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“Físico-Química e Termodinâmica dos Sólidos - SFI5769”

Thermodynamics of mechanochemistry in solid state reactions

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Introduction & Motivation

Theoretical background

The Arrhenius Equation

- Proposed in 1889 by Svante Arrhenius
- Arrhenius used his equation to develop the concept of activation energy

$$k = A\mathrm{e}^{-\frac{E_\mathrm{a}}{(RT)}}$$

k Rate constant of the reaction

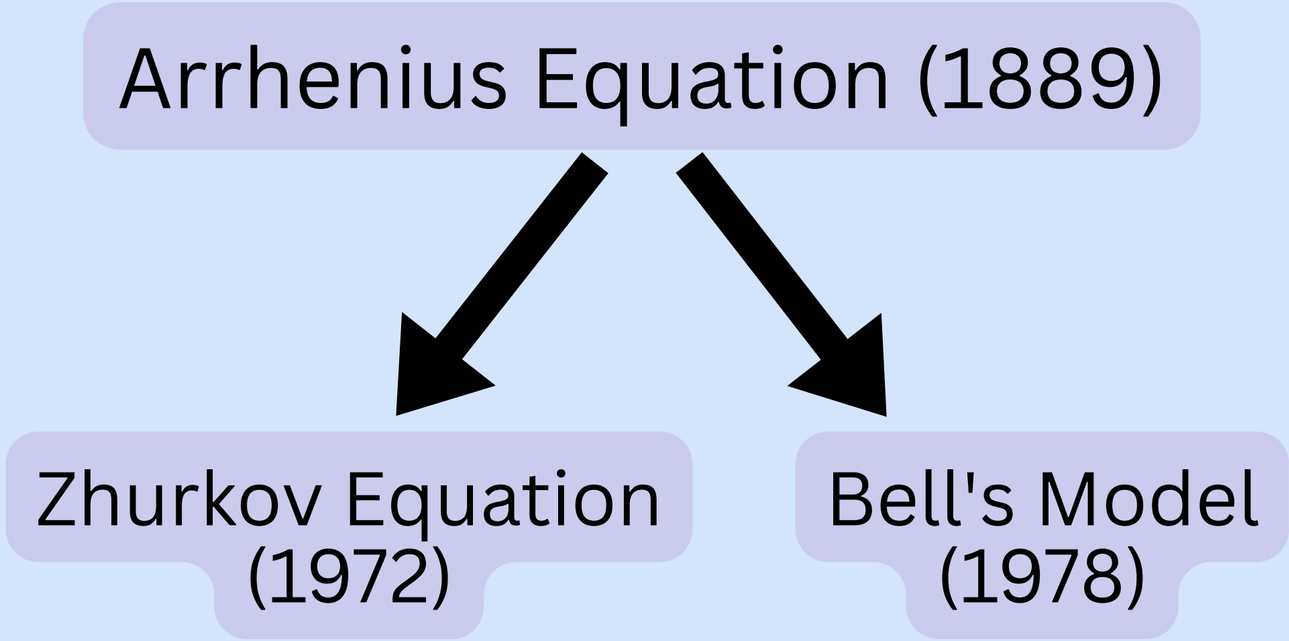
A Pre-exponential factor

R Universal gas constant

T Temperature

E_a Activation Energy

Descendents of the Arrhenius equation



Zhurkov Equation

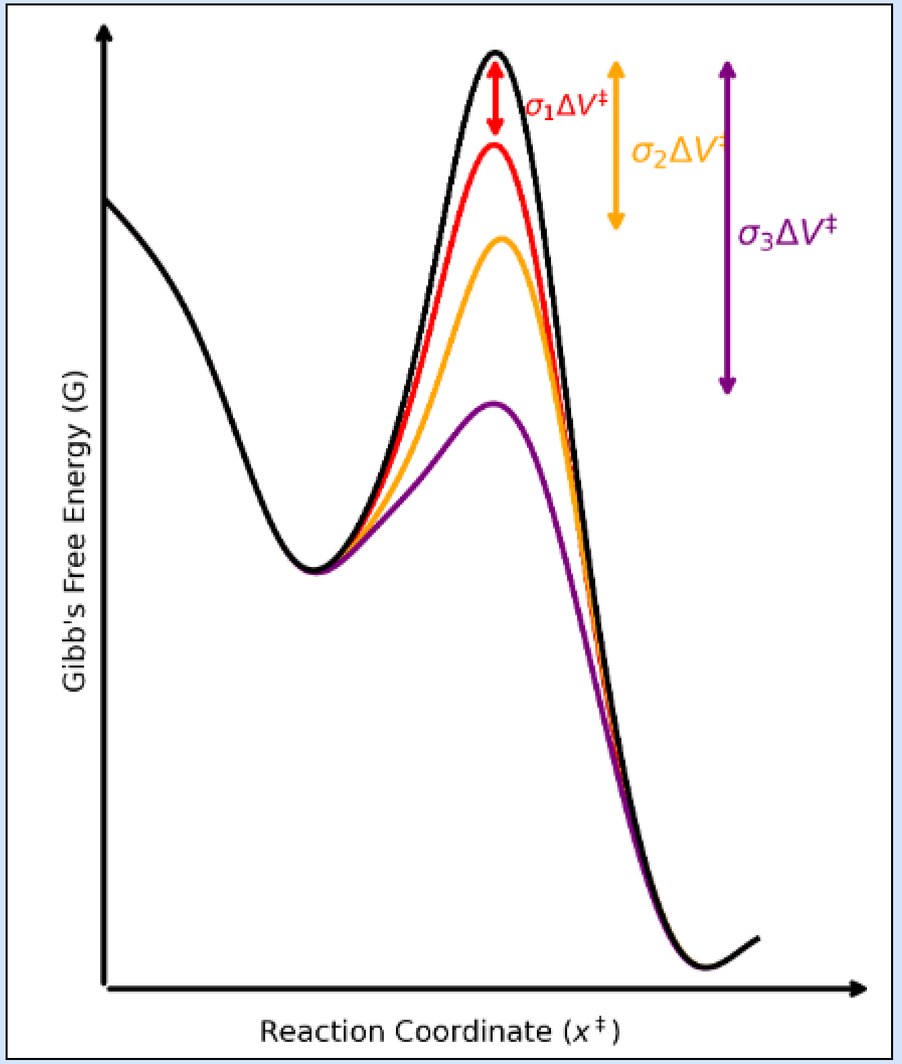
- Generalizes Arrhenius law to model fractures in solids
