Figure 1b, the edge view, we observe evidence for both parallel alignment and weak transverse alignment.

We can show the orientation more clearly by showing the azimuthal angle dependence of the first order maximum, $I_{int,}(\mu)$, which we define by

$$I_{int}(\mu) = \int_{q_1}^{q_2} I(q,\mu)dq \tag{1}$$

where q is magnitude of the scattering vector and q_1 and q_2 are the upper and lower bounds of q for the first order scattering maximum. $q=4\pi/\lambda \sin(\theta/2)$ where λ is the wavelength of the X-rays and θ is the scattering angle. Note that the angle $\mu=0$ is defined as horizontal, parallel to the z axis in Figure 1a and y axis in Figure 1b. See the inset in Figure 2 for a schematic defining μ. In order to compare data from different measurements we normalized the data with the formulas:

$$\overline{I}_{int,\ through}(\mu) = \frac{I_{int,\ through}(\mu)}{\int_0^{2\pi} I_{int,through}(\mu)d\mu} \times \frac{\ln(t_{edge})}{\ln(t_{through})} \tag{2}$$

and

$$\overline{I}_{int,\ edge}(\mu) = \frac{I_{int,\ edge}(\mu)}{\int_0^{2\pi} I_{int,through}(\mu)d\mu} \times \frac{\ln(t_{edge})}{\ln(t_{edge})} \tag{3}$$

where $\overline{I}_{int,through}(\mu)$ and $\overline{I}_{int,edge}(\mu)$ are the normalized data for $I_{int,through}(\mu)$ and $I_{int,edge}(\mu)$ for the through and edge views, respectively. t_{edge} and $t_{through}$ are the measured values of the X-ray transmission and the ratio of their logarithms is used to correct for differences in the scattering volume between the edge and through views. Normalized intensity data $\overline{I}_{int,through}(\mu)$ and $\overline{I}_{int,edge}(\mu)$ are presented in the following figures.

Figure 2 shows the $\overline{I}_{int}$ as a function of azimuthal angle taken from the data of Figures 1a. and 1b From this plot, we can clearly see that the orientation is predominately perpendicular with peaks at azimuthal angles of 0° and 180° in the through view, that is, the lamellar normals are along the vorticity (neutral) direction. In addition, there is evidence for weak parallel orientation, shown by peaks at 0° and 180° for the edge view (lamellar normals parallel to the gradient direction). Finally, there is some slight evidence of transverse alignment in the edge view as evidenced by very weak peaks around 90° and 270° (lamellar normals along the flow direction). For a magnified view of the edge view data of all three samples, see Figure 4.

In figure 3, we show the azimuthal angle dependence of the scattered intensity for three samples sheared under the same conditions (1.5 hours, 153° C, 0.1 Hz), but with the strain amplitudes of 1.50 (also shown in Figure 2), 0.96 and 0.70. Here, we see that there is again predominately perpendicular alignment due to peaks at 0° and 180° in the through view, with weak parallel alignment (0° and 180° in the edge view), and some small evidence of transverse alignment (90° and 270° in the edge view) in the edge view of these samples. The edge view data is shown on an expanded scale in Figure 4. In all the samples described here, we only see transverse alignment in the edge view, though in principle, we should see it in the through view measurements as well. We suspect that due to the strong perpendicular alignment dominating the scattering in the through view the transverse alignment cannot be clearly discerned. More detailed X-ray experiments, necessary to check this

point, are currently underway.

The predominately perpendicular alignment mixed with some parallel alignment is consistent with results measured by birefringence from shear on other SI diblocks at temperatures close to the ODT temperature [9,10]. In the case of the measurements presented here, the shearing temperature is close to the ODT temperature (T/T_{ODT}=0.96). The frequency is also low, below the critical frequency observed by Gupta et. al. for a similar SI diblock [7], again suggesting perpendicular alignment dominates. It has also been shown previously by birefringence measurements that the transverse alignment is suppressed first, followed by suppression of parallel alignment during the shear alignment of SI diblocks to the perpendicularly aligned condition [5]. Here, we observe that the intermediate alignments are suppressed most, that is, alignments that are neither parallel, nor perpendicular, nor transverse, closely followed by the transverse alignment, and finally by the parallel alignment, suggesting agreement with the in situ birefringence measurements [5]. By using X-ray scattering, we are able to discern more details concerning the alignment than is possible with birefringence measurements.

