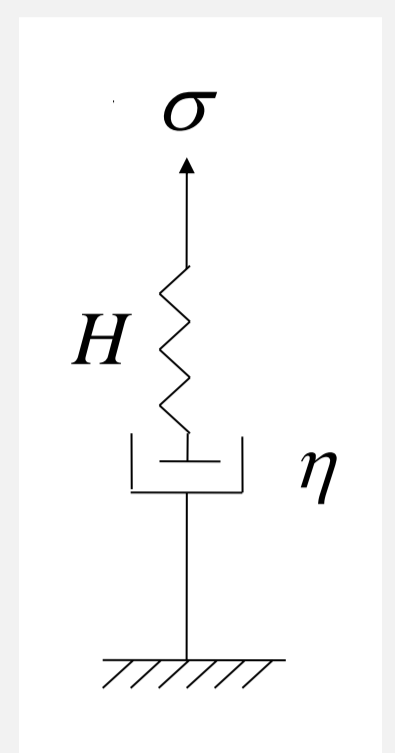


Based on a simple molecular model, a mechanism of rubber deformation characterized by a viscosity increasing during the reversible highly elastic deformation is proposed. It is associated with activation energy of viscous flow which increases by the amount proportional to the external stress due to the entropy elasticity of macromolecules. This increase of the activation energy for jumping of molecular-kinetic units of a polymer network into vacancies during the rubber deformation process is caused by an increasing resistance of the stretching macromolecular network due to the entropy nature of macromolecule deformation.

Maxwell model



$$\varepsilon = \varepsilon_e + \varepsilon_\eta$$

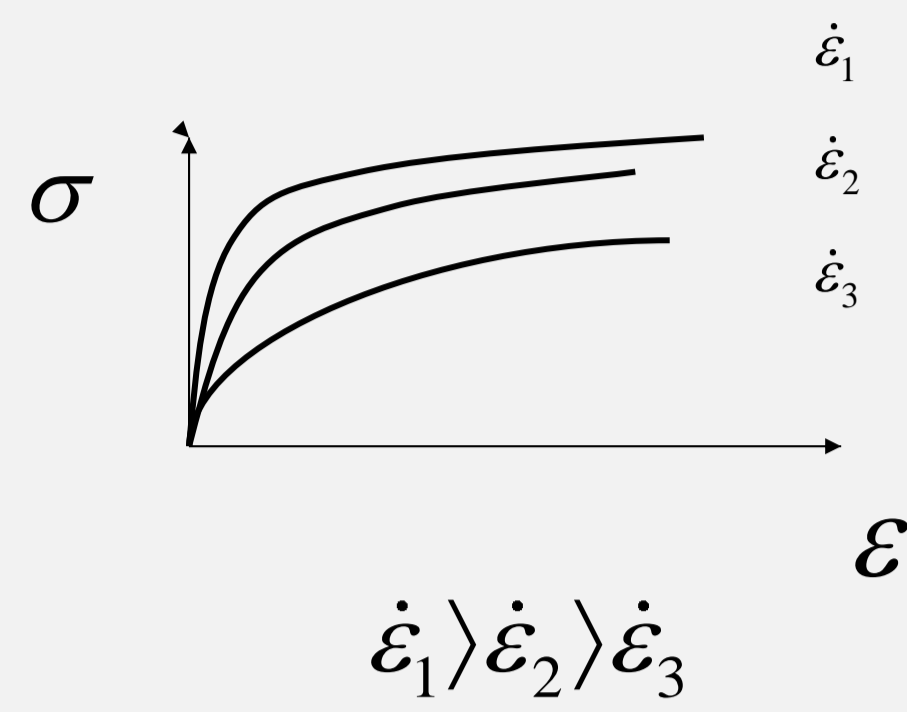
$$\dot{\varepsilon} = \frac{1}{H} \dot{\sigma} + \frac{\sigma}{\eta}$$

$$\dot{\sigma} = H \dot{\varepsilon} - \frac{\sigma}{\eta}$$

$$\dot{\sigma} = 0 \quad \dot{\varepsilon} = \frac{\sigma}{\eta}$$

$$\dot{\varepsilon} = \frac{\sigma}{A \sigma \exp \frac{E_0 - b\sigma}{k_B T}}$$

$$\ln \dot{\varepsilon} = \ln \frac{1}{A} - \frac{E_0}{k_B T} + \frac{\delta}{k_B T} \sigma$$

