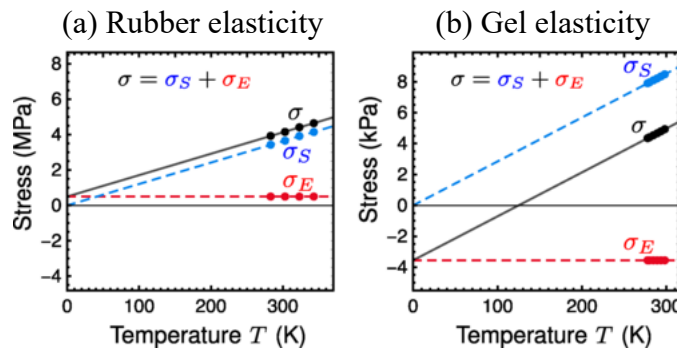


Negative energy elasticity in polymer gel elasticity

Takamasa Sakai and Naoyuki Sakumichi

Graduate School of Engineering, The University of Tokyo, Japan

In thermodynamics and statistical mechanics, elasticity of rubber appears as a representative example of "entropic force" arising from the thermal motion of chains. To confirm that "entropic force" dominates the elasticity of real rubber, it is enough to measure the temperature (T) dependence of the shear modulus (G) under constant volume conditions. This is because the relationship equation $G_S = TdG/dT$ derived from the general theory of thermodynamics can be used to separate the elasticity G into entropic elasticity G_S and energy elasticity G_E ($G = G_S + G_E$) originating from changes in entropy and internal energy, respectively. This equation has been experimentally confirmed that the elasticity of natural and synthetic rubber is mostly entropic ($G \approx G_S$) [1,2].



On the other hand, for polymer gels (hereinafter simply referred to as gels), a model of rubber elasticity theory is conventionally used without experimental verification, assuming that its elasticity is entropic [3,4]. Usually, the elastic modulus of gels is predicted based on classical rubber elasticity models (affine network models, phantom network models, etc.) [3,4]. The central assumption of these models is that "elasticity is mostly determined by entropic elasticity."

Recently, we have discovered that the assumption that the elasticity of polymer gels is solely due to entropy changes is incorrect and that the elasticity of polymer gels also includes a large "negative energy elasticity" G_E from the solvent in addition to entropy elasticity G_S [5-7]. The elasticity of the gel can be approximated as a linear function of temperature ($G = aT + b$), with the first term ($G_S = aT$) corresponding to the contribution of entropy and the second term ($G_E = b$) corresponding to the contribution of internal energy. A large negative energy elasticity means that b has a significant negative value. In the first report of negative energy elasticity, the ratio $|G_E|/G$ reached 1.8 at the maximum. When the polymer concentration of the gel is increased, or in other words, when the gel is made closer to rubber by reducing the solvent, the negative energy elasticity b approaches zero. Thus, the conventional understanding that rubber's elasticity is mainly determined by entropy elasticity ($G \approx G_S$) is consistent with this. Conversely,

negative energy elasticity originates from the solvent and gives the fundamental difference between rubber and gel elasticities.

The negative energy elasticity was first discovered in hydrogels with polyethylene glycol (PEG) as the main chain [5], and has since been reported in other gels such as PDMS gels [8]. Although it is not yet clear whether negative energy elasticity is present in all gels, it is expected to be universally present in many gels that have good solvents and low polymer concentrations.

REFERENCES

1. K. H. Meyer and C. Ferri, *Helv. Chim. A.* **18**, 570 (1935).
2. R. L. Anthony, R. H. Caston, and E. Guth, *J. Phys. Chem.* **46**, 826 (1942).
3. Y. Osada, K. Dusek, M. Shibayama, K. Urayama, "Gel no Kagaku" Kodansha, 2020.
4. M. Zhong, J. A. Johnson, *et al.*, *Science* **353**, 1264 (2016).
5. Y. Yoshikawa, N. Sakumichi, U. Chung, and T. Sakai, *Phys. Rev. X* **11**, 011045 (2021).
6. N. Sakumichi, Y. Yoshikawa, and T. Sakai, *Polymer J.* **53**, 1293 (2021).
7. T. Fujiyabu, T. Sakai, R. Kudo, Y. Yoshikawa, N. Sakumichi, *et al.*, *Phys. Rev. Lett.* **127**, 237801 (2021).
8. T. Aoyama, K. Urayama, Abstract of Gel Symposium 2M06 (2023).