1. Introduction and Basic Thermodynamics
Lectures: Friday 12.00 – 16.00 o‘clock
Room: TK 17

Schedule

from 17. of April until 22. of May 2009

1. of May is official holiday
Polymer Thermodynamics

Prof. Dr. rer. nat. habil. S. Enders

Faculty III for Process Science
Institute of Chemical Engineering
Department of Thermodynamics

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opening hours: Wednesday 9.30-11.30 o’clock
Room TK 111

actual information's:

http://www.thermodynamik.tu-berlin.de
Polymer Thermodynamics

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Material: available as downloads

Downloads  http://www.thermodynamik.tu-berlin.de/

Lehre → Polymer Thermodynamics

✓ News
✓ lecture presentations and exercises
✓ internet Links
Polymer Thermodynamics

Recommended literature

Attention: We have prepared all materials with great care. Nevertheless some errors can be involved.

Invitation

3. Error Challenge

If you have found an error, please send my an E-Mail.
sabine.enders@tu-berlin.de

Please use in the title: Error_Polymer

The student, having found the most errors, will win a price.
Examination

Time: 25. of May until 29. of May 2009

- oral, individual examination
- duration 30 minutes
- content: topics of the lecture
- Please, bring along student ID and personal ID
- Please, make a appointment in my office or via email
Why do we need polymer thermodynamics?

„If you do not know thermodynamics you would not get a bad design, you would get a wrong design!“

M. Parker, CEO Dow Chemical Company (2002)
Why do we need polymer thermodynamics?

Which liquid can be put in cups made from polystyrene?

Interaction of liquids (solvent) with polymers

solubility of polymers
thermic stability of polymers
Polymer Thermodynamics

Why do we need polymer thermodynamics?

Polymer Production: based on Petrol (Petrol distillation)

Which polymers can be produced? At which temperature?

Is the polymerization reaction an voluntary process?

Which solvent should be used?
Why do we need polymer thermodynamics?

The most industrial polymer production processes take place in solutions. How is it possible to remove the solvent? Which solvent should be used? How can we avoid undesired phase separation in the production plant? What are the thermodynamic properties (i.e. heat capacity, vapor pressure) of polymer solutions?
Polymer Thermodynamics

Why do we need polymer thermodynamics?

1. example: foam polystyrene = expanded polystyrene = EPS

Application of EPS

construction (heat, sound and tension insulation)

street building
insulating slab
Polymer Thermodynamics

Why do we need polymer thermodynamics?

1. example: foam polystyrene = expanded polystyrene = EPS construction (heat, sound and tension insulation)

Building by F. Hundertwasser (1928-2000) (Austrian artist) in Darmstadt (Germany)
Polymer Thermodynamics

Why do we need polymer thermodynamics?

1. example: foam polystyrene = expanded polystyrene = EPS

Application of EPS packaging

- blister packaging material of any shape
- safety helmet for bikers
Polymer Thermodynamics

Why do we need polymer thermodynamics?

1. example: foam polystyrene = expanded polystyrene = EPS

Application of EPS

- **Red**: construction
  - (heat and sound insulation)
- **Blue**: packaging
- **Yellow**: cups
- **Grey**: others

1. Europe
2. North-America
3. Africa/West-Asia
4. Latin-America
5. Japan
6. Asia
7. World

Caused by the great climatic differences the application depends strongly on the region.
Polymer Thermodynamics

Why do we need polymer thermodynamics?

1. example: foam polystyrene = expanded polystyrene = EPS

polystyrene plant (Dow Chemical Company)

Thermodynamic task: Description of the involved phase equilibria during the whole production process.
Polymer Thermodynamics

Why do we need polymer thermodynamics?

1. example: foam polystyrene = expanded polystyrene = EPS

Expansion: Polystyrene particle having a diameter of 1mm will be expanded using pentane.
first step: Heating of PS to 100-120°C (T>T_g) using hot water vapor
second step: Pentane will be evaporated and pressed into polymer particles. This leads to new particle (pearls) having a diameter of 3 mm.

Thermodynamic task:
Can we predict the glass temperature of polymers?
What is the vapor pressure of pentane?
Does the interfacial properties play an important role?
Polymer Thermodynamics

Why do we need polymer thermodynamics?