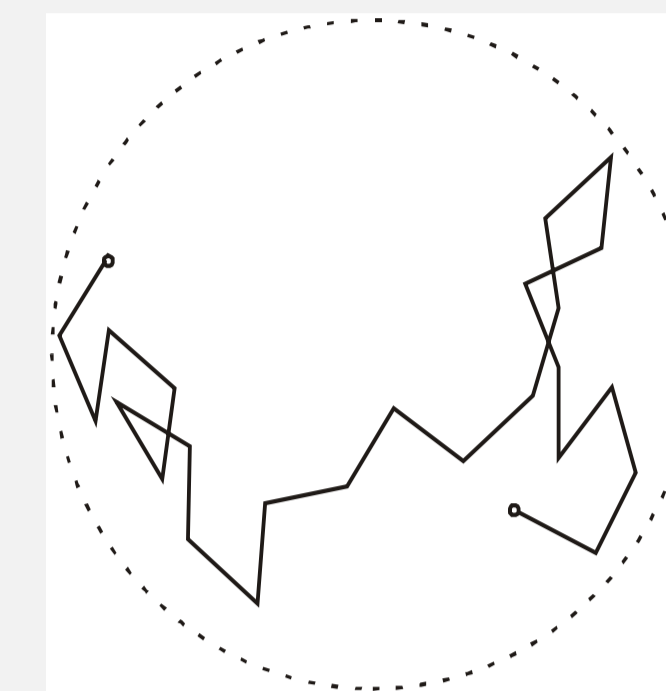


Ludwik, P. $\sigma_\gamma = a + b \lg \dot{\varepsilon}$

Eyring, H. $\eta = A \sigma \exp \frac{E_0 - b\sigma}{k_B T}$ (1) [1]

$$\sigma = \frac{k_B T}{b} \left(\frac{E_0}{k_B T} - \ln \frac{1}{A} \right) + \frac{k_B T}{b} \ln \dot{\varepsilon}$$

Kinetic theory of rubber-elasticity



$$f_e = \frac{3k_B T}{Nl^2} r$$

$$f_e \sim \gamma_e$$

Figure 3.

The force of entropic elasticity of the chain:

