A size-independent law to describe the alignment of shape-anisotropic objects

Ulla Vainio
Institute of Materials Research, Helmholtz-Zentrum Geesthacht Centre for Materials and Coastal Research, Max-Planck-Str. 1, 21502 Geesthacht, Germany

Current address: Department of Applied Physics, Aalto University, Espoo, Finland

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A major challenge in the field of nanosciences is the assembly of anisotropic nano objects into aligned structures. The way the objects are aligned determines the physical properties of the final material. In this work, we take a closer look at the shapes of orientation distributions of aligned anisotropic nano and macro objects by examining previously published works. The data shows that the orientation distribution shape of anisotropic objects aligned by shearing and other commonly used methods varies size-independently between Laplace and Gaussian depending on the distribution width and on the cohesivity of the particles.

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INTRODUCTION

Production of aligned arrangements of anisotropic objects is a challenging task. While for example carbon nanotubes and silicon nanowires can be conveniently grown into arrays, the alignment of these structures is often far from perfect. \[1\] When oriented growth is not an option, anisotropic objects can be aligned by mechanical agitation such as shear \[3\] \[4\], flow, \[5\] or vibration \[6\], and sometimes a magnetic or electric field can act as the orientating agent. \[7\] Both in the macro scale and nano scale, most methods fail to give perfect alignment. The factors limiting the alignment are not fully understood.

In a composite material, the shape and width of the orientation distribution of its building blocks translates directly into other physical properties of the material. For example, the orientation distribution of carbon nanotubes within fibre ropes has a significant effect on the mechanical properties of the ropes. \[8\] Theoretical studies show that the orientation distribution shape selected for simulation of a carbon nanotube film has a drastic effect on the electrical properties of the film. \[9\] Nevertheless, instead of carefully examining the shape of the orientation spread, most experimental studies on alignment of nano and macro scale objects have been focused on obtaining a single number, an average alignment or an order parameter. In some cases, the orientation distributions of particle assemblies have been described with Gaussians \[4\] \[10\], Lorentzians \[11\], the combination of both \[12\] \[13\], and even with squared Lorentzians \[14\]. Typically, these functions did not fit the data perfectly but discrepancies between the data and the model were not discussed. Recently, a new better-fitting function, the generalized normal distribution, was applied to carbon nanotube orientation distributions which had been measured with high statistical accuracy using synchrotron radiation. \[2\] If this function could be applied also to other systems, it could be a game-changer for the study of aligned structures. In this contribution, we show that the generalized normal distribution fits to previously published data for many objects from nanometre to centimetre sizes, and we can now compare the shapes of the different orientation distributions to each other by using the same set of parameters.

EXPERIMENTAL

A survey of the literature shows that one of the most common ways to define the orientation of particle assemblies from X-ray scattering experiments or the like is by calculating the Hermans orientation parameter \[15\] \[16\]

\[
f = \frac{1}{2} \left(3 \langle \cos^2 \varphi \rangle - 1 \right),
\]

where the mean-square cosine is calculated from the scattered intensity \(I(\varphi)\) by integrating over the azimuthal angle \(\varphi\).

\[
\langle \cos^2 \varphi \rangle = \frac{\int_0^{\pi/2} I(\varphi) \sin \varphi \cos^2 \varphi d\varphi}{\int_0^{\pi/2} I(\varphi) \sin \varphi d\varphi}.
\]

For perfect vertical orientation \(f = 1\), for isotropic orientation \(f = 0\), and for perfect horizontal orientation \(f = -0.5\). In the following analysis, we have calculated the orientation parameter for all distributions as if they were perfectly vertically centred by shifting the \(\varphi = 0^\circ\) accordingly in order to compare the orientation degree rather than direction of alignment. The orientation parameter can be calculated for any orientation distribution regardless of their shape.

In the next step, we compare the values of Hermans orientation parameter to parameters describing the shape of the orientation distribution for different experimentally observed particle assembly systems by refitting literature data. Recently, it was identified that the shape of the orientation distribution of multiwalled carbon nanotube arrays (MWCNTs) can be modelled accurately with a family of symmetric distributions that include all shapes between Laplace and Gaussian. \[2\] This generalized normal
distribution (GND), also called exponential power distribution in the literature [17–19] has the form

\[ p_\alpha(\varphi) = \frac{\beta}{2\alpha \Gamma(1/\beta)} \exp \left( -\left( \frac{|\varphi - \mu|}{\alpha} \right)^\beta \right), \]

where \( \alpha \) is a scaling factor related to the width, \( \beta \) is the shape parameter determining the sharpness, and \( \mu \) is the mean of the distribution. \( \Gamma \) denotes the gamma function. The GND reduces to the normal distribution when \( \beta = 2 \) and to Laplace distribution when \( \beta = 1 \). Due to its generality, this distribution has actually been invented several times in the course of history. In diffusion studies it is known as the stretched exponential function with \( 0 < \beta < 1 \), and in the field of relaxation dynamics in materials, it is also called the Kohlrausch function [or Kohlrausch-Williams-Watts function (KWW)] after the physicist Rudolf Kohlrausch who applied it in the 19th century to describe electric charge decay. [20, 21]

