Supporting Information

Hygroscopic Swelling Determination of Cellulose Nanocrystal (CNC) Films by Polarized Light Microscopy Digital Image Correlation

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Herman Order Parameter (S)[1]

The equations used for the integration of the 2D XRD intensity (I) versus azimuthal angle (ϕ) was performed from 0° to 180° around (200) plane present at 2θ for cellulose Iβ are given by:

$$S = \frac{3\langle cos^2\gamma\rangle - 1}{2} \quad \text{(S1)}$$

$$\langle cos^2\gamma\rangle = 1 - 2\langle cos^2\phi\rangle \quad \text{(S2)}$$

$$\langle cos^2\phi\rangle = \frac{\int I(\phi)cos^2\phi\ sin\phi\ \mathrm{d}\phi}{\int I(\phi)sin\phi\ \mathrm{d}\phi} \quad \text{(S3)}$$

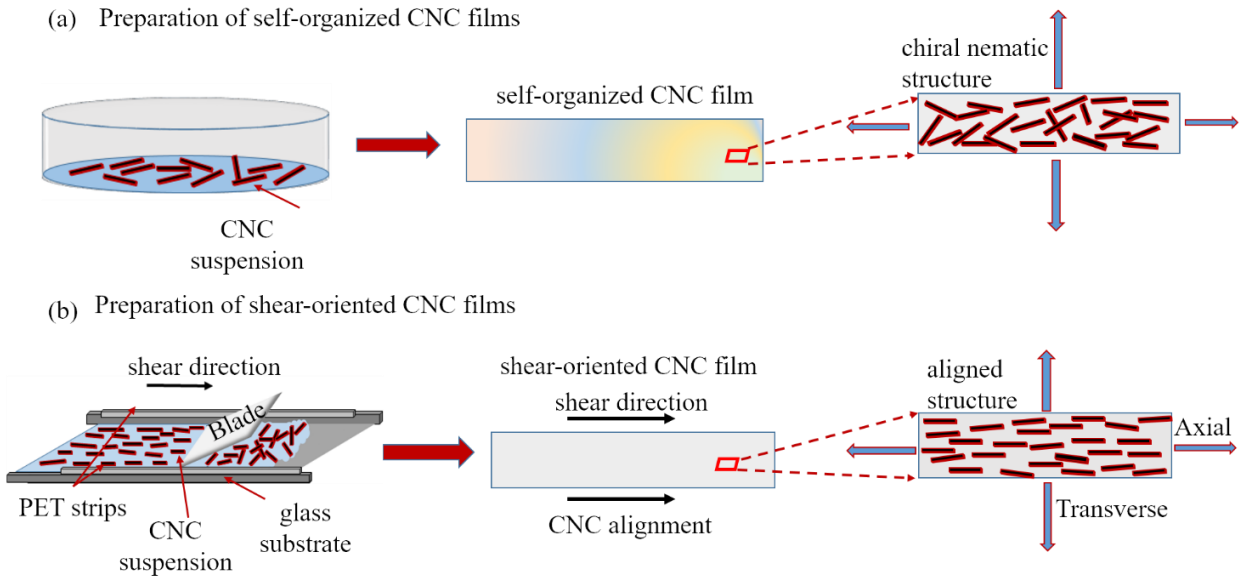

Figure S1. Schematic of preparation of the CNC films by casting method for (a) self-organized and (b) shear-oriented films. The directionality of the shear cast films was defined as "axial" or "transverse" for the direction parallel to or perpendicular to the shear direction.