One interesting observation is that the presence of weak transverse alignment. However, this is not unprecedented. Gupta et. al. [12] observed the predominance of transverse orientation at the expense of perpendicular orientation during evolution of parallel lamellar orientation. Furthermore, Okamoto et. al. observed biaxial parallel and transverse orientation after shear of an SEP sample [8] in the strong segregation limit. Here, we observe transverse orientation during what evolution of perpendicular orientation. We also note, in all cases presented here that the transverse orientation is quite weak compared

to perpendicular or parallel orientation.

From figure 4, the edge view data, no clear trend is apparent, probably due to the relatively weak scattering from the sample in this orientation. This point is worth future study. However, from figure 3, we see qualitatively that increased strain increases the sharpness of the perpendicular orientation distribution of these diblocks.

In order to quantitatively compare the sharpness of the perpendicular orientation, we fit the through view data in figure 3 with a gaussian function and obtained the square of the peak half-width at half-height as a measure of sharpness. These results are plotted in figure 5. We see that increased strain at constant duration leads to sharper orientation as indicated by the decreasing value of the peak half-width at half-height with increasing strain.

In these samples, there is no reason to believe that these results are terminal. That is, we expect that longer shearing times would lead to more perfectly aligned samples. However, these results do capture the alignment of these samples at intermediate shear duration and show that: (a) large strain oscillatory shear of this diblock at 153 ^{o}C leads to perpendicular alignment (b) shear leads to alignment in all principal directions, at the expense of intermediate orientations, however, parallel and transverse alignment is much weaker than perpendicular alignment (c) larger strain amplitude at constant time leads to stronger perpendicular alignment.

REFERENCES

1. See, for example: T. Hashimoto, in *Thermoplastic Elastomers*, N. R. Legge, G. Holden, and H. D. Schroeder, Eds. (Hanser Publishers., Munich Vienna, New York, 1987), p. 349.
2. See, for example: F. S. Bates and G. H. Fredrickson, *Annu. Rev. Phys. Chem.* **41**: 525 (1990).
3. A. Keller, E. Pedemonte, and F. M. Willmouth, *Nature* **225**: 538 (1970).
4. G. Hadziioannou, C. Picot, A. Skoulios, M.-L. Ionescu, A. Mathis, R. Duplessix, Y. Gallot, and J.-P. Lingelser, *Macromolecules* **15**: 263 (1982).
5. V. K. Gupta, R. Krishnamoorti, J. A. Kornfield, and S. D. Smith, *Macromolecules* **29**: 1359 (1996).
6. K. Koppi, M. Tirrel, and F. S. Bates, *Phys. Rev. Lett.* **70**: 1449 (1993).
7. V. K. Gupta, R. Krishnamoorti, Z.-R. Chen, J. A. Kornfield, S. D. Smith, M. M. Satkowski, and J. T. Grothaus, *Macromolecules* **29**: 875 (1996).
8. S. Okamoto, K. Saijo, and T. Hashimoto, *Macromolecules* **27**: 5547 (1994).
9. S. S. Patel, R. G. Larsen, K. I. Winey, and H. Watanabe, *Macromolecules* **28**: 4313 (1995).
10. B. L. Riise, G. H. Fredrickson, R. G. Larson, and D. S. Pearson, *Macromolecules* **28**: 7653 (1995).
11. R. M. Kannan and J. A. Kornfield, *Macromolecules* **27**: 1177 (1994).
12. V. K. Gupta, R. Krishnamoorti, J. A. Kornfield, and S. D. Smith, *Macromolecules* **28**: 4464 (1995).

13. B. S. Pinheiro, D. A. Hajduk, S. M. Gruner, and K. I. Winey, *Macromolecules* **29**: 1482 (1996).

14. Y. Zhang, U. Wiesner, and H. W. Speiss, *Macromolecules* **28**: 778 (1995).

15. D. Maring and U. Wiesner *Macromolecules* **30**: 660 (1997).

16. N. Sakamoto and T. Hashimoto, *Macromolecules* **28**: 6825 (1995).

17. J. Bodycomb, D. Yamaguchi, and T. Hashimoto *Polym. J.* **28**: 821 (1996).

FIGURE CAPTIONS

Figure 1a. 2-D scattering pattern from shear oriented sample, γ_0=1.50, through view.