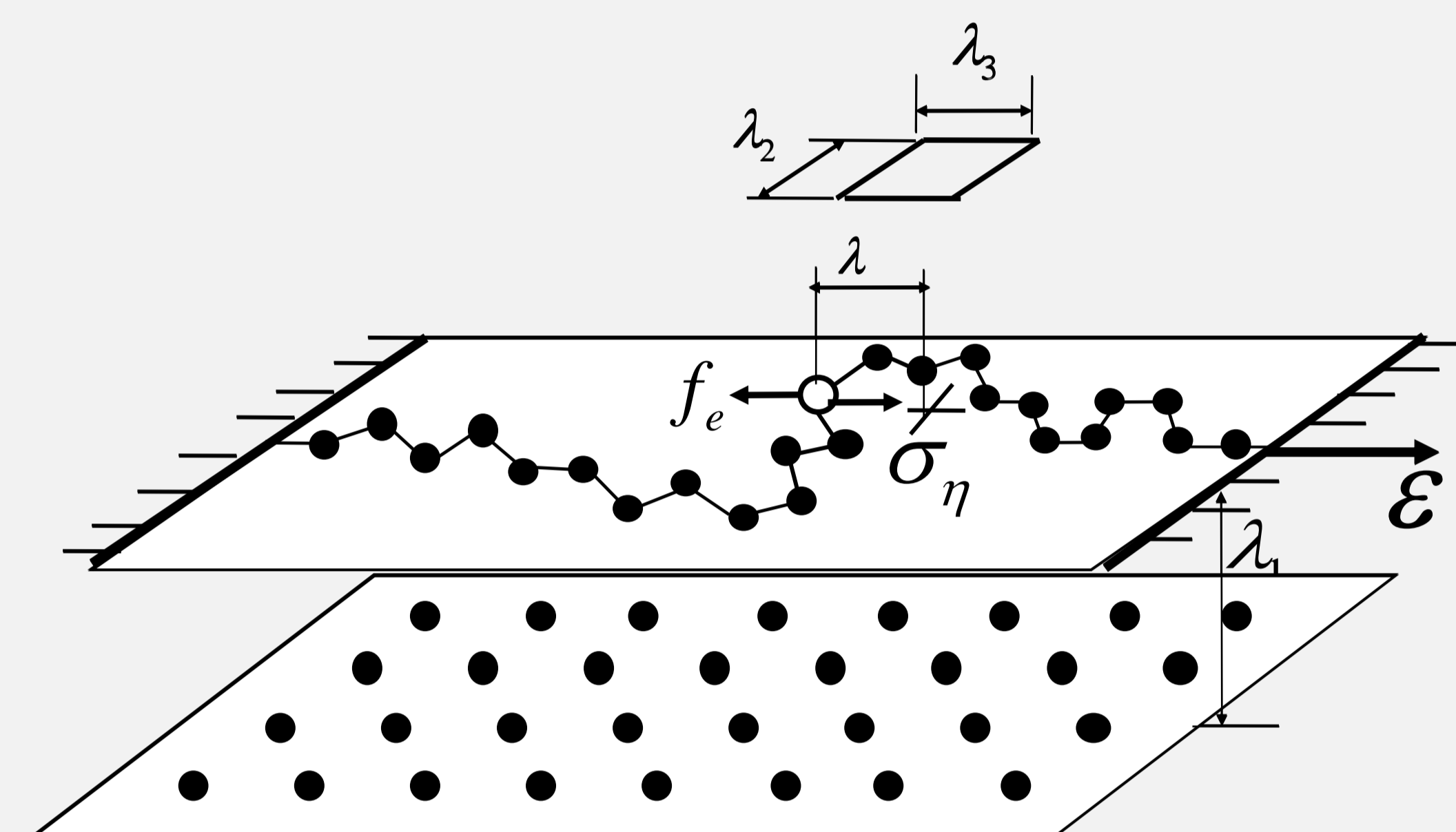
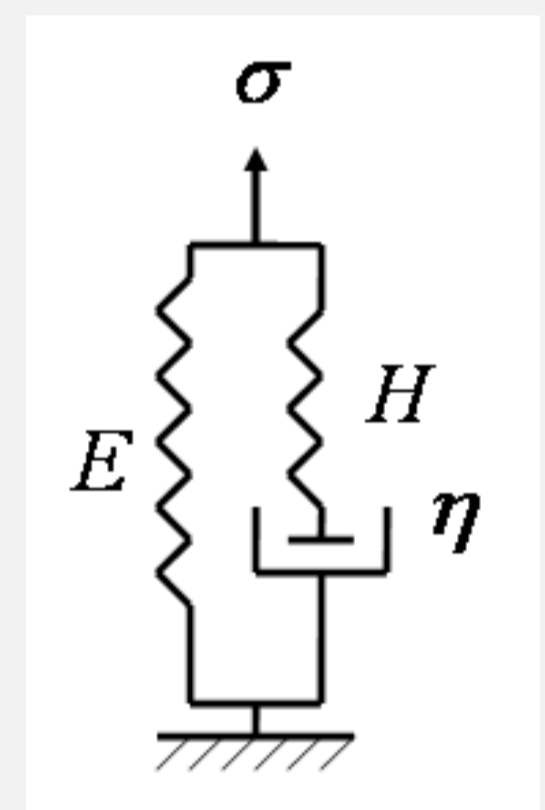


Figure 4. Transition of molecular-kinetic unit of the expanded polymeric chain into the new equilibrium state during the flow of the two liquid planes at different related to each other speeds [2,3].

$$\eta = A \sigma \exp \frac{E_0 + b f_e}{k_B T} \quad (9) \quad [2]$$

$$A = \frac{1}{k_a} = \frac{\lambda_1 h}{\lambda k_B T} \cdot \frac{F}{F_a} \quad (10) \quad b_i = \frac{1}{2} \lambda_2 \lambda_3 \lambda \quad (11)$$

Model of a standard linear solid



$$\eta(H + E)\dot{\varepsilon} + HE\varepsilon = \eta\dot{\sigma} + H\sigma \quad (2)$$

$$\frac{H(\sigma - E\varepsilon)}{(H + E)\dot{\varepsilon} - \dot{\sigma}} = \eta \quad (3)$$

$$\sigma_\eta = \sigma - \sigma_{en} = \sigma - E\varepsilon \quad (4)$$

$$\eta = A_i (\sigma - E\varepsilon) \exp \left(\frac{E_0 + b_i (\sigma - E\varepsilon)}{k_B T} \right) \quad (5)$$

$$\frac{H(\sigma - E\varepsilon)}{(H + E)\dot{\varepsilon} - \dot{\sigma}} = A_i (\sigma - E\varepsilon) \exp \left(\frac{E_0 + b_i (\sigma - E\varepsilon)}{k_B T} \right) \quad (6)$$

$$\frac{1}{(H + E)\dot{\varepsilon} - \dot{\sigma}} = C_i \exp \left(\frac{E_0 + b_i (\sigma - E\varepsilon)}{k_B T} \right) \quad (7)$$

$$\ln \frac{1}{(H + E)\dot{\varepsilon} - \dot{\sigma}} = (\ln C_i + \frac{E_0}{k_B T}) + \frac{b_i}{k_B T} (\sigma - E\varepsilon) \quad (8)$$