1. Example: foam polystyrene = expanded polystyrene = EPS

Expansion: Polystyrene particle having a diameter of 1mm will be expanded using pentane.
Third step: Expanded polymer particle will be given in the desired forming.
Fourth step: Little holes will be made on the polymer wall.
Fifth step: Hot air will be pressed in the system in order to remove the pentane.
Sixth step: Heating the polymer well above the glass transition temperature in order to increase the volume by the factor 2 – 2.5.
Seventh: Cooling down the whole system. The foam takes his final shape.
Eight: The product will be stored several days in order to allow the completely remove of pentane.

Thermodynamic task:
At which conditions will the air be able to replace pentane?
How will the volume of the polymer be changed during heating and cooling procedures?
Does a special interaction between the polymer and the fluid plays a role?
At which temperature the critical state of the gas can be found?
Is there a potential for simplification or improvement of the process?
What is the role of permeation in the procedure?
Polymer Thermodynamics

Why do we need polymer thermodynamics?

1. example: foam polystyrene = expanded polystyrene = EPS

Foaming of Polymers

Thermodynamic task:
It is possible to use an alternative gas (hydrogen, nitrogen, carbon dioxide)?
At which pressure can the foaming process be carried out?
Polymer Thermodynamics

Why do we need polymer thermodynamics?

1. example: foam polystyrene = expanded polystyrene = EPS

Application for heat insulation:
Important property: heat conductivity

<table>
<thead>
<tr>
<th>Material</th>
<th>Polymer density [g/m³]</th>
<th>Heat conductivity [W/mK]</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPS</td>
<td>30</td>
<td>0.032</td>
</tr>
<tr>
<td>polyurethane-foam</td>
<td>30</td>
<td>0.019 to 0.024</td>
</tr>
<tr>
<td>air</td>
<td></td>
<td>0.025</td>
</tr>
</tbody>
</table>

Thermodynamic task: Why? Which difference in layer thickness follows from the different heat conductivities, if the insulation power should be identical?
Polymer Thermodynamics

Why do we need polymer thermodynamics?

2. example: polymers for medical applications

- glasses, contact lenses, denture
- valve, blood vessels, disc, artificial nerves
- dialysis membranes, dialysis tubes, artificial hip joint endoprosthesis
- implant for skin
- artificial knee joint

Diagram showing percentages of different polymers used in medical applications:
- PVC 29%
- PS 21%
- PE 29%
- PP 13%
- Others 11%

Diagram of a human figure with arrows pointing to different medical applications.
Polymer Thermodynamics

Why do we need polymer thermodynamics?

2. example: polymers for medical applications

PVC = poly(vinyl chloride)

Application: bags for blood, drug-formulations, safety gloves, tubes, blister-package

Advantage: suitable for thermic formability, high flexibility, excellent chemical resistance, very low potential for allergy

Disadvantage: phthalates is used as softener, but they can be toxic (teratogen and cancerogen) for humans

Challenge for thermodynamics:
How can we produce ultra pure PVC with a negligible amount of softener?
How are the relation between polymer properties (i.e. molecular weight distribution) and flexibility?
Can we use phase equilibria (demixing of polymer solution) to made tailor-made polymers?
Which procedure can be applied for sterilization?
Polymer Thermodynamics

Why do we need polymer thermodynamics?

2. example: polymers for medical applications

PE – poly(ethylene)

Application: foil, packaging, containers
tubes, bottles, implant (knee, hip)
Advantage: excellent chemical resistance
high stiffness

Challenge for thermodynamics:
How we can produce ultra pure PE?
What are the relations between polymer
properties (i.e. molecular weight distribution)
and other physical properties, like permeation, solubility?
Can we use phase equilibria (demixing of polymer solution) to made tailor-made polymers?
Which procedure can be applied for sterilization?
LDPE is produced via high-pressure polymerization. What do we know about the influence of pressure on the phase equilibria?
Polymer Thermodynamics

Why do we need polymer thermodynamics?

2. example: polymers for medical applications

PS = polystyrene

Application: package, infusion equipment, tubes

Advantage: chemical resistance
   excellent deformability
   excellent transparency

Thermodynamic challenge
How can we produce tailor-made polymers based on polystyrene, maybe copolymerization?
Which copolymer should be applied for which purpose?
What is the influence of chemical composition on the properties of the copolymer?
Polymer Thermodynamics

Why do we need polymer thermodynamics?