Figure 1b. 2-D scattering pattern from shear oriented sample, γ_0=1.50, edge view

Figure 2. Azimuthal angle dependence of the first order maximum from shear oriented sample,γ_0=1.50

Figure 3. Azimuthal angle dependence of the first order maximum from shear oriented samples at various strains. Sparse markers are used to differentiate data from different values of γ_0.

Figure 4. Comparison of azimuthal angle dependence of the first order maxima, edge views. Sparse markers are used to differentiate data from different values of γ_0.

Figure 5. Width of perpendicular orientation peaks in $\overline{I}_{int,through}(\mu)$ as in the a function of strain at constant shear duration, temperature, and frequency.

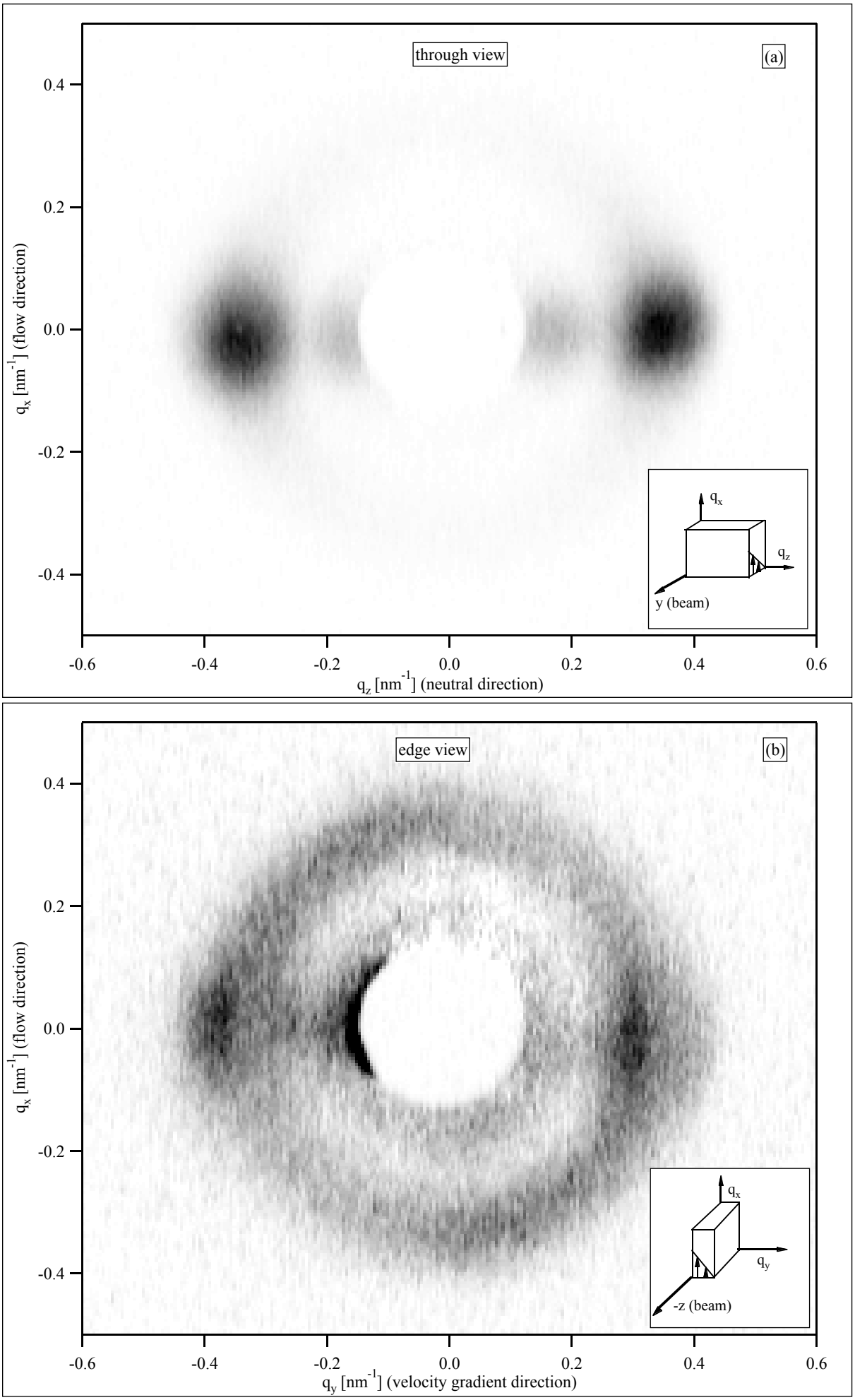
through view
(a)
0.4
0.2
0.0
-0.2
-0.4
q_x [nm^{-1}] (flow direction)
q_x
q_z
y (beam)
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
q_z [nm^{-1}] (neutral direction)
edge view
(b)
0.4
0.2
0.0
-0.2
-0.4
q_x [nm^{-1}] (flow direction)
q_x
q_y
-z (beam)
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
q_y [nm^{-1}] (velocity gradient direction)