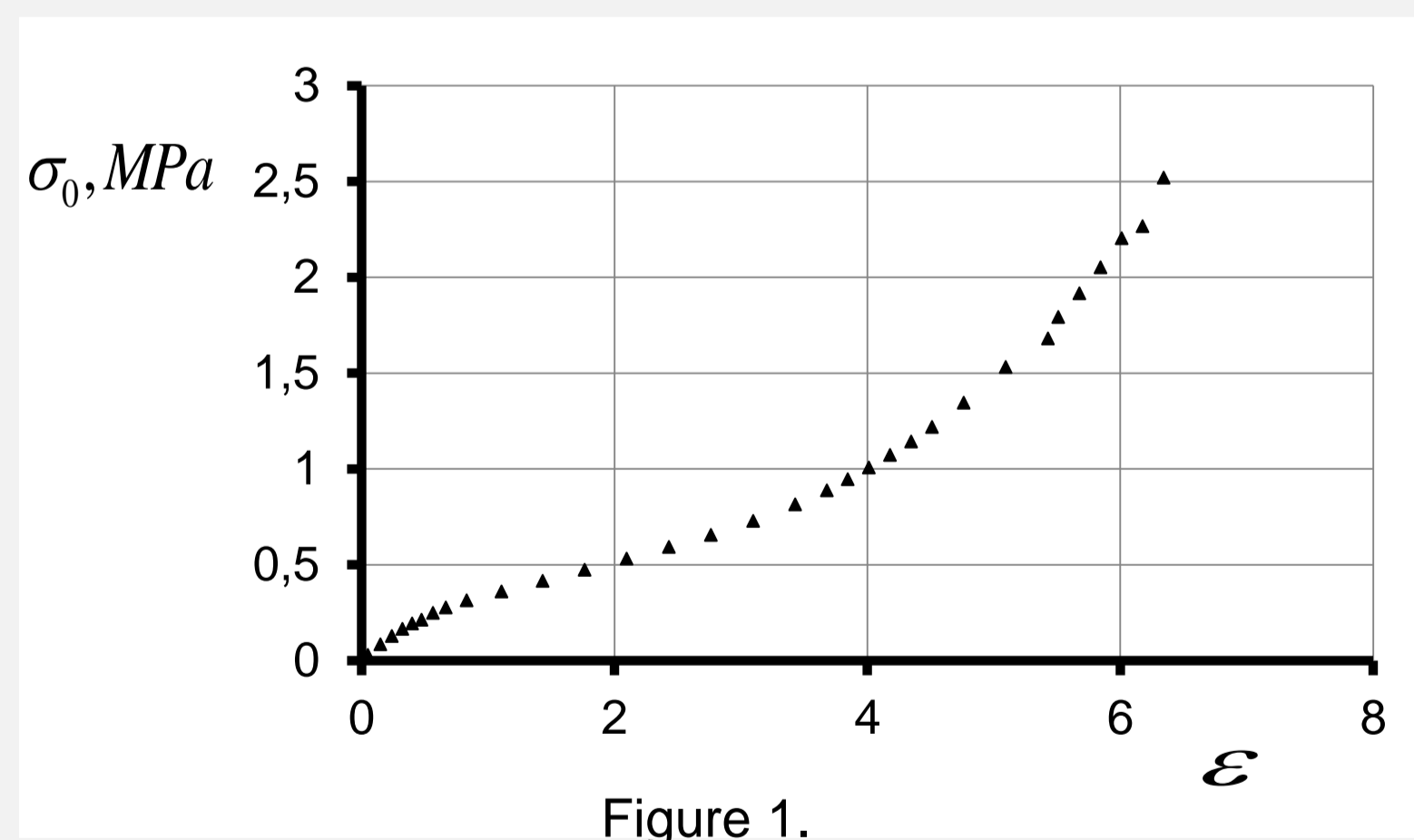


Figure 1. The dependence of nominal stress during the elongation of rubber with stretching of the specimen at a rate of 0.1667 s⁻¹

