An Outlook to Biothermodynamics

J. U. Keller, Inst. Fluid - and Thermodynamics
University of Siegen, 57068 Siegen, Germany
keller@ift.maschinenbau.uni-siegen.de

Biothermodynamics
Overview, Historical Remarks

1. Photosynthesis

2. Lipid Membranes : Phase Transition
DMPC-EOS (E2)

3. Proteins : Thermal Denaturation

4. Metabolism of Bacteria
Kleiber's Law

Bacteria Escherichia Coli
Th. Escherich, 1919

Biothermodynamics (BTH):

Application of Thermodynamics, i.e.Thermostatics (TST) and Thermodynamics of Irreversible Processes (TIP) to Biological and Bioengineering Systems.

Biotechnology (BT):
Technology using living systems like cells, bacteria, fungi etc. as chemical reactors.

White BT	Industrial sized biocatalytic processes (fermentation) Breweries, Production vitamine B12, steroid hormones etc.;
Green BT	Plants and transgene variations for production of biofuels etc. in biorefineries;
Red BT	Medical applications of substances and processes related to living organisms, as for example interferones etc. (cancer,viruses)
Yellow BT	Pharmaceutical molecules, recombinant proteins, penicilline and other fungi;
Blue BT	Seawater based microorganisms as reactors; extremophiles... Extraction noble metals from seawater, production of new molecules

Fields of Research in Biothermodynamics

3rdInt. Symposium on Biothermodynamics
DECHEMA, Bologna, September 2010

Biomolecules

 # Protein adsorption on surfaces

 # Protein folding, interactions and stability

Bacteria

 # Active masstransport in biological membranes

 # Thermodynamics of metabolic pathways

 # Intracellular Thermodynamics

Bioreactors

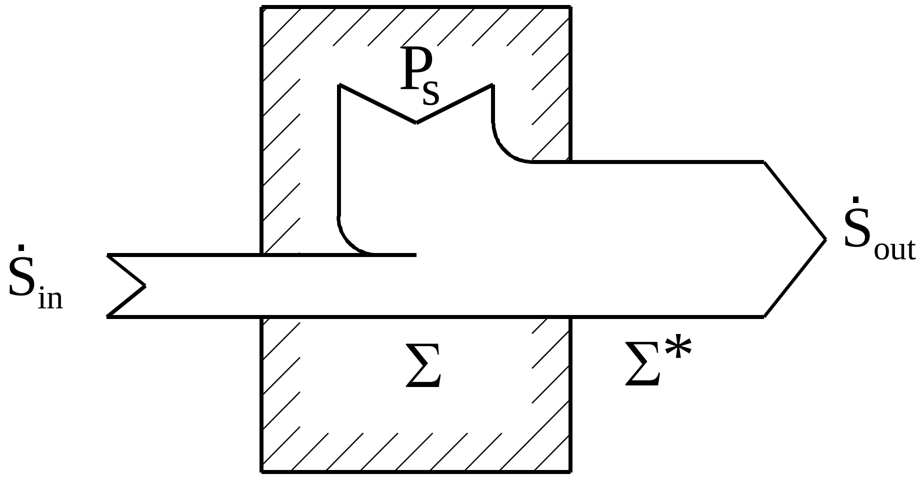
 # Biocalorimetry

 # Thermodynamics of downstream processing

 # Thermodynamics in biological energy conversion processes

 # Thermodynamic aspects of Systems Bilogy

1. Thermodynamics of Photosynthesis



Evaporation of Additional Water:

$$\dot{S}_{in} = \dot{S}_{out} + 0.24 \frac{kJ}{mol\,K} \cdot \dot{n}_{GL}$$

$$2.2 \,|\, \dot{S}\; H_2O\;_{L} = \dot{S}\; H_2O\;_{V} - 0.11 \frac{kJ}{mol\,K} \cdot \dot{n}_{W}$$

$$\dot{n}_W = 2.2 \cdot \dot{n}_{GL}$$

E. Schrödinger (~1940)

$$\underbrace{6\,CO_2 + 6\,H_2O}_{\dot{S}_{in}} \rightarrow \underbrace{C_6H_{12}O_6 + 6\,O_2}_{\dot{S}_{out}}$$