Figure 1

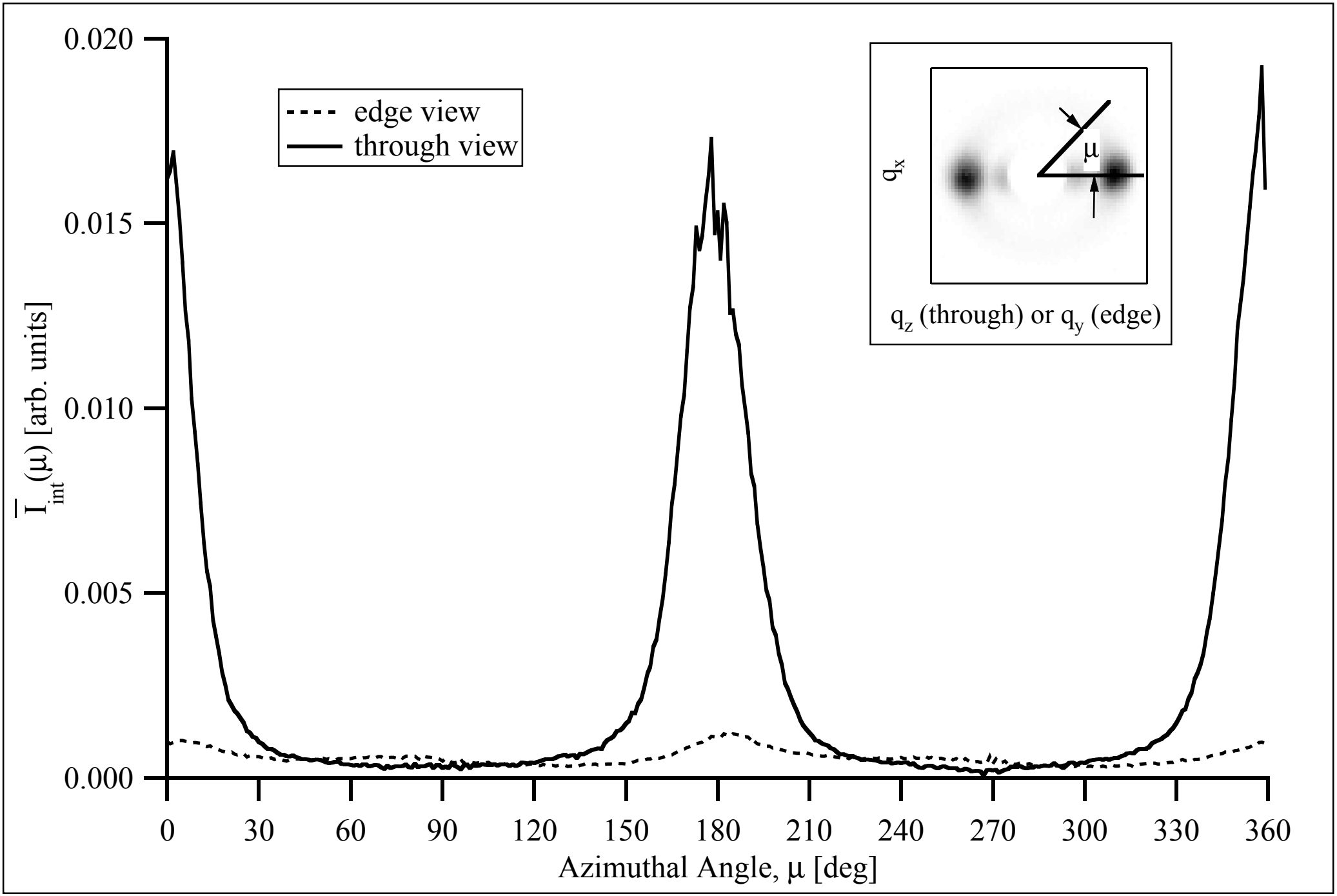
0.020
0.015
0.010
0.005
0.000
$\bar{I}_{int}(\mu)$ [arb. units]
edge view
through view
q_x
μ
q_z (through) or q_y (edge)
0
30
60
90
120
150
180
210
240
270
300
330
360
Azimuthal Angle, μ [deg]