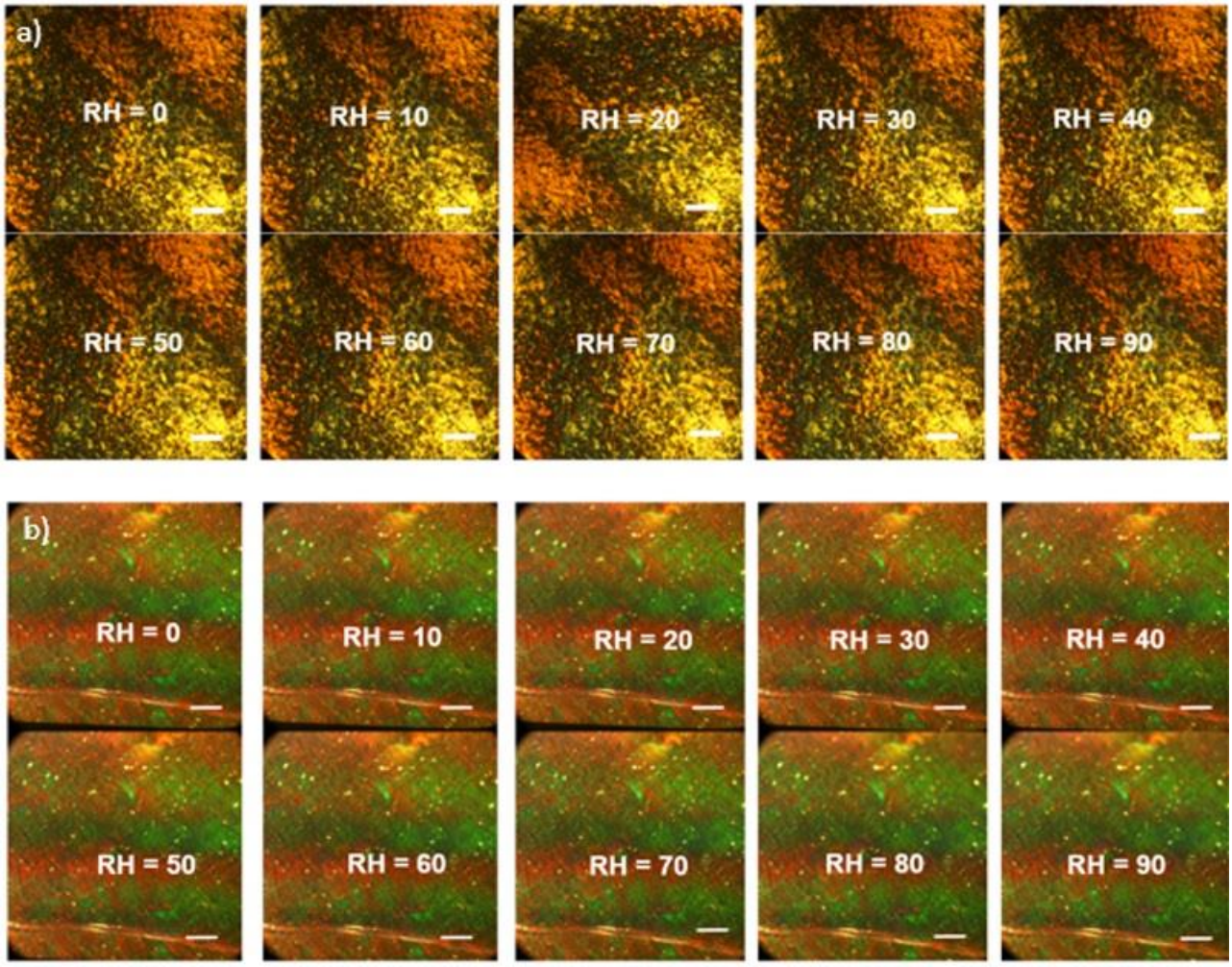

Figure S2. (a) self-organized CNC films (b) shear-oriented CNC films imaged under polarized light (PL) modes at different relative humidity. Scale bar 500 μm.