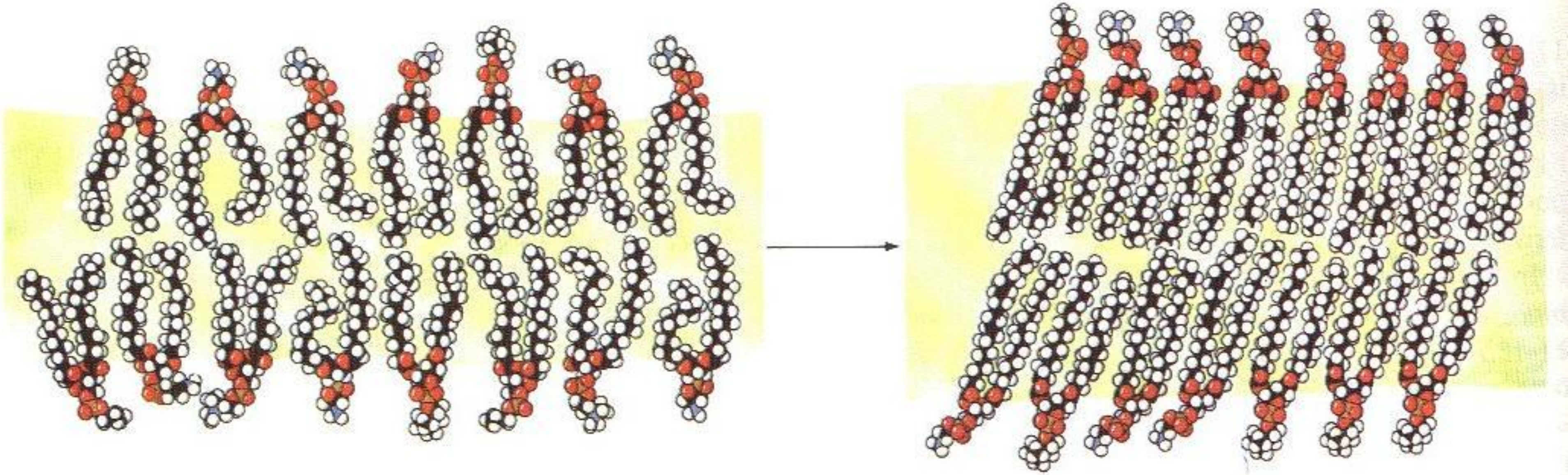
$$\dot{S}_{in} = \dot{S}_{out} + 0.24 \frac{kJ}{mol\,K} \cdot \dot{n}_{GL}$$

2nd Law: $\dot{S}_{in} \leq \dot{S}_{out}$?

$$\left\| \begin{array}{l} 6\,CO_2 + 6\,H_2O \rightarrow C_6H_{12}O_6 + 6\,O_2 \\ + 2.2\; H_2O\;_{L} \rightarrow 2.2\; H_2O\;_{V} \end{array} \right\|$$