Figure 2

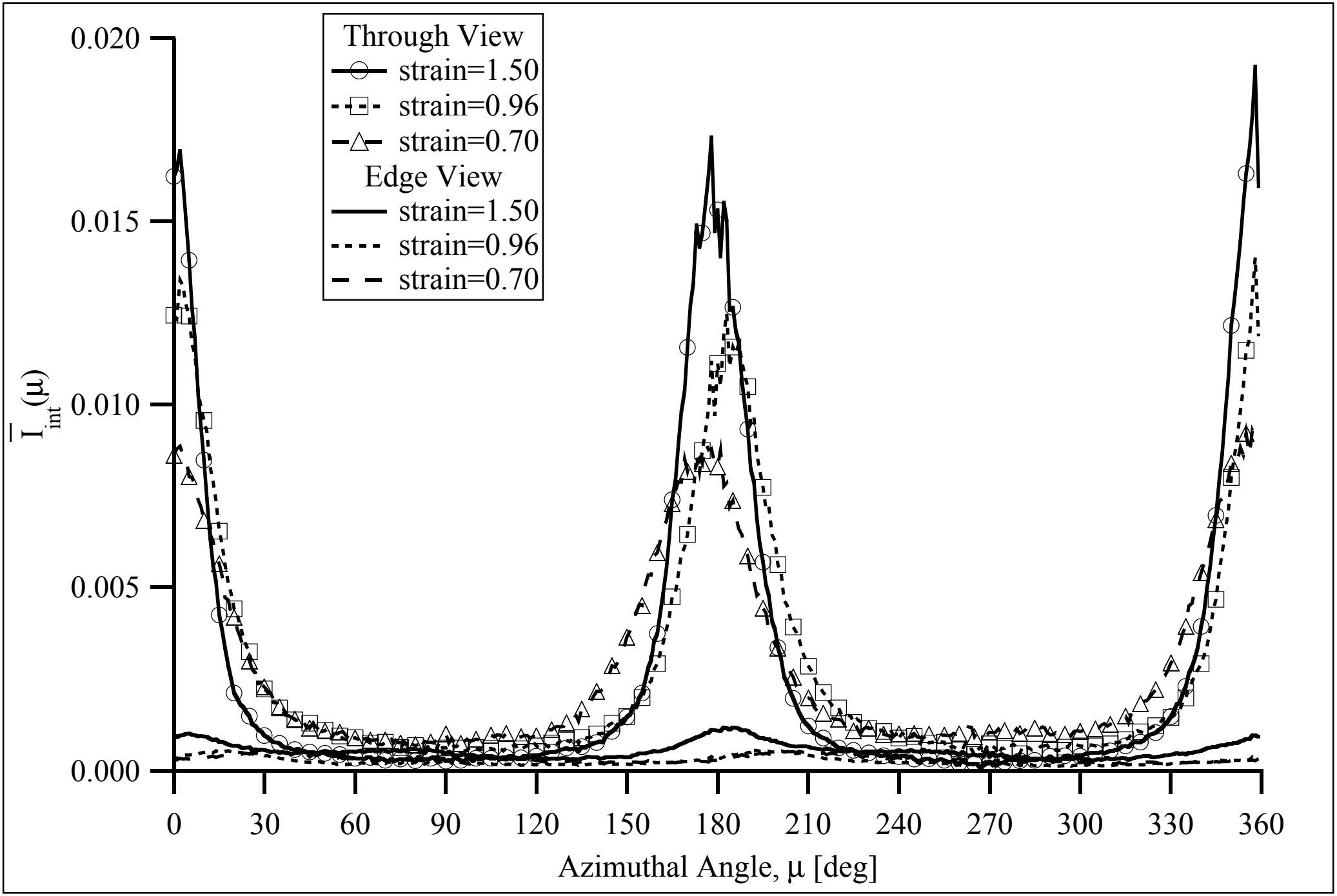
Through View
strain=1.50
strain=0.96
strain=0.70
Edge View
strain=1.50
strain=0.96
strain=0.70
0.020
0.015
0.010
0.005
0.000
$\bar{I}_{int}(\mu)$
0
30
60
90
120
150
180
210
240
270
300
330
360
Azimuthal Angle, μ [deg]