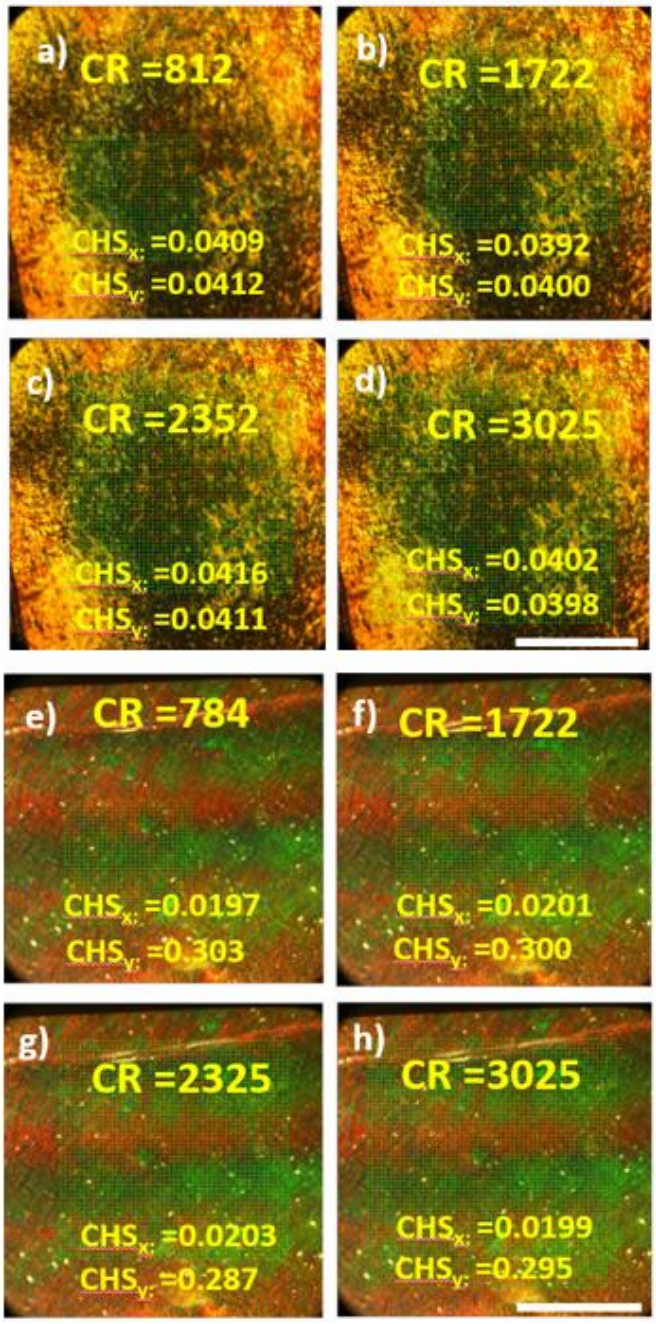

Figure S3. Image Correlation as a function of position and number of correlation points for a self-organized (a-d) and shear-oriented (e-h) CNC film. CR: Number of correlation points. CHS_x: Coefficient of hygroscopic swelling in axial direction. CHS_y: Coefficient of hygroscopic swelling in the transverse direction. Scale bar 1 mm. ($CHS_x = CHS_{axial}$ and $CHS_y = CHS_{trans}$)

Table S1. DIC parameters used in CHS determination of self-organized and shear-oriented CNC films.

CNC film	Sample[1]	ROI	CHS [%strain/ %C]	Cpcorr Size	Grid Spa.	Corr. Pts
Self-organized	S1-1-x	A1	0.0409	60	30 x 30	2352
	S2-2-x	B1	0.0392	60	30 x 30	1722
	S2-3-y	C1	0.0412	60	30 x 30	1722
	S3-1-y	D1	0.0400	60	30 x 30	812
	S1-2-y	E1	0.0416	60	30 x 30	3025
Shear-oriented	S1-1-x	A2	0.0203	60	30 x 30	2304
	S1-2-x	B2	0.0202	60	30 x 30	1722
	S1-3-x	C2	0.0201	60	30 x 30	1722
	S2-1-x	D2	0.0197	60	30 x 30	784
	S3-2-x	E2	0.0199	60	30 x 30	3025
	S1-1-y	A3	0.287	90	30 x 30	2304
	S3-3-y	B3	0.310	60	30 x 30	1764
	S2-1-y	C3	0.298	60	30 x 30	1764
	S1-2-y	D2	0.303	30	30 x 30	784
	S3-3-y	E3	0.295	60	30 x 30	3080