2. example: polymers for medical applications

PP = polypropylene

Application: artificial thread, artificial tissue membranes for dialysis heart valve, syringe

Advantage: chemical resistance excellent deformability

Challenge for thermodynamics:
How can we produce ultra pure PP?
What are the relations between polymer properties (i.e. molecular weight distribution) and other physical properties, like permeation, solubility crystallinity?
Can we use phase equilibria (demixing of polymer solution) to made tailor-made polymers?
Which procedure can be applied for sterilization?
Polymers Thermodynamics

Why do we need polymer thermodynamics?

2. example: polymers for medical applications

PLA = poly(lactic acid)

Application: tissue-engineering, artificial bone and articular

Advantage: biological degradation is possible

two optical isomers poly( L-lactic acid) and poly( D-lactic acid)

Properties: partial crystalline melting temperature 180°C

Properties: amorphous melting temperature 75°C

copolymerization in order to tune the physical properties

Thermodynamic challenge: How is the influence of copolymer composition on physical properties (crystallinity, degradation, pH-stability)?
Polymer Thermodynamics

Why do we need polymer thermodynamics?

2. example: polymers for medical applications

PLA = poly(lactic acid) as controlled drug delivery systems

encapsulation of drugs

Advantage:
long-term therapy over months
is possible

Diseases: chemotherapy, hormone therapy

Thermodynamic challenge: Can we predict the maximal amount of drug in the polymer particles? Do we have any influence on this amount? What do we know about the involved swelling equilibria? How can we optimized the degradation behavior?
Polymer Thermodynamics

Why do we need polymer thermodynamics?

Let us start to learn something about polymer thermodynamics!

The department of Thermodynamics und Thermic Engineering wishes you a lot of fun with thermodynamics and complete success.

Let us start to repeat the basics of thermodynamics, namely some basic terms, the first and second law of thermodynamics.
Polymer Thermodynamics

Basic terms of Thermodynamics

System and Surrounding

**System**: certain sector of matter containing a large number of particles ($\approx 10^{23}$)

Examples: content of beaker, content of thermos bottle, chemical reactor, steam engine

- **System**: certain sector of matter containing a large number of particles ($\approx 10^{23}$)
- **Surrounding**: environment outside the system

**System**
- **Open System**: allows material and energy transfer
- **Closed System**: allows material transfer but not energy transfer
- **Isolated System**: neither material nor energy transfer

For heat and work holds the definition that heat or work put into the system has a positive sign.

\[
\text{from surrounding to system} \rightarrow dW \text{ or } dQ > 0 \rightarrow \text{endothermic}
\]

\[
\text{from system to surrounding} \rightarrow dW \text{ or } dQ < 0 \rightarrow \text{exothermic}
\]
Phase: Phase is a substance (pure phase) or a mixture of substances having spatial constant properties. The area, where the properties will be changed is called interphase.
phase: Phase is a substance (pure phase) or a mixture of substances having **spatial constant properties**. The area, where the properties will be changed is called interphase.
**Phase**

Phase is a substance (pure phase) or a mixture of substances having **spatial constant properties**. The area, where the properties will be changed is called interphase.

**Example:** oil + water

<table>
<thead>
<tr>
<th>Liquid 1 $L_1$</th>
<th>$L_1$ liquid density $\rho^{L_1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid 2 $L_2$</td>
<td>$L_2$ liquid density $\rho^{L_2}$</td>
</tr>
</tbody>
</table>
Polymer Thermodynamics

Basic terms of Thermodynamics

State

state: Thermodynamic state of system is characterized by its state variables (i.e. temperature, pressure, density, composition, energy).

state functions (i.e h,u,f,g,s) depend on state variables (i.e. T,P,V, n_i).