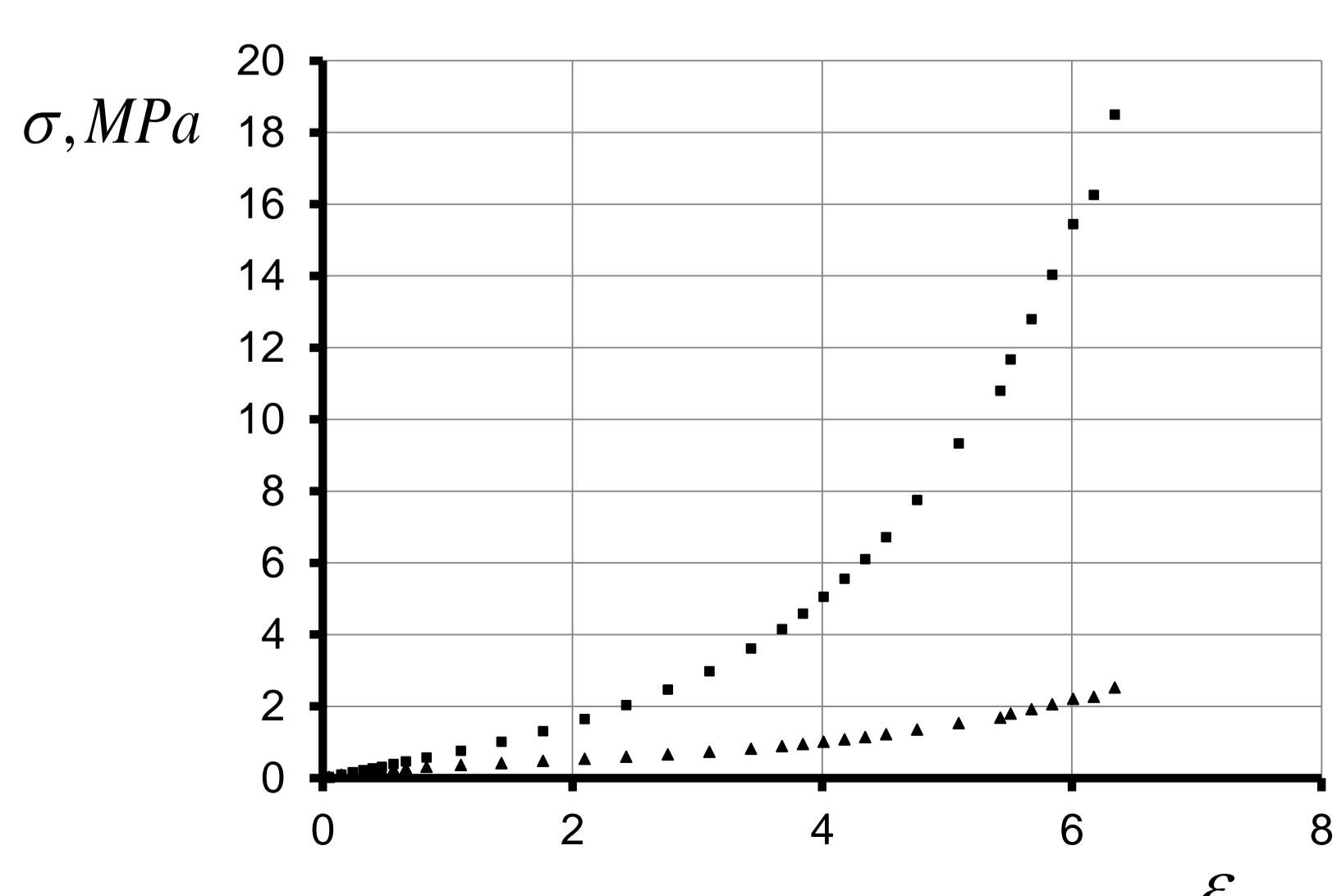


Figure 2. The dependence of true stress (squares) and nominal stress (triangles) during the elongation of rubber with stretching of the specimen at a rate of 0.1667 s⁻¹