2. Lipid Membranes, Phase Transition Fluid - Gel

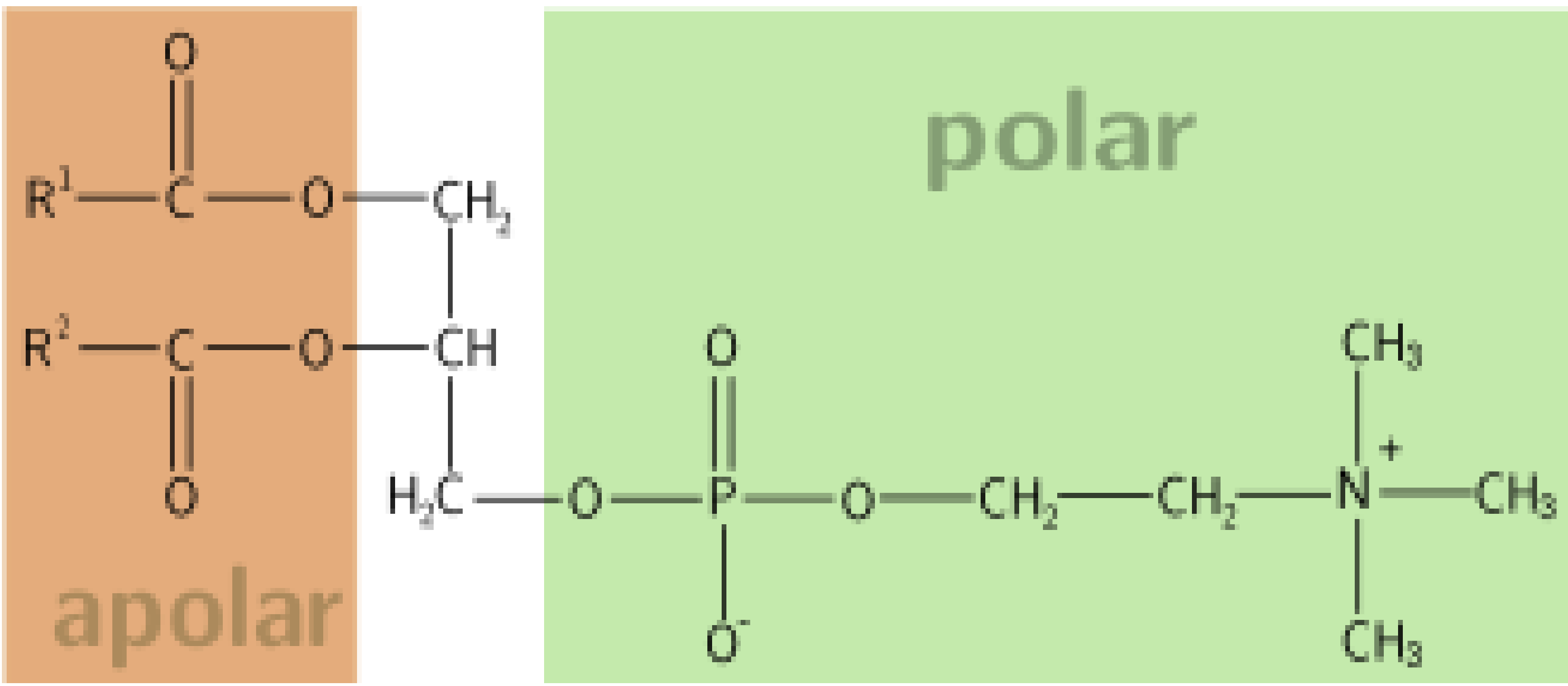
$T > T_t(p, ...)$ $T < T_t(p, ...)$



Lipid by-layer formed of phosphatidylcholine (Voet & Voet, p. 288)