[1] Sample#-Run#-direction

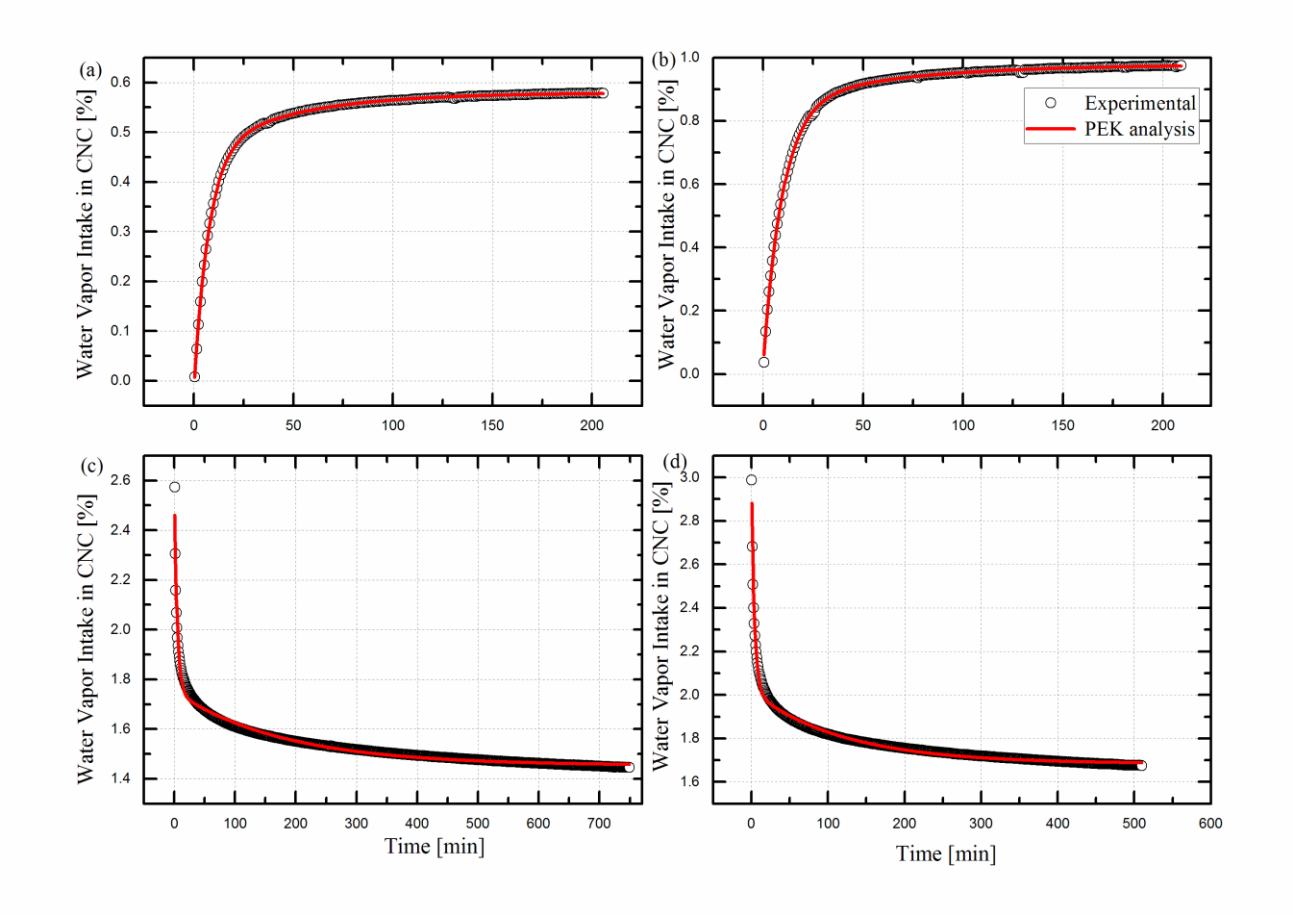

Figure S4. PEK simulation of experimental data of adsorption-desorption for self-organized (a) and (c) and shear-oriented (b) and (d) CNC films 30% RH and 23°C.