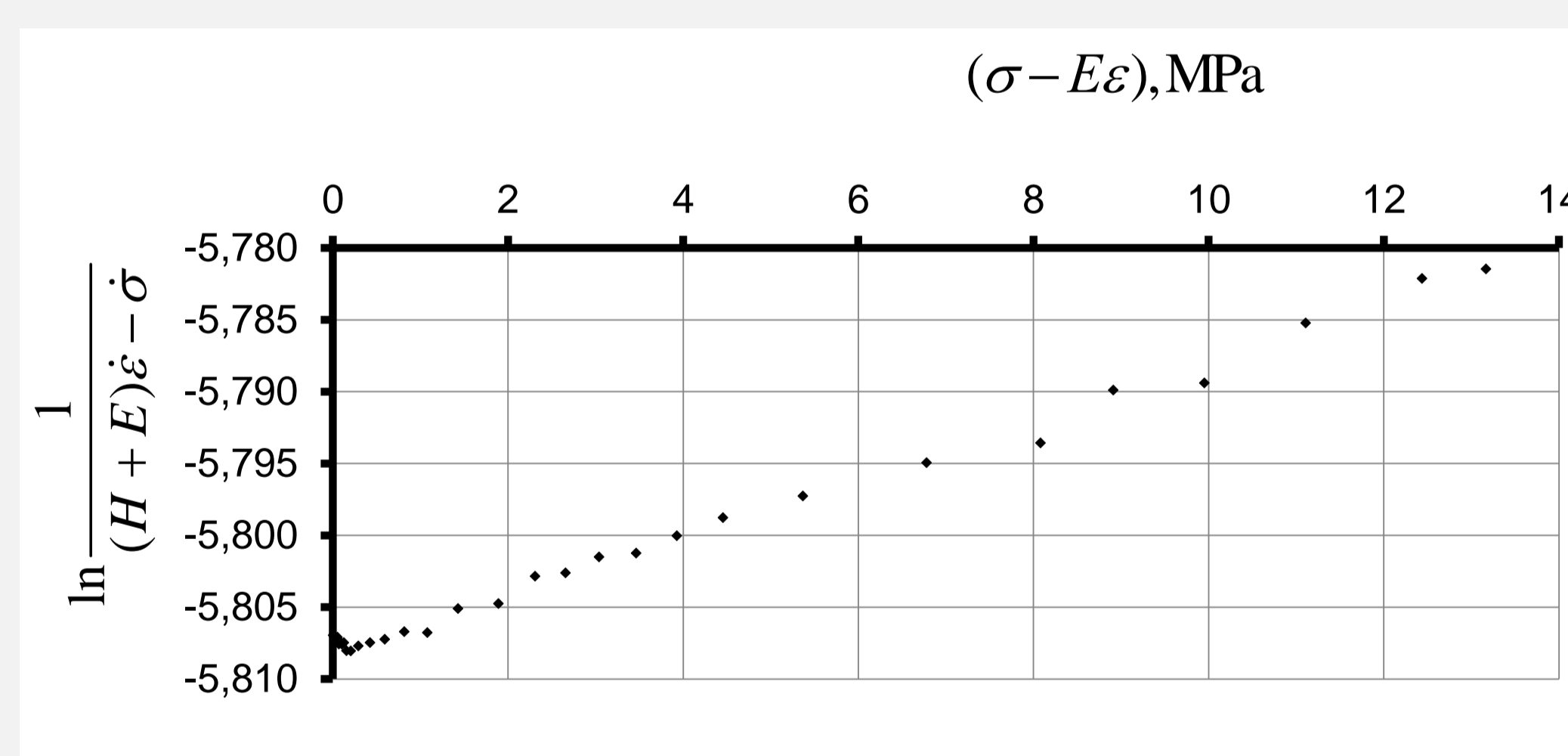


Figure 5. The dependence of $\ln \frac{1}{(H + E)\dot{\varepsilon} - \dot{\sigma}}$ on $(\sigma - E\varepsilon)$ for the stress-strain curve of rubber