DMPC – Strukture: Phosphatidylcholine / Lecithine

Fatty acids

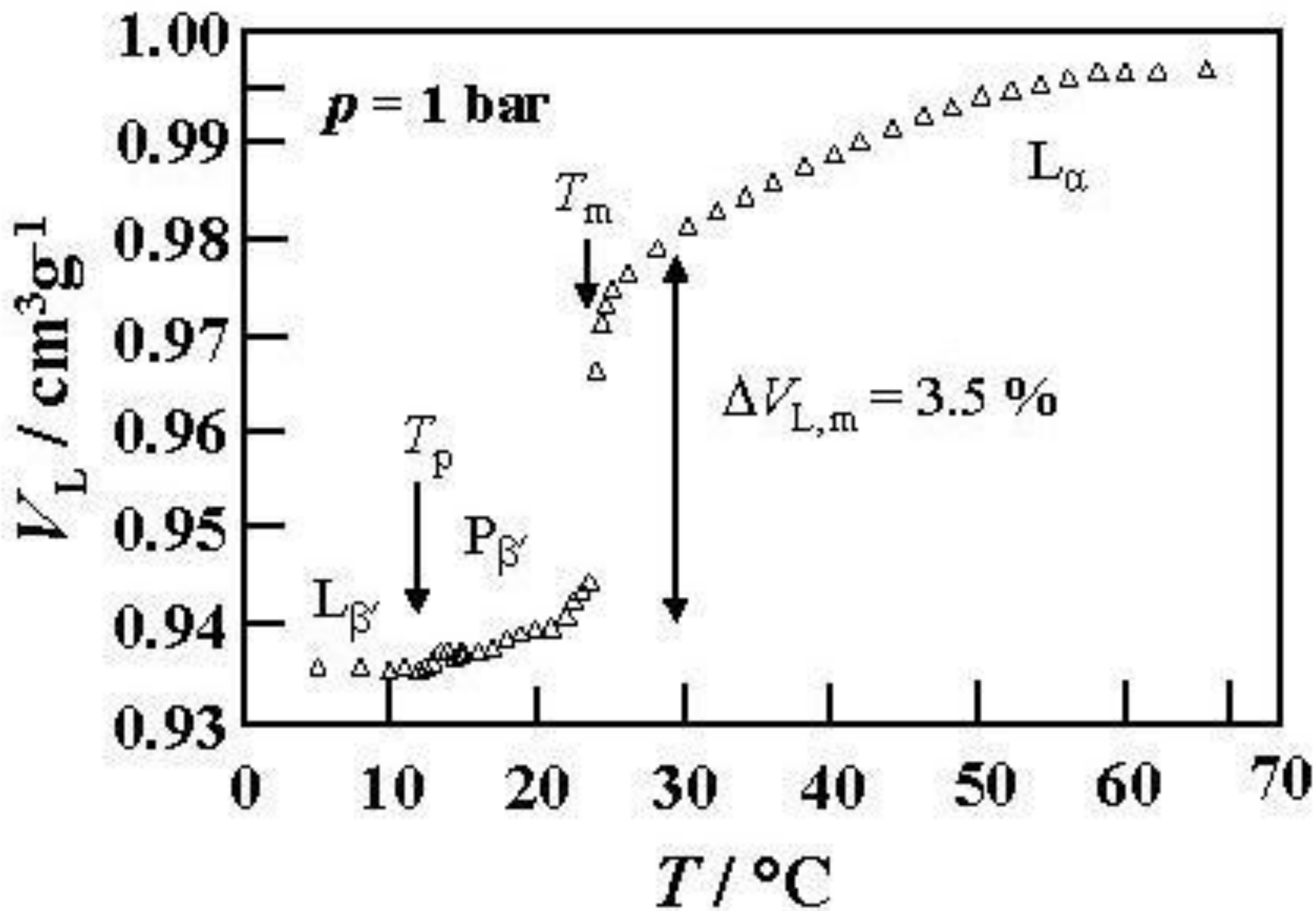


Glycerine CH2 – CH – CH2

/ / /

OH OH OH

Choline



Temperature and pressure dependence of the specific volume of DMPC*) in water.
(R. Winter, JNE 6-22, 2007) *)1,2-dimyristoyl-s,n-glycero-3-phosphatidylcholine

DMPC Thermal Equation of State (EOS)

Aliphatic tails of DMPC-molecules may aggregate/adsorb on each other.

Degree of aggregation:

$$\alpha(v) := \frac{v_{.0} - v}{v_{.0} - b_{.0}} \qquad 0 < \alpha(v) < 1$$

Fluid state   Gel state

Free volume

$$\beta(v) := \frac{v - b_{.0}}{v_{.0} - b_{.0}}$$

Fractality

EOS:

$$p(\alpha, T) := A(T)\cdot\alpha + B(T)\cdot\alpha^2 + D(T)\cdot\alpha^3 + C(T)\cdot\frac{\alpha^\gamma}{1-\alpha^\gamma} \qquad \gamma := 1$$