- Used mainly in polymers

$$k = k_0 \mathrm{e}^{-\left(\frac{E_\mathrm{A} - \alpha\sigma}{RT}\right)}$$

Bell's Model

- Usually used to describe mechanochemical processes
- Rarely applied in a way that considers the impact of the crystalline structure in the force dissipation

$$k(\sigma) = A \exp(\frac{\sigma \Delta V^{\ddagger} - E_{\mathrm{act}}}{k_B T})$$



Lowering of the activation barrier by Bell’s model

Hertzian contact

Describes impacts to solids

$$\sigma = \frac{3F_{\text{impact}}}{2\pi R_{\text{impact}}^2}$$

$$F_{\text{impact}} = ma_{max}$$

$$R_{\text{impact}} = (rd)^{\frac{1}{2}}$$

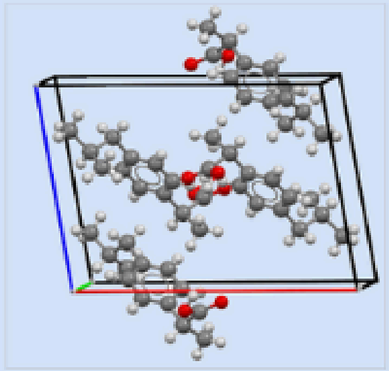
$$d = \left(\frac{3}{4}\frac{F_{\text{impact}}}{E^* r^{\frac{1}{2}}}\right)^{\frac{2}{3}}$$