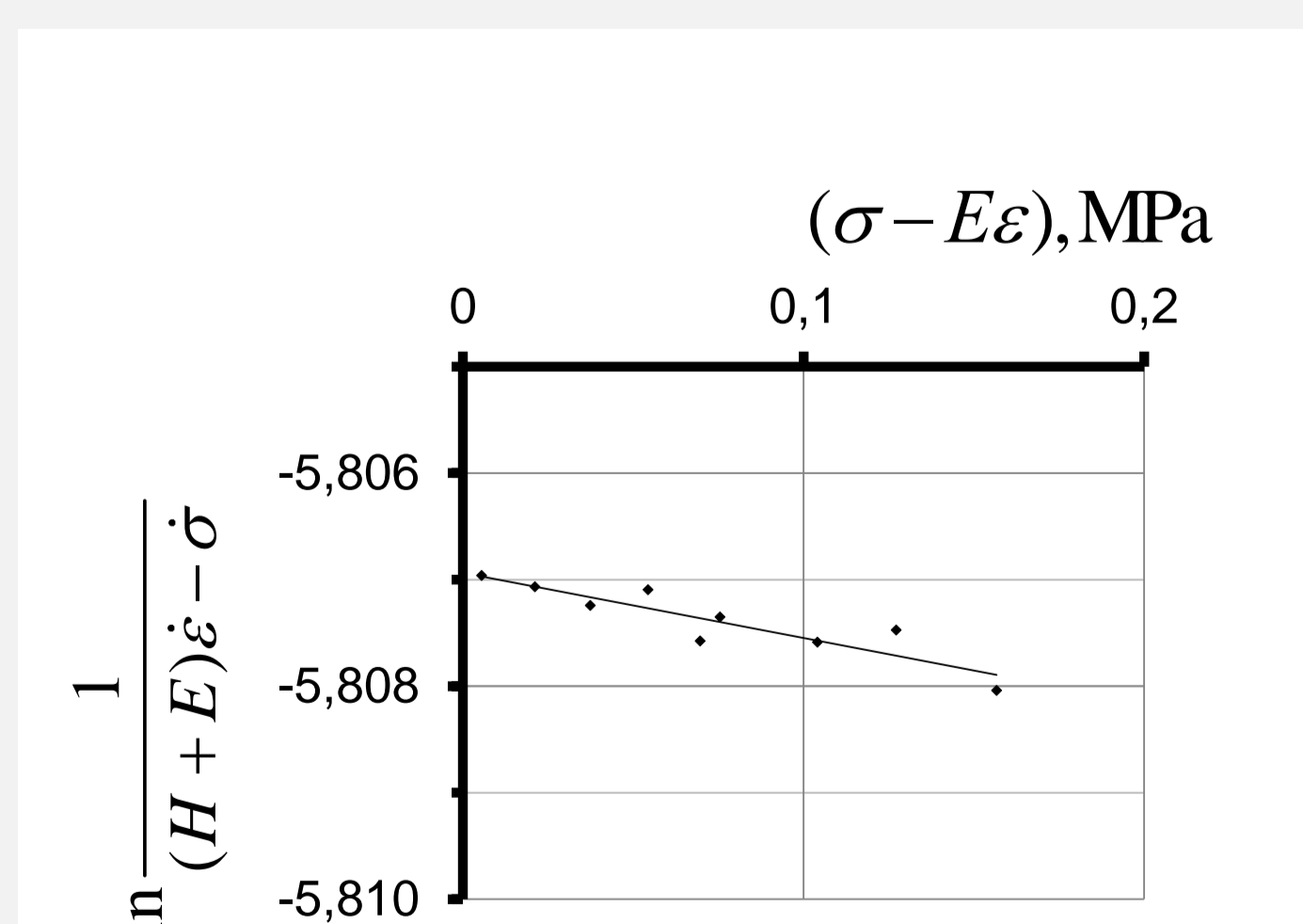


Figure 6. The dependence of $\ln \frac{1}{(H + E)\dot{\varepsilon} - \dot{\sigma}}$ on $(\sigma - E\varepsilon)$ for the stress-strain curve of rubber (initial section)

$$\ln \frac{1}{(H + E)\dot{\varepsilon} - \dot{\sigma}} = (\ln C_d + \frac{E_0}{k_B T}) - \frac{b_d}{k_B T} (\sigma - E\varepsilon) \quad (12)$$