Virial expansion ...   **Adsorption term**

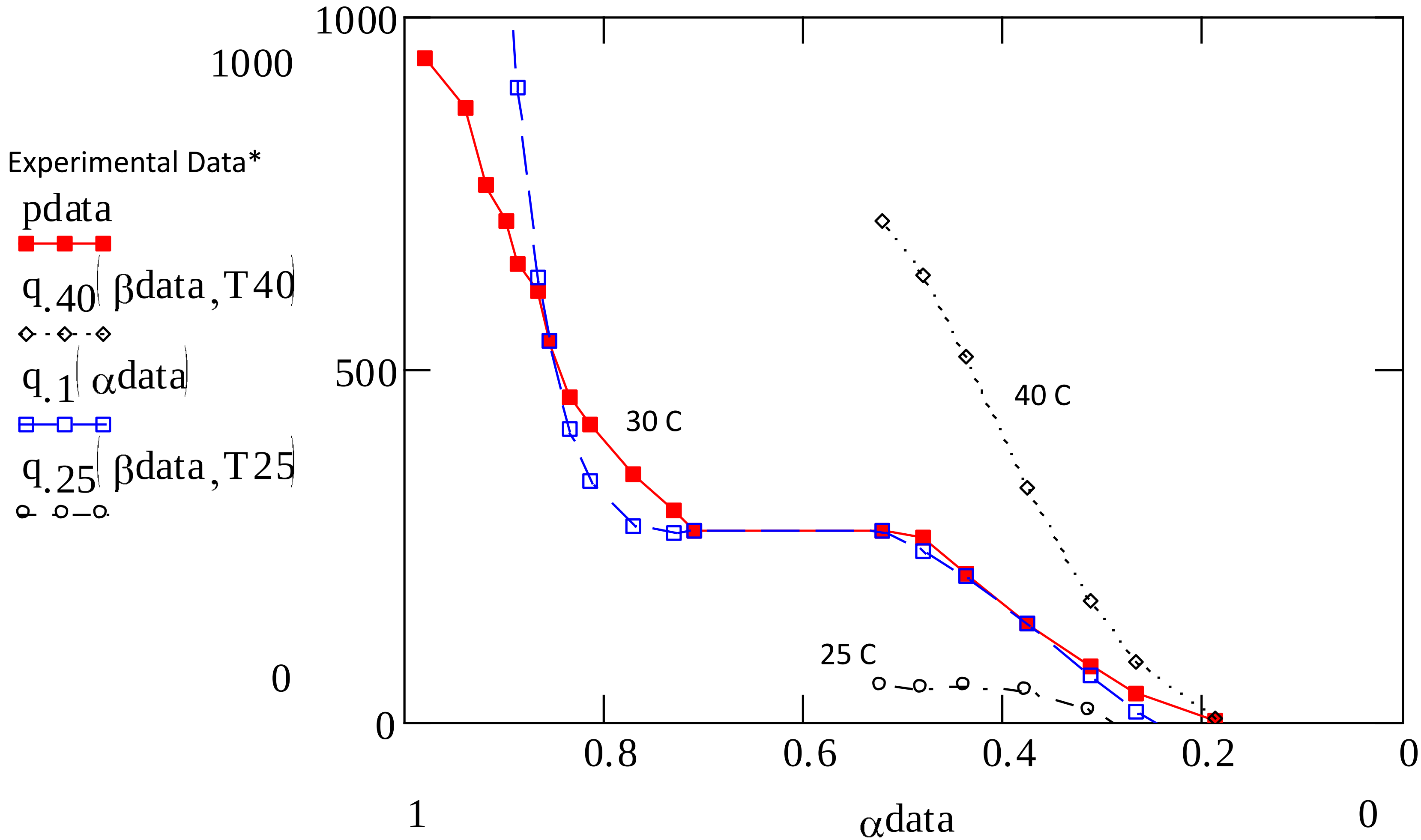
$$A(T) := A_{.0}\cdot\left[1 + a\cdot\left(T - T_{.0}\right)\right]$$

....

$$D(T) := D_{.0}\cdot\left[1 + d\cdot\left(T - T_{.0}\right)\right]$$

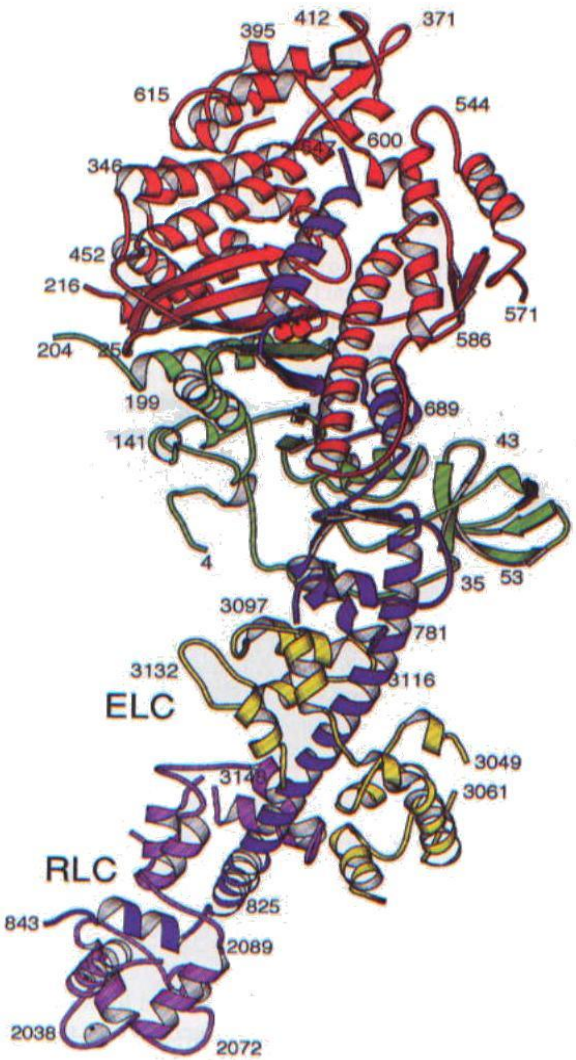
A= -1873 bar	a=-0.54
B=7942	b=-0.051
D=-8997	d=-0.429
C=333.34	c=-2.534