General: \( z=f(x,y) \)

Change of state functions \( dz \) → exact differential

\[
\left( \frac{\partial z(x,y)}{\partial x} \right)_y = \lim_{\Delta x \to 0} \frac{z(x+\Delta x,y) - z(x,y)}{\Delta x} \\
\left( \frac{\partial z(x,y)}{\partial y} \right)_x = \lim_{\Delta y \to 0} \frac{z(x,y+\Delta y) - z(x,y)}{\Delta y}
\]

\[
\left( \frac{\partial z(x,y)}{\partial y} \right)_y \ dx = z(x+dx, y) - z(x, y) \\
\left( \frac{\partial z(x,y)}{\partial y} \right)_x \ dy = z(x, y+dy) - z(x, y)
\]

\[
dz(x,y) = \left( \frac{\partial z(x,y)}{\partial x} \right)_y \ dx + \left( \frac{\partial z(x,y)}{\partial y} \right)_x \ dy \\
\text{exact differential}
\]
Polymer Thermodynamics

Basic terms of Thermodynamics

State

state: Thermodynamic state of system characterized by its state variables (i.e. temperature, pressure, density, composition, energy).

state functions (i.e. h, u, f, g, s) depend on state variables (i.e. T, P, V, n_i).

General: z = f(x, y)

Change of state functions $dz \rightarrow$ exact differential

$$dz = \left( \frac{\partial z}{\partial q} \right)_{r,s} dq + \left( \frac{\partial z}{\partial r} \right)_{q,s} dr + \left( \frac{\partial z}{\partial s} \right)_{r,q} ds$$

partial differential coefficient $\rightarrow$ related to experimental quantities

i.e. $$\left( \frac{\partial H}{\partial T} \right)_P = c_P \quad \left( \frac{\partial S}{\partial T} \right)_P = \frac{c_P}{T} \quad \left( \frac{\partial H}{\partial P} \right)_T = V - T \left( \frac{\partial V}{\partial T} \right)_P$$
Polymer Thermodynamics

Basic terms of Thermodynamics

State

state functions: example

\[ z(x, y) = 3x^2 + 2xy + \frac{3}{2}y^2 \]

\[ dz = \left( \frac{\partial z}{\partial x} \right)_y dx + \left( \frac{\partial z}{\partial y} \right)_x dy \]

\[ \left( \frac{\partial z}{\partial x} \right)_y = 6x + 2y \]

\[ \left( \frac{\partial z}{\partial y} \right)_x = 2x + 3y \]

\[ dz = (6x + 2y)dx + (2x + 3y)dy \]
Polymer Thermodynamics

Basic terms of Thermodynamics

State
Polymer Thermodynamics

Basic terms of Thermodynamics

State

\[ \Delta Z = Z_{\text{end}} - Z_{\text{beginning}} \]

\[ \Delta Z = \Delta_1 Z = \Delta_2 Z = \Delta_3 Z \]

State functions depend **not** from the route.
Polymer Thermodynamics

Basic terms of Thermodynamics

State – Functions

Calculation of changes in state functions

Example:

\[ z(x, y) = 3x^2 + 2xy + \frac{3}{2}y^2 \]

change in state = state at end – state at beginning

i.e. state at beginning: \( x=2, \ y=4 \)
state at end: ~ \( x=5, \ y=1 \)

\[ \Delta z = z(5, 1) - z(2, 4) = 86.5 - 52 = 34.5 \]
Polymer Thermodynamics

Basic terms of Thermodynamics

State – Change

i.e. What is the change in volume, if the substance is transferred from state \( V(P,T,n) \) into state \( V(P+\Delta P, T+\Delta T,n) \) ?

\[
V = f(T, P, n)
\]

\[
dV = \left( \frac{\partial V}{\partial T} \right)_{P,n} dT + \left( \frac{\partial V}{\partial P} \right)_{T,n} dP + \left( \frac{\partial V}{\partial n} \right)_{T,P} dn
\]

Ideal gas law:

\[
P V = nRT \rightarrow V = \frac{nRT}{P}
\]

\[
\left( \frac{\partial V}{\partial T} \right)_{P,n} = \frac{nR}{P} \quad \left( \frac{\partial V}{\partial P} \right)_{T,n} = -\frac{nRT}{P^2} \quad \left( \frac{\partial V}{\partial n} \right)_{P,T} = \frac{RT}{P}
\]

\[
dV = \frac{nR}{P} dT - \frac{nRT}{P^2} dP + \frac{RT}{P} dn
\]
Polymer Thermodynamics

Basic terms of Thermodynamics

**State – Functions**

\[ \Delta Z = Z^{\text{end}} - Z^{\text{beginning}} \]