Figure 3

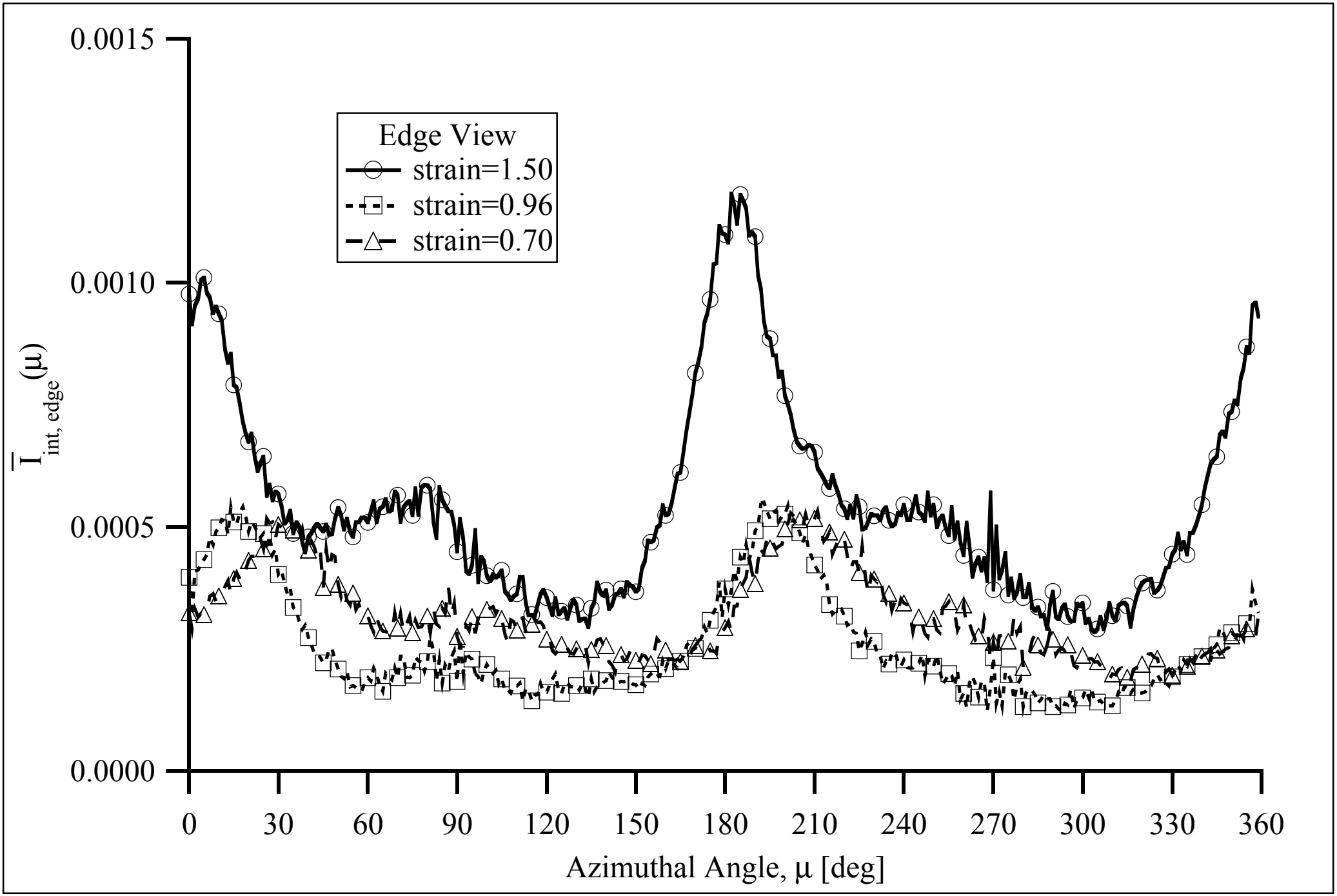
Edge View
strain=1.50
strain=0.96
strain=0.70
0.0015
0.0010
0.0005
0.0000
$\bar{I}_{int, edge}(\mu)$
0
30
60
90
120
150
180
210
240
270
300
330
360
Azimuthal Angle, μ [deg]