DMPC Thermal Equation of State (EOS)
Correlation of Isothermal Data



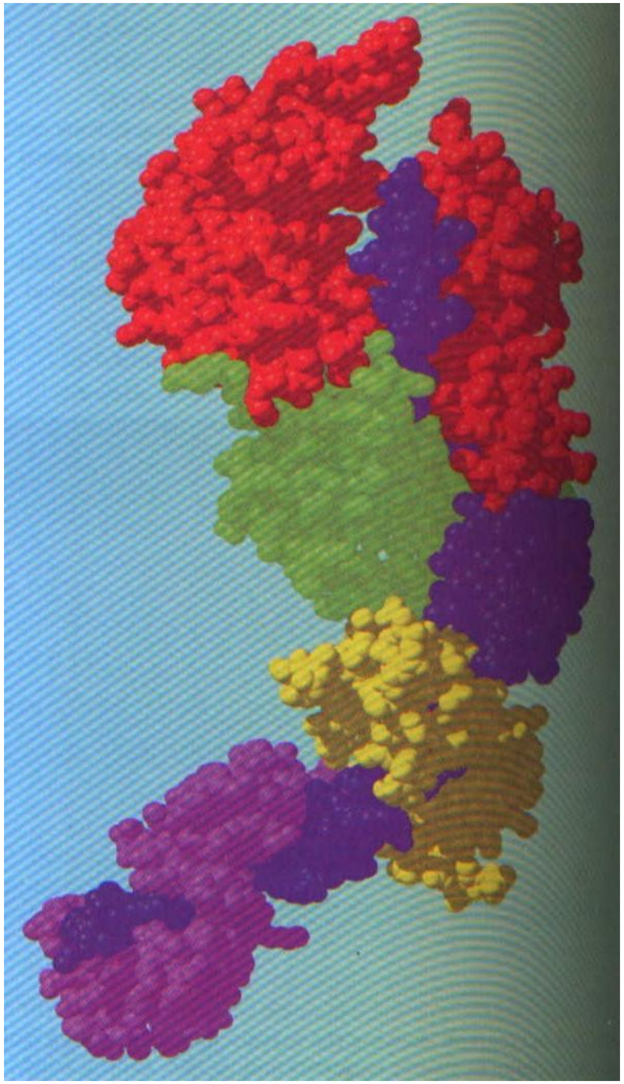
* R. Winter et al.,JNE 32(2007),p.41

3. Proteins (Example): Myosin from Chicken Muscle



Secondary Structure

Voet&Voet
Biochemistry
Wiley,N.Y.
1995

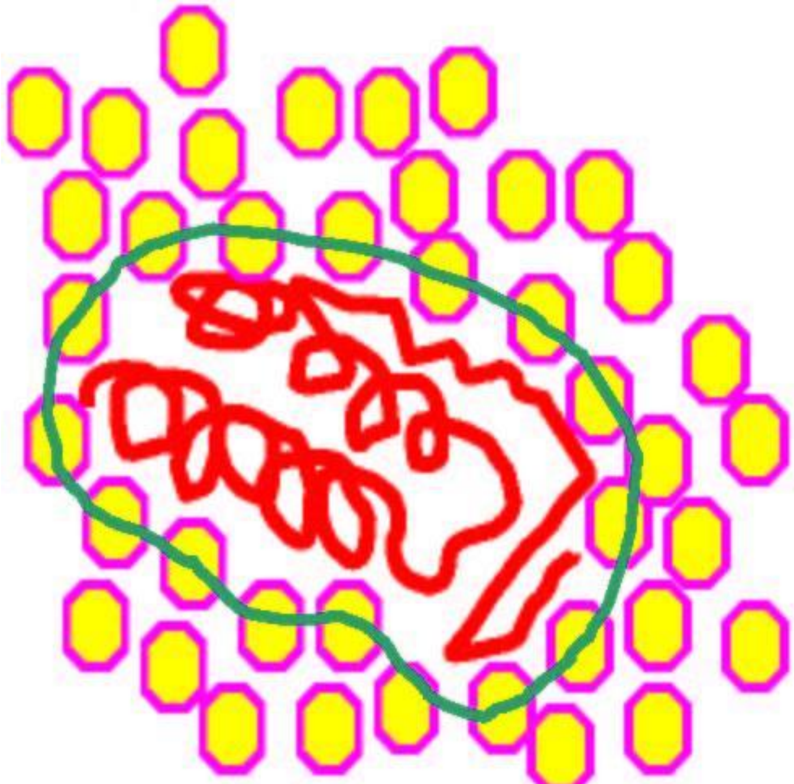


Tertiary Structure (X-Ray)

Protein(P) - Water(W) Interactions (E4)