- State functions depend *not* from the route

**Law of Schwarz:** The sequence of differentiation can be interchanged.

For \( z = f(q, r) \) is valid

\[
\begin{align*}
dz &= \left( \frac{\partial z}{\partial q} \right)_r \, dq + \left( \frac{\partial z}{\partial r} \right)_q \, dr \\
\end{align*}
\]

\[
\left( \frac{\partial}{\partial r} \left( \frac{\partial z}{\partial q} \right)_r \right)_q = \left( \frac{\partial}{\partial q} \left( \frac{\partial z}{\partial r} \right)_q \right)_r
\]

\[
\left( \frac{\partial^2 z}{\partial q \partial r} \right) = \left( \frac{\partial^2 z}{\partial r \partial q} \right)
\]
Polymer Thermodynamics

Basic terms of Thermodynamics

State – Functions

\[ \Delta Z = Z^{\text{End}} - Z^{\text{Beginning}} \]

Rule for differentiation of products

\[ z(x, y) = f(x, y)g(x, y) \quad y' = uv' + vu' \]

\[ dz(x, y) = g(x, y)df(x, y) + f(x, y)dg(x, y) \]

with

\[ df(x, y) = \left( \frac{\partial f(x, y)}{\partial x} \right)_y dx + \left( \frac{\partial f(x, y)}{\partial y} \right)_x dy \]

\[ dg(x, y) = \left( \frac{\partial g(x, y)}{\partial x} \right)_y dx + \left( \frac{\partial g(x, y)}{\partial y} \right)_x dy \]
Polymer Thermodynamics

Basic terms of Thermodynamics

State – Quantities

State quantities can be extensive or intensive.

Extensive state quantities will double their value if two equal systems will be united to one new system. 

i.e. mass m, volume V, energy U

Intensive state quantities will keep their value if two equal systems will be united to one new system.

i.e. temperature T, pressure P, molar volume v, specific volume $v_{sp}$

Molar quantities

Density $[\text{g/l}]$ 

Concentration $[\text{mol/l}]$

$$v = \frac{V}{n}$$

$n$ = amount of substance

Specific quantities

$$v_{sp} = \frac{V}{m} = \frac{v}{M}$$

$m$ = mass, $M$ = molar mass
The equilibrium state is the final state of the process. At equilibrium no changes can be observed, experimentally.
Polymer Thermodynamics

Basic terms of Thermodynamics

Processes

Processes: Transfer from initial (beginning) state to the final (end) state.

<table>
<thead>
<tr>
<th>isobar</th>
<th>isotherm</th>
<th>isochore</th>
<th>adiabatic</th>
</tr>
</thead>
<tbody>
<tr>
<td>constant</td>
<td>constant</td>
<td>constant</td>
<td>no heat exchange</td>
</tr>
<tr>
<td>pressure</td>
<td>temperature</td>
<td>volume</td>
<td></td>
</tr>
</tbody>
</table>

Process quantities: depend on the route
they are related to a process and not to a system
i.e. work and heat

extensive quantities
i.e. work W, heat Q

intensive quantities
i.e. molar enthalpies of chemical reactions
Processes

**heat and work**

from mechanics

\[ dW = F ds \]

force  \rightarrow route

i.e. to uplift of mass \( m \) from the height \( h_1 \) to the height \( h_2 \)

\[ W_{HUB} = \int_{h_1}^{h_2} Gdh = mg \int_{h_1}^{h_2} dh = mg(h_2 - h_1) \]

i.e. Acceleration of mass \( m \) from speed \( v=0 \) to speed \( v_1 \)

\[ a = \frac{dv}{dt} \quad v = \frac{ds}{dt} \quad W_{Be} = \int_{s_0}^{s_1} mads = \int_{0}^{v_1} m \frac{dv}{dt} vdt = \int_{0}^{v_1} mvdv = \frac{1}{2}mv_1^2 \]
Polymer Thermodynamics

Basic terms of Thermodynamics

Processes

\[ dW = Fds \]

thermodynamics: mechanical work \( W_{\text{vol}} \) caused by the movement of the system limits via volume change.