Reduced Young's Modulus

Parameters can be obtained from the elastic tensor

$$\frac{1}{E^*} = \frac{1-\mu_1^2}{E_1} + \frac{1-\mu_2^2}{E_2}$$

The State Of the Art



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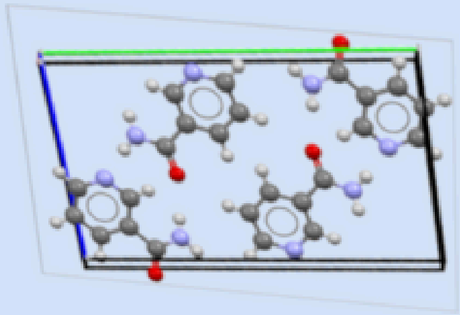

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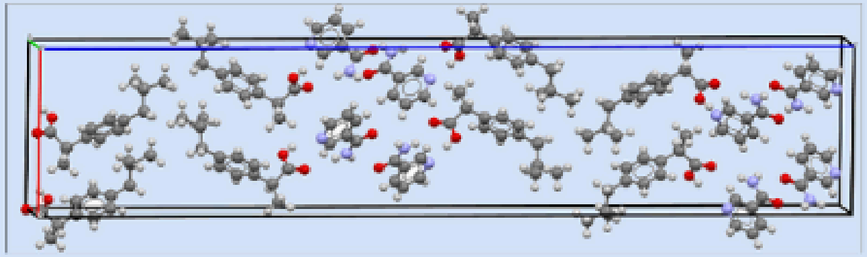
$$E_a = 15 \pm 6 \text{ kJ} \cdot \text{mol}^{-1}$$



The determination of activation energy in ibu:na co-crystal

- Fischer, Franziska, *et all* [1]. Measured the activation energy of a mechanochemical reaction.
- They used normalized Raman Peak intensities at constant temperatures to determine the activation energy using the Arrhenius law: $k = A\mathrm{e}^{-\frac{E_\mathrm{a}}{(RT)}}$
- They only determined the activation energy at 50 Hz on their apparatus (which has a different mechanism than the one commented later)