In most cases in the literature, uncertainties for the data were not available so goodness-of-fit is not reported here, but the relative likelihoods for model selection were calculated from the residual sum of squares \( \text{RSS} = \sum_{n=1}^{N} (y_n - p(\varphi_n))^2 \). We use the Akaike information criterion, \( \text{AIC} = 2k - N \ln(\text{RSS}) \), to compare the relative likelihoods, \( \exp((\text{AIC}_\text{min} - \text{AIC})/2) \), of the Gaussian, Lorentzian and generalized normal distribution for the model selection. Here, \( k \) is the number of free parameters, \( N \) the number of data points, \( p(\varphi) \) is one of the three models, and \( \text{AIC}_\text{min} \) is the smallest AIC value obtained for the models. Fig. 2 visualises the data presented in Table I. The contour lines mark the Hermans orientation parameter and this shows that the best orientation is found for high \( \beta \) and low \( \alpha \) values, in the upper left corner of the graph. All of the experimental data is located in the lower right corner of the graph and there seems to be no prominent difference between nano and macro scale particles. The dashed line showing a fit to a few data points in which alignment has been obtained by shearing shows a sort of a limit to the orientation distribution shape. It is possible to achieve near to perfect alignment using these commonly used methods for alignment but then, according to this graph, we should expect the orientation distribution to be more Laplace like than Gaussian.

In the case of \( \text{Al}_2\text{O}_3 \) platelets intercalated with poly-
FIG. 2. Orientation distribution of wooden pegs in a rheometer [4] fitted with (a) a Gaussian and (b) a generalized normal distribution.

TABLE I. Descriptions of objects and shape, $\beta$, and scale, $\alpha$, parameters of their orientation distributions according to a fit with the generalized normal distribution. $D$ denotes the diameter of the object and $L/D$ its aspect ratio. For MWCNTs and Al$_2$O$_3$ platelets the range of values show the variation within one sample. Bad fit with the generalized normal distribution is marked with a dash (-) for $\alpha$ and $\beta$.

| Objects               | $D$ (µm) | $L/D$ | Alignment  | $\beta$ | $\alpha$ (°) | Method  | Ref  |
|-----------------------|----------|-------|------------|---------|--------------|---------|------|
| CdSe nanorods         | 0.008    | 2.75  | rubbing    | 1.83    | 31           | GIWAXS  | [21] |
| Polymer cryst.        | < 0.017  | -     | strain     | -       | -            | XRD     | [25] |
| MWCNTs                | 0.040–0.070 | -     | grown      | 1.37–1.65 | 26–38        | SAXS    | [2]  |
| Cellulose whiskers 1  | 1.95     | 4.1   | magnetic   | 1.35    | 12           | XRD     | [7]  |
| Cellulose whiskers 2  | 7.18     | 3.2   | magnetic   | 1.19    | 21           | XRD     | [7]  |
| Al$_2$O$_3$ platelets 1| 10       | 0.03–0.05 | sediment  | 1.21–1.55 | 19–28       | XRD     | [26] |
| Al$_2$O$_3$ platelets 2| 10       | 0.03–0.05 | pressed    | 1.55±0.06 | 17.4±0.4    | XRD     | [26] |
| Cellulose whiskers 3  | 16.1     | 6.4   | magnetic   | 2.07    | 42           | XRD     | [7]  |
| Rice 1                | 1600     | 4.5   | shear      | 1.59    | 20           | optical | [4]  |
| Glass cylinders       | 1900     | 3.5   | shear      | 1.63    | 27           | optical | [4]  |
| Rice 2                | 2000     | 3.4   | shear      | 1.63    | 23           | optical | [4]  |
| Rice 3                | 2800     | 2.0   | shear      | 1.69    | 28           | optical | [4]  |
| Wooden pegs           | > 5000   | 5.0   | shear      | 1.39    | 15           | X-ray CT | [4]  |
| Simulation 1          | -        | 10    | gravitation (Bo$_g$=0) | 1.48    | 18           | 2d simulation | [23] |
| Simulation 2          | -        | 10    | gravitation (Bo$_g$=10$^3$) | 1.36    | 20           | 2d simulation | [23] |
| Simulation 3          | -        | 10    | gravitation (Bo$_g$=10$^4$) | 1.62    | 35           | 2d simulation | [23] |

**mer, two data sets for same particle type are available.** The first one of sedimented particles shows poorer alignment than a second set where the sedimented particle assembly was further compressed. The orientations of sedimented Al$_2$O$_3$ platelets should be dominated more by cohesive forces than the sedimented and pressed platelets. Effect of a moderate amount of cohesion is seen both in simulation [23] and experiment as a decrease in $\beta$ and increase in $\alpha$. The simulation with most sticky particles results in a broad orientation distribution with increased $\beta$. The carbon nanotube forests could be described effectively as very sticky granular systems. The most prominent result from cohesion is the decrease in the overall orientation degree of the particles.