P: Conformational Changes, Unfolding

W: Adsorption, Intrusion, Coating of (P) > Stabilization



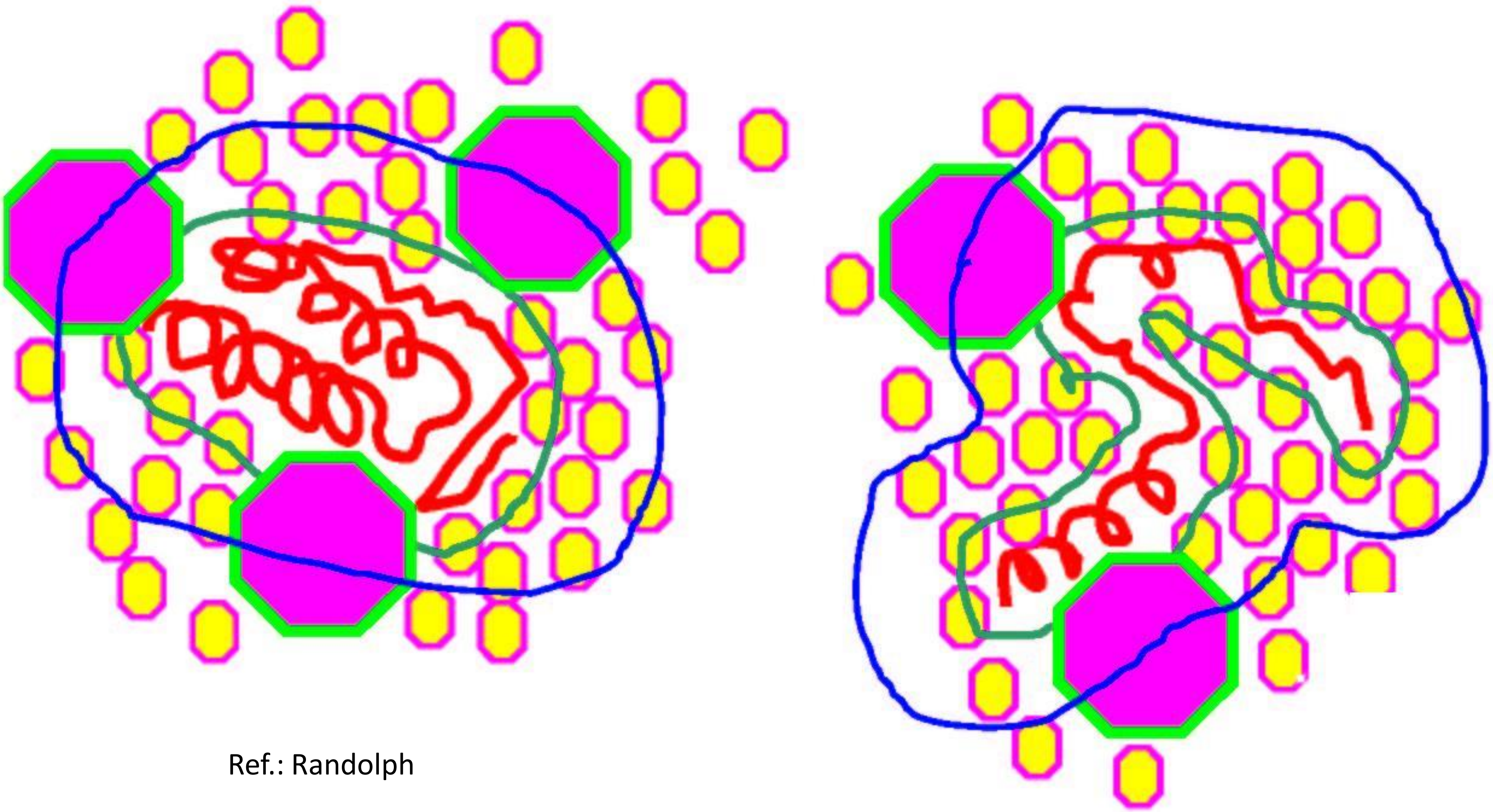
Ref.:Randolph

Native State (N):
compact, surface area small

Unfolded State (D):
expanded, surface area high

Protein(P) - Water(W) – Sugar(S) Interactions

S: Adsorption, Desorption upon unfolding of protein.



Ref.: Randolph

S-W: Coadsorption on surface may stabilize (P).

Thermal Denaturation of Myoglobin

Experimental Data

153 Amino acids

Seize: (44x44x25)Å^3

Molecular Weight $\approx$ 18kD

N ... Native (folded) State

D ... Denaturated (unfolded) State

Equilibrium at T=const, p=const

$$\Delta G_{DN}(p,T) = -RT\ln\left(\frac{\gamma_D x_D}{\gamma_N x_N}\right)$$