During expansion of an ideal gas against an outside acting force \( F \) caused by the weight, \( G \), the work is given by:

\[
W_{\text{Vol}} = - \int_{S_1}^{S_2} Fds \\
F = PA \\
dV = A ds
\]

\[
W_{\text{Vol}} = - \int_{V_1}^{V_2} PA \frac{dV}{A} \\
W_{\text{Vol}} = - \int_{V_1}^{V_2} PdV
\]

Mechanical work is always connected with a vectored movement of particles.
Polymer Thermodynamics

Basic terms of Thermodynamics

Processes

Thermodynamics: mechanical work, $W_{vol}$

$$W_{vol} = - \int_{S_1}^{S_2} F ds = - \int_{V_1}^{V_2} P dV$$

The sign of mechanical work:

$$V_2 > V_1 \rightarrow \Delta V > 0 \rightarrow W_{vol} < 0$$

$\rightarrow$ work done by the system

$$V_1 > V_2 \rightarrow \Delta V < 0 \rightarrow W_{vol} > 0$$

$\rightarrow$ work done on the system
Polymer Thermodynamics

Basic terms of Thermodynamics

Processes

mechanical work at constant extern pressure (i.e. atmospheric pressure)

\[ W_{vol} = - \int_{s_1}^{s_2} F ds = - \int_{v_1}^{v_2} P dV \]

\[ W_{vol} = -P(V_2 - V_1) \]

\[ V_2 > V_1 \rightarrow W_{vol} < 0 \]

The work is done by the system.
The work is done on the system.
Polymer Thermodynamics

Basic terms of Thermodynamics

Processes

mechanical work at variable extern pressure

\[ W_{Vol} = -nRT \ln \left( \frac{V_2}{V_1} \right) \]

\[ P_1 = \frac{nRT}{V_1} \quad P_2 = \frac{nRT}{V_2} \]

Isotherme

\[ P = \frac{nRT}{V} \]
Polymer Thermodynamics

Basic terms of Thermodynamics

Processes

Two groups of hikers would like to go to mountain. The first group takes the direct way. The second group uses the serpentines. On the top of the mountains both groups have the same state (the same height), but the second group has done more work.

Change in state variables (i.e. height): depends not on the route
Change in process quantities (i.e. work): depends on the route
**Polymer Thermodynamics**

**Basic terms of Thermodynamics**

**Processes**

**Heat**: is equal to the change of energy related to the energy of molecular motion.
- process quantity \( \rightarrow \) depends on the way
- is related to processes and not to systems

heat exchanges with change of temperature

i.e. Heating of liquid in beaker

\[
dQ = CdT
\]

heat capacity \( C \)

specific heat capacity:

\[
c = \frac{C}{n}
\]

\[
c_{sp} = \frac{C}{m}
\]

heat exchanges without change of temperature

latent heat

i.e. phase change, chemical reaction, solution, adsorption

\[
dQ = qd\zeta
\]

q molare heat of reaction

\( \zeta \) reaction coordinate

**\( dQ < 0 \) exothermic**

**\( dQ > 0 \) endothermic**
Polymer Thermodynamics

Basic terms of Thermodynamics

Processes

Heat $Q$

$T \, [°C]$

ice

water + ice

water

water + vapor

vapor

-20 0 20 40 60 80 100
Polymer Thermodynamics

Basic terms of Thermodynamics

Processes

work

heat
Polymer Thermodynamics
Basic terms of Thermodynamics

Equilibrium

a) thermic equilibrium: \( T^I = T^{II} = \ldots = T \)
   \( \rightarrow \) constant temperature
b) mechanical equilibrium: \( P^I = P^{II} = \ldots = P \)
   \( \rightarrow \) constant pressure
c) material equilibrium: \( \mu_i^I = \mu_i^{II} = \ldots = \mu_i^n \)
   \( \rightarrow \) The chemical potential of the component, i, is equal in all present phases.
Polymer Thermodynamics

Basic terms of Thermodynamics

**Equilibrium**

\[ E_{\text{Pot}} = mgh \]

stable
\[ E_{\text{Pot}} \rightarrow \text{global minimum} \]
stable against all perturbations

instable
\[ E_{\text{Pot}} \rightarrow \text{global maximum} \]
instable against all perturbations

metastable
\[ E_{\text{Pot}} \rightarrow \text{local minimum} \]
stable against small perturbations