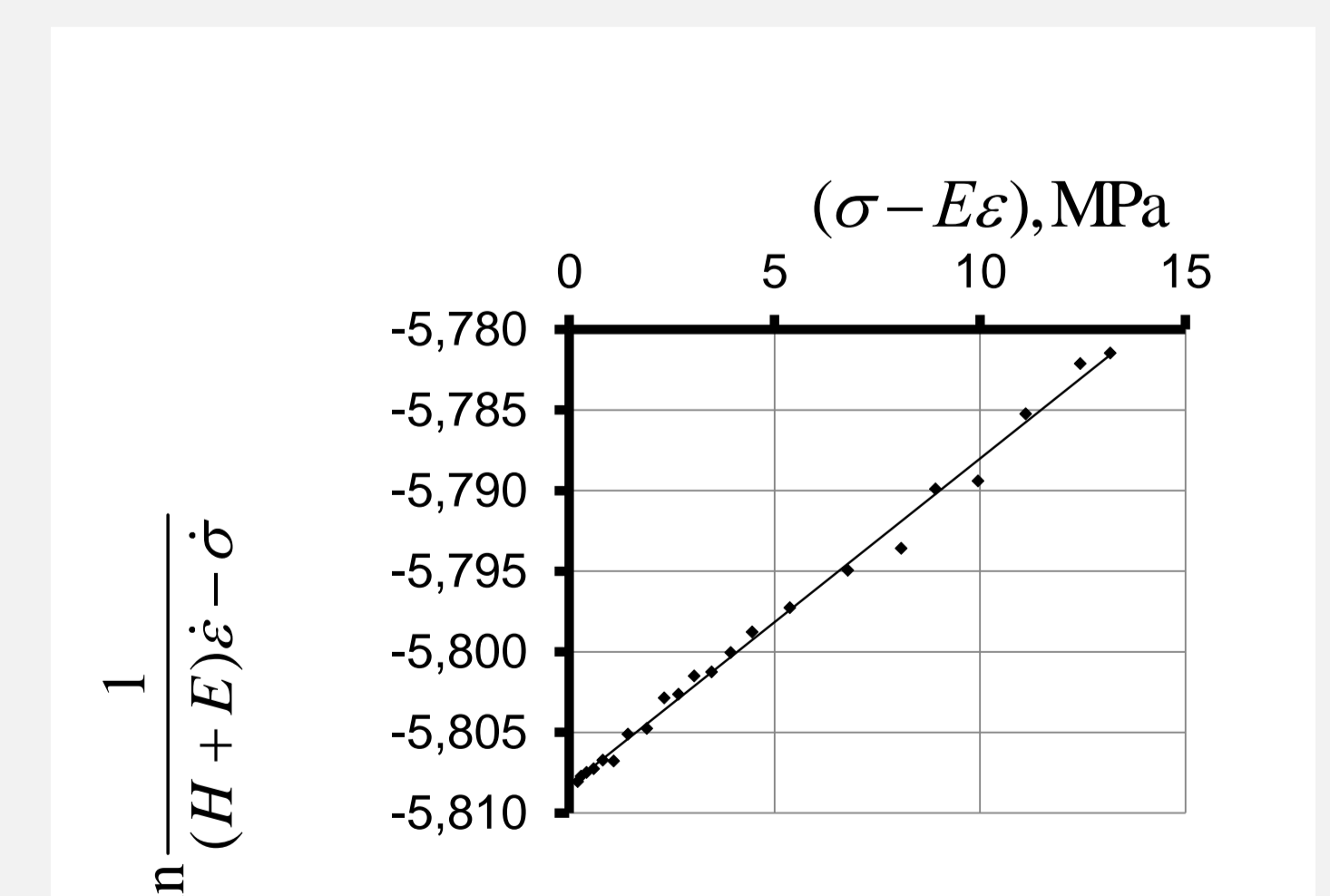


Figure 7. The dependence of $\ln \frac{1}{(H + E)\dot{\varepsilon} - \dot{\sigma}}$ on $(\sigma - E\varepsilon)$ for the stress-strain curve of rubber (second section)

$$\ln \frac{1}{(H + E)\dot{\varepsilon} - \dot{\sigma}} = (\ln C_i + \frac{E_0}{k_B T}) + \frac{b_i}{k_B T} (\sigma - E\varepsilon) \quad (13)$$

calculations of parameters of the equation (5) From experiment (Fig.7):

$$b_i = 8.17 \cdot 10^{-24} \text{ cm}^3 \quad A_i = 1.228 \cdot 10^{-3} \text{ sec} \quad \text{if } E_0 = 5 \text{ kcal/mol} = 20.93 \text{ kJ/mol}$$

if $\varepsilon = 6.177$ hence $\eta = 4.06 \cdot 10^4 \text{ Pa} \cdot \text{sec}$
 $\tau_r = 2.03 \cdot 10^{-2} \text{ sec}$

if $\varepsilon = 1.765$ hence $\eta = 1.27 \cdot 10^3 \text{ Pa} \cdot \text{sec}$
 $\tau_r = 6.38 \cdot 10^{-4} \text{ sec}$

References:

- Glasstone, S.; Laidler, K. J.; Eyring, H. *The theory of rate processes*; McGraw-Hill: New York, 1941, Chap. IX.
- V. I. Kartsovnik, Changes of Activation Energy during Deformation of Rubber. *J. Macromol. Sci., Part B: Physics*, 50:75-88, 2011.