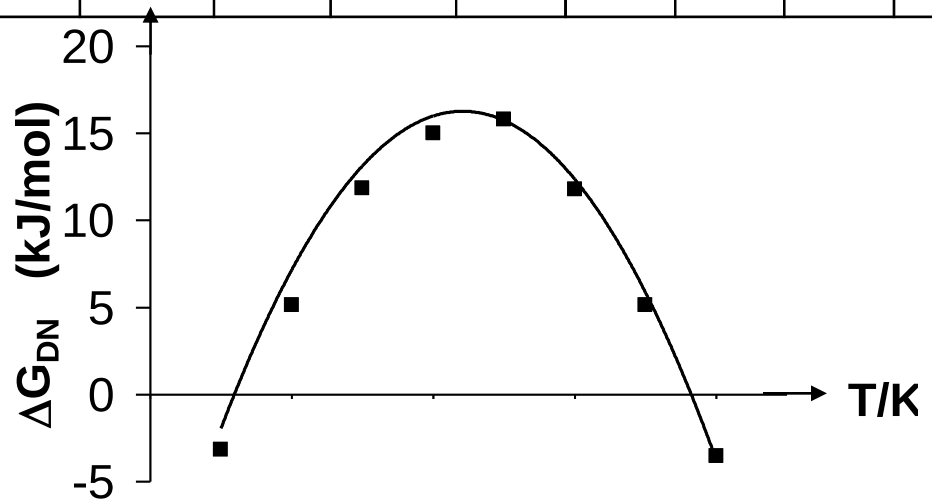
$$\Delta G_{DN} = \mu_{D0} - \mu_{N0}$$

Approx.: $\gamma_D = \gamma_N = 1$

$\Delta G_{DN} > 0 \rightarrow x_D \ll x_N$...N...stable

$\Delta G_{DN} < 0 \rightarrow x_D \gg x_N$...N...unstable

T/K	270	280	290	300	310	320	330	340
ΔG_{DN} (kJ/mol)	-3.16	5.13	11.8	15	15.8	11.8	5.13	-3.53
ΔH_{DN} (kJ/mol)	-289.	-204	-115	-23	72.2	170	272	376
ΔS_{DN} (kJ/mol K)	-1.06	-0.75	-0.44	-0.13	0.18	0.49	0.81	1.12



(U.von Stockar,EPFL,et al., MV Seminar,2000)

4. Kleiber's Law of Metabolism in Aerobic Living Systems

Allometry

Metabolic Rate

$$\Gamma = a\ (T, T_0)\ M^{\gamma}$$

$$a \cong (1-2) mW/g$$

$$\frac{2}{3} < \gamma \leq 1$$

$$\gamma \cong \frac{3}{4}$$

B. Ahlborn, Zoological Physics