Figure 4

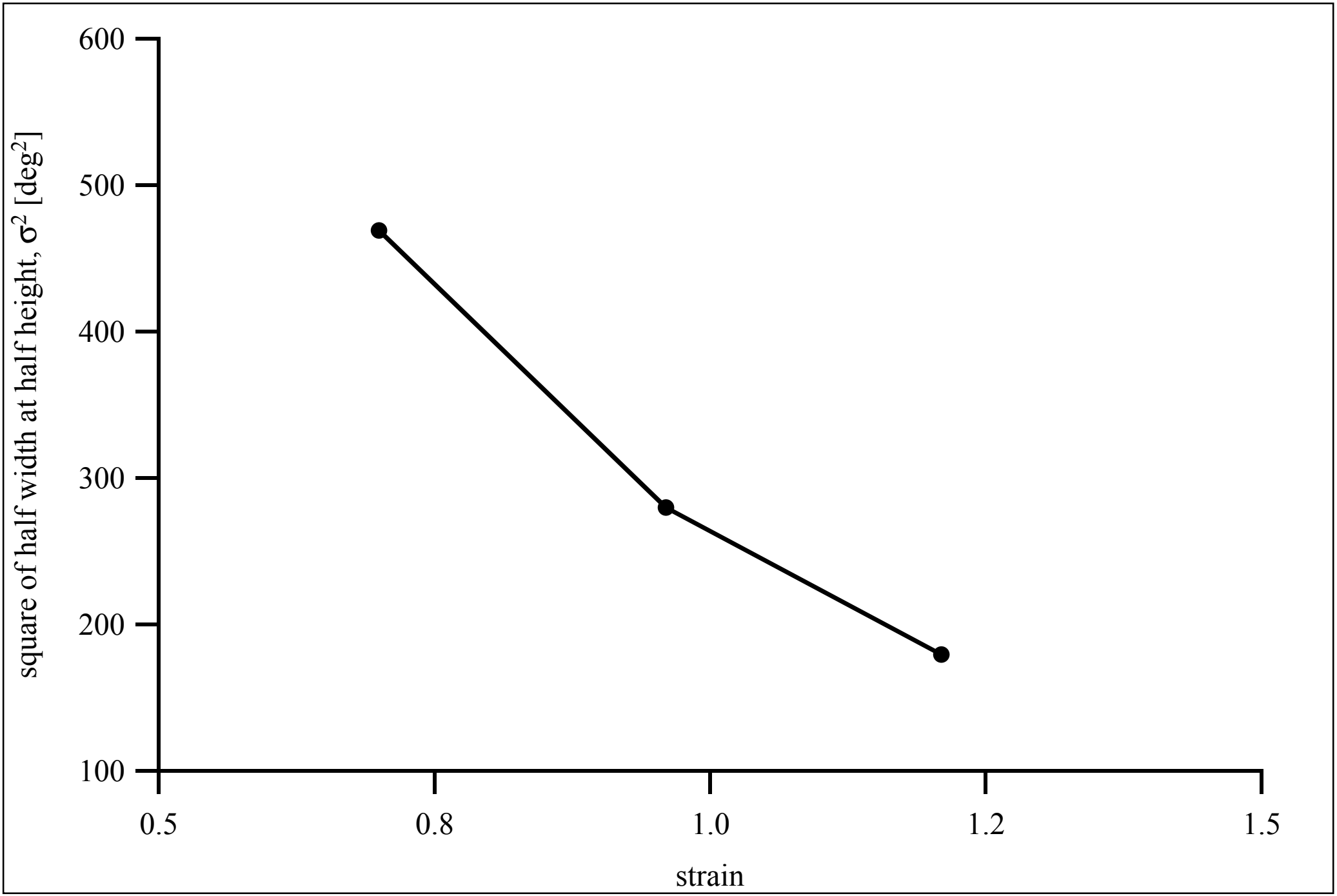
600
500
400
300
200
100
square of half width at half height, σ² [deg²]
0.5
0.8
1.0
1.2
1.5
strain

Figure 5