Despite the success in fitting most of the data presented in table I, there is also one data set which could not be fitted with the GND. In case of polymer crystallites of poly(ε-caprolactone) oriented under strain, [25]
the orientation of crystallites did not follow the generalized normal distribution. This is an example of a system which is composed of particles that are interconnected. This situation is very different from all the other cases presented here. The applicability of the generalized normal distribution may very well be limited only to particle assemblies which allow free movement of the particles.

### DISCUSSION

Now that we have identified the generalized normal distribution to be a feasible model for a multitude of particulate systems, we need to consider its physical meaning. There exist several theoretical models for orientation distributions of particles in different environments, and it is not clear if some of them could actually have the same shape as the generalized normal distribution. Fitting a non-cyclic function to the orientation distribution as a function of azimuthal angle \( \phi \) is not fully correct, because it cannot describe all the situations between isotropically oriented and fully oriented systems. A mathematically correct model would need to have cyclic properties. Next, we inspect cyclic functions found in the literature to see if they could actually reproduce the shape of the generalized normal distribution. Theoretical framework for the orientation distribution shape exists for example in the case of spheroidal particles in dilute suspension under shear. The function describing the orientation of spheroids of aspect ratio \( r_\alpha \) is given \[ p_1(\varphi) \propto \frac{1}{r_\alpha^2 \cos^2 \varphi + \sin^2 \varphi}, \]\ (4) where \( \varphi \) is the misorientation of the symmetry axis of the particle compared to the flow direction. This shape should be valid also for other centrosymmetric particles, such as cylinders and discs, but fitting this function with the generalized normal distribution did not produce satisfying results.

The Maier-Saupe distribution, which can be applied to describe the orientation distributions in liquid crystals and to study the chain orientation in cholesterol-lipid systems, \[ p_2(\varphi) = \exp \left( \frac{m \cos^2 \varphi}{2} \right) I_0 \left( \frac{m \cos^2 \varphi}{2} \right), \] \( m \) is a parameter related to the width of the distribution. For simplicity, we have omitted the normalization factor in equation (5) but it can be found in the original publication. While \( p_2 \) can be fitted to great accuracy (but not perfectly) with the generalized normal distribution, the shape factor, \( \beta \), remains above 1.73 for all parameter values of the Maier-Saupe distribution and hence the
Maier-Saupe model cannot be the correct model to use in the case of most of the systems presented here.

A special orientation distribution has been used to simulate acoustic non-woven fibre systems consisting of cylindrical subunits. [29] This distribution is characterized mainly by the anisotropy parameter $p$:

$$p_3(\theta, \varphi) = \frac{p \sin \theta}{4\pi \left[1 + (p^2 - 1) \cos^2 \theta\right]^{3/2}}. \quad (6)$$

Here, $\theta \in [0, \pi)$ and $\varphi \in [0, 2\pi)$ are the altitude and longitude in spherical coordinates. The $\sin \theta$ term in this equation is responsible for assigning the correct probability to each $\theta$ when we are interested in the volume orientation distribution but we may compare the number orientation distributions to each other without this normalization such that $p_3(\theta, \varphi)/\sin \theta$ is constant for $p = 1$. For $p < 1$, the cylinders are more oriented along the symmetry axis. Again, $p_3(\theta, \varphi)/\sin \theta$ does not have the shape of the generalized normal distribution.

For modelling of orientations of graphene layers, the projected von Mises-Fisher distribution has been introduced [30]

$$p_4(\varphi, \gamma) = \frac{\kappa}{4 \sinh \kappa} L_{-1}(\kappa \cos(\gamma - \varphi)). \quad (7)$$

Here $\varphi \in [0, \pi]$ is the azimuthal angle, $\gamma \in [0, \pi]$ represents the angle of preferred orientation, $\kappa$ is a concentration parameter, and $L_{-1}$ is the modified Struve function. The von Mises-Fisher distribution is a directional analogue of the Gaussian distribution and hence it cannot reproduce the shapes of the generalized normal distribution, apart from $\beta = 2$.

None of the cyclic functions, $p_1 - p_4$, presented above are able to capture the range of distribution shapes which we found in real systems. In conclusion, despite the shortcomings due to non-cyclicity, the generalized normal distribution is at the moment the most suited function for the study of moderately aligned systems, even if it cannot be used to describe systems close to isotropic alignment.

CONCLUSIONS

Here we have shown that alignment of freely moving anisotropic objects both in nano and macro scale can be described by one function, the generalized normal distribution. Spread of the experimental data in Fig. 3 allows us to draw some general conclusions about the alignment of anisotropic objects. We observe that the projection of orientation distribution of anisotropic particles is close to the Laplace distribution ($e^{-x^2}$) when very good alignment is achieved. Exponential decay occurs commonly in the field physics, and the Laplacian orientation distribution may be a manifestation of an underlying relaxation processes, which follow an exponential decay. Moderate or poor alignment will lead to a more Gaussian distribution ($e^{-x^2}$) but slightly cohesive particles may behave differently. These findings should be taken into account in future studies of materials consisting of aligned anisotropic particles.

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