Table S2. Computed values of GAB parameters and correlation coefficients obtained from analysis of moisture sorption isotherms of CNC films.

CNC Films		Crystallinity (%)	W_m (g/g)	W_m^{Corr} (g/g)	C_G	K	Ref.
self-organized	adsorption	72[2]	0.033	0.124	6.518	0.912	this work
	desorption		0.052	0.186	5.129	0.867	
shear-oriented	adsorption	72[2]	0.035	0.125	6.004	0.913	
	desorption		0.048	0.172	5.896	0.882	

Table S3. Amount of water sorbed by various celluloses at the monolayer corrected for degree of crystallinity.[3]

Sample	Crystallinity (%)	W_m (g/g)	W_m^{Corr} (g/g)	Ref.
Cotton	70	0.032	0.107	4
Cellophane	70	0.059	0.098	5
Microcrystalline Cellulose	63	0.036	0.096	6
Microcrystalline Cellulose	40	0.066	0.107	4

Table S4. Computed values of PEK's model parameters M_1, M_2, τ_1 and τ_2, corresponding to fast (1) and slow (2) kinetics for lower RH of 30%.

Relative Humidity 30%					
CNC Films	M_1	τ_1	M_2	τ_2	R^2
self-organized	0.782 ± 0.00128	59.7 ± 0.570	0.131 ± 0.00121	8.92 ± 0.0347	0.997
shear-oriented	0.825 ± 0.00324	60.97 ± 2.12	0.132 ± 0.00293	9.06 ± 0.0631	0.999

Table S5. Computed values of PEK's model parameters M_1, M_2, τ_1 and τ_2, corresponding to fast (1) and slow (2) kinetics for higher RH of 90%.

Relative Humidity 90%					
CNC Films	M_1	τ_1	M_2	τ_2	R^2
self-organized	0.972 ± 0.0061	14.8 ± 0.085	5.04 ± 0.0151	245.8 ± 3.34	0.999
shear-oriented	0.946 ± 0.0054	14.5 ± 0.061	5.31 ± 0.0177	240.7 ± 2.76	0.998