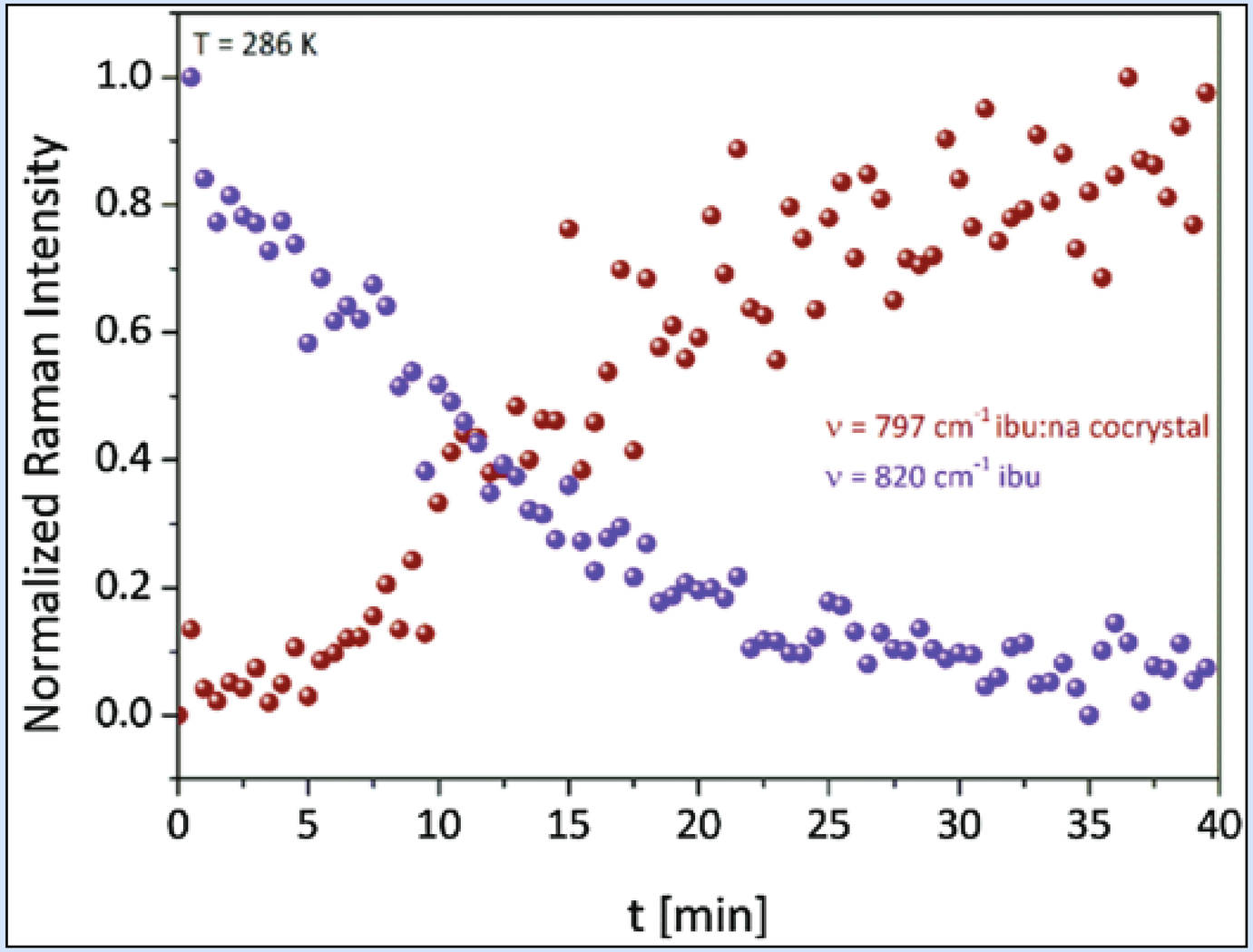
