Enantiomorphic symmetry breaking in crystallization of molten sodium chlorate

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A. Poisson model for symmetry breaking

We assume two choices of enantiomorph, *d* or *l*, for a nucleus, so for *r* nuclei there are 2^r permutations. Probability that all of the *r* nuclei are *d* is therefore 2^{-r}. Probability of a mixed nucleus (*dl*) is therefore

$$1-2\cdot 2^{-r} = 1-2^{(1-r)}. \qquad \text{(S1)}$$

The Poisson probability $P(r,\lambda) \sim \frac{\lambda^r}{r!}$, where λ is the Poisson parameter.[1] If we normalize the sum we have $\sum_{r=1}^{\infty} P(r,\lambda) = \mathrm{e}^{\lambda} - 1$, so that normalized probability is found to be

$$P(r,\lambda) = \frac{\lambda^r}{(\mathrm{e}^{\lambda}-1)r!}. \qquad \text{(S2)}$$

Note that this distribution differs from the regular Poisson expression in that it explicitly excludes *r* = 0, i.e., we are assuming that nucleation definitely occurs.

The probability of obtaining an overall mixed (*dl*) sample is obtained as follows,

$$\begin{aligned} P_{\mathrm{dl}}(\lambda) &= P(1,\lambda)\cdot(1-2^0) + P(2,\lambda)\cdot(1-2^{-1}) + \cdots \\ &= \sum_{r=1}^{\infty} P(r,\lambda)\cdot\left(1-2^{(1-r)}\right) = \frac{\mathrm{e}^{\lambda/2}-1}{\mathrm{e}^{\lambda/2}+1} \end{aligned} \qquad \text{(S3)}$$

Similarly, the probability of a pure (*d* or *l*) sample is obtained as,

$$P_{\mathrm{d\ or\ l}}(\lambda) = \frac{2}{\mathrm{e}^{\lambda/2}+1}. \qquad \text{(S4)}$$

The final expressions S3 (solid curve) and S4 (dashed curve) are plotted in Fig. 1 of the accompanying communication.

B. Poisson arrival process

For a Poisson arrival process, the *inter-arrival* times (i.e., time between events) are exponentially distributed as:[1,2]

$$f(t) = \lambda e^{-\lambda t}. \tag{S5}$$

The mean inter-arrival time is related to the Poisson rate, $\langle t \rangle = 1/\lambda$.

We model the experimental times to nucleate, taking $t = 0$ as the time that the sample first reaches 248 °C during cooling. The data can be represented as a histogram, with equal bin-widths in time (Δt), for which we find:

$$F(t) = \int_{t-\Delta t}^{t+\Delta t} f(t)\mathrm{d}t = \mathrm{e}^{-\lambda t} 2\sinh(\lambda \Delta t). \tag{S6}$$

The histogram of experimental inter-arrival times was fitted by Eqn. S6 with $\Delta t = 10$ s using a nonlinear least squares fitting procedure, to obtain $\lambda = 0.011 \pm 0.001$ s^{-1}, see Fig. S1.

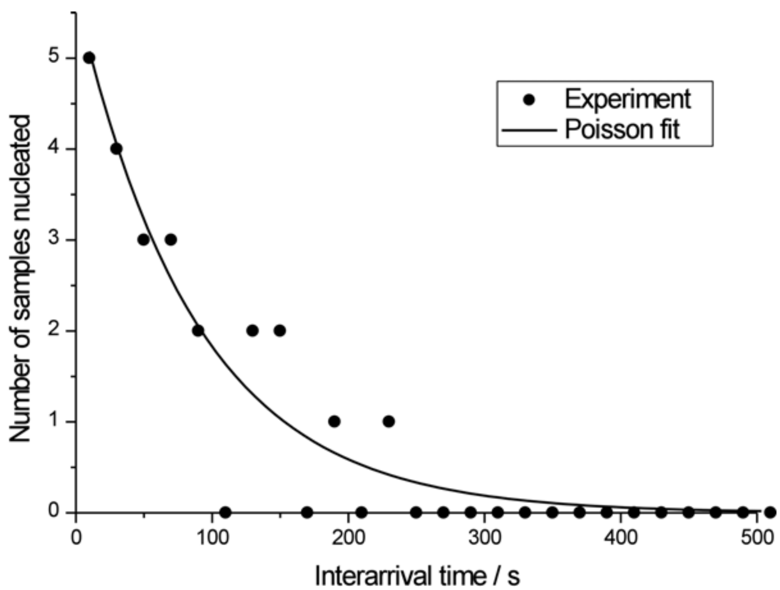

Fig. S1. Plot of number of samples nucleated versus interarrival time for 26 samples cooled to 248 °C and maintained at this temperature until nucleation (see Table 1 and text of accompanying communication for details). Note that 3 samples nucleated at times, $t > 500$ s, which were included in the fit but are not shown.

References

[1] F. A. Haight, *Handbook of the Poisson Distribution*, John Wiley & Sons, New York, 1967.
[2] J. K. Lindsey, *Introduction to Applied Statistics: a Modelling Approach*, 2nd ed., Oxford University Press, Oxford, 2004.