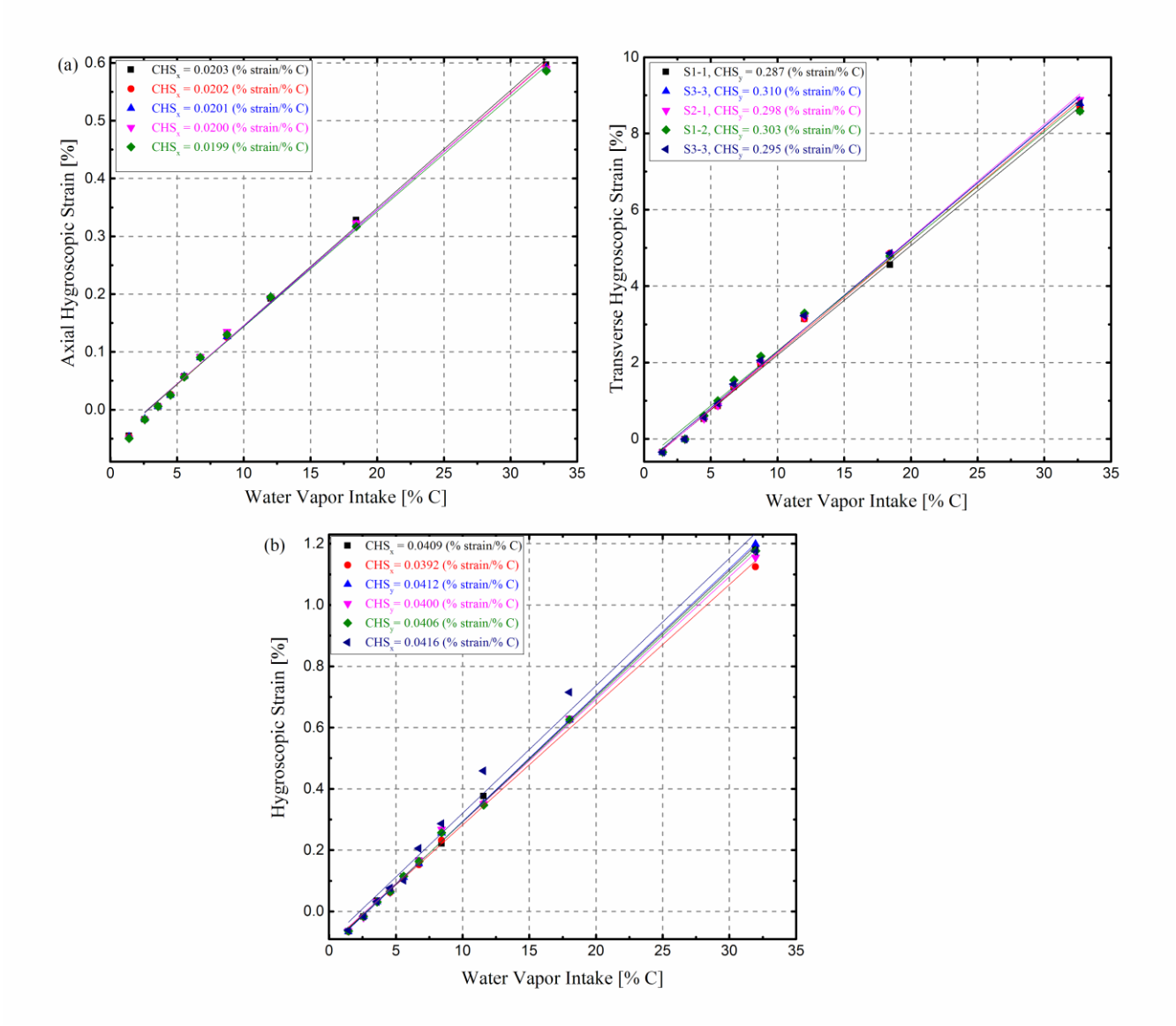

Figure S5. Determination of Coefficient of hygroscopic swelling in (a) shear-oriented (b) self-organized CNC films with different direction. ($CHS_x = CHS_{axial}$ and $CHS_y = CHS_{trans}$).

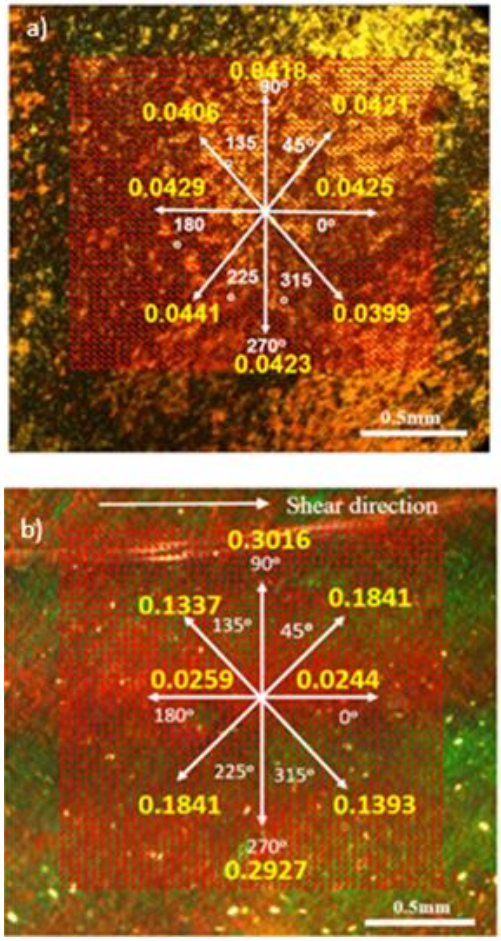

Figure S6. In-plane coefficient of hygroscopic swelling values for (a) self-organized and (b) shear-oriented CNC films at an angular increment of 45°. The CHS of self-organized film is isotropic whereas that of shear-oriented is anisotropic.

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