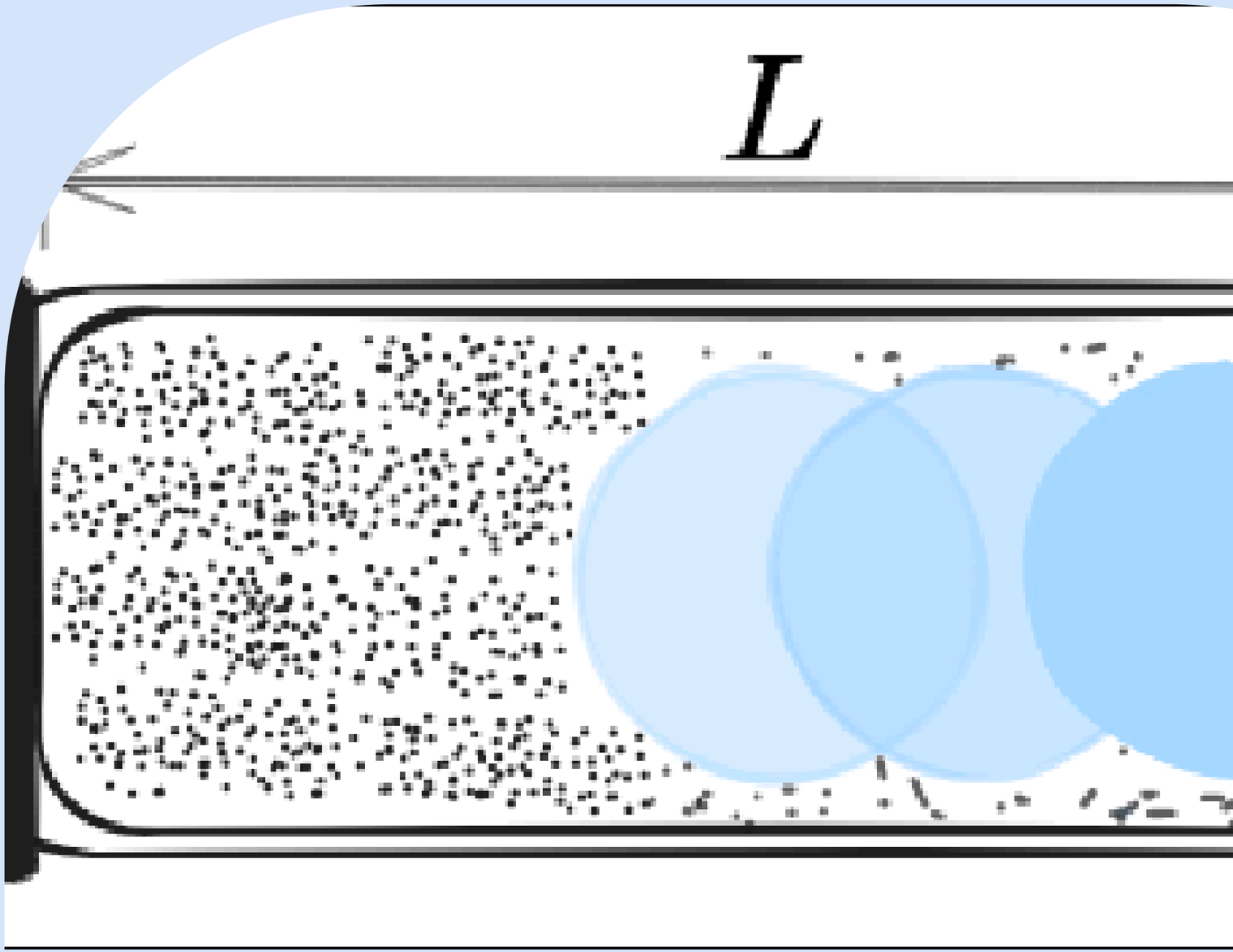


Figure 1: Rates of Ibuprofen and Ibuprofen-Nicotinamide in function of time. Obtained from Fischer, F. *Et all* [1]. Licensed under CC.

Mechanochemical parameters on conversion of polyolefins

Hergesell, *et all*[3], described the influence of ball milling parameters using the Zhurkov equation. They found similar results to what was found in this work for polymers. Some additional experimental conclusions they came to must be analized for 3d crystals

Modelling



Harmonic approximation

In this model, a sinusoidal movement is assumed. An harmonic like solution is chosen because it models the mill operating with just one frequency.

$$x(t) = x_{\max} \cdot \sin(2\pi f_{\text{mill}} t)$$

$$\ddot{x}_{\max} = -x_{\max} \cdot (2\pi f_{\text{mill}})^2$$

$$a_{\max} = |\ddot{x}_{\max}|$$

Harmonic approximation

$$F_{\text{impact}} = ma_{\max}$$

$$x_{\max} = \frac{L}{2}$$

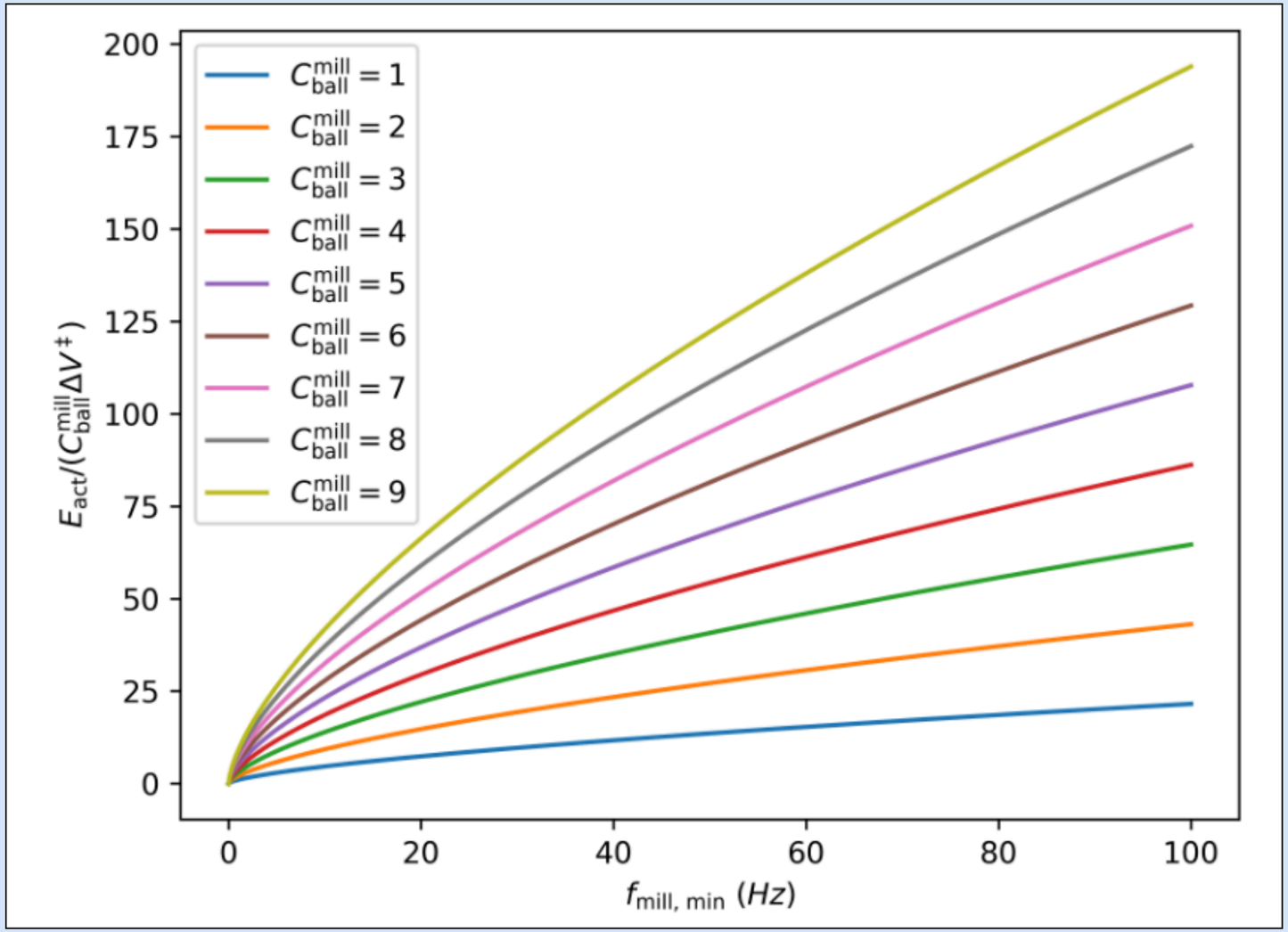
$$m = \rho\frac{4}{3}\pi r^3$$

$$F_{\text{impact}} = \frac{2}{3}\rho\pi r^3 L \cdot (2\pi f_{\text{mill}})^2$$

$$\sigma = \left(\frac{6}{\pi^3}\frac{E^{*2}}{r^2}\frac{2}{3}\rho\pi r^3 L \cdot (2\pi f_{\text{mill}})^2\right)^{1/3}$$

$$\boxed{\sigma = \left(16E^{*2} r\rho L f_{\text{mill}}^2\right)^{1/3}}$$

$$\boxed{\sigma = C_{\text{ball}}^{\text{mill}} f^{2/3}}$$



Minimum activation frequency for arbitrary constants

Conclusion

- It was possible to establish a possible relationship between activation energy and frequency for the system
- More work is needed for generalizing it for more mechanochemical methods with more than one frequency
- It may be possible to limit the frequency so a system doesn’t reach a stable but undesired crystalline phase.

Bibliography

1. Fischer, F., Wenzel, K.-J., Rademann, K., Emmerling, F., 2016. Quantitative determination of activation energies in mechanochemical reactions. Physical Chemistry Chemical Physics 18, 23320–23325. https://doi.org/10.1039/C6CP04280E
2. Laidler, K.J., 1984. The development of the Arrhenius equation. J. Chem. Educ. 61, 494. https://doi.org/10.1021/ed061p494
3. H. Hergesell, A., L. Seitzinger, C., Burg, J., J. Baarslag, R., Vollmer, I., 2025. Influence of ball milling parameters on the mechano-chemical conversion of polyolefins. RSC Mechanochemistry 2, 263–272. https://doi.org/10.1039/D4MR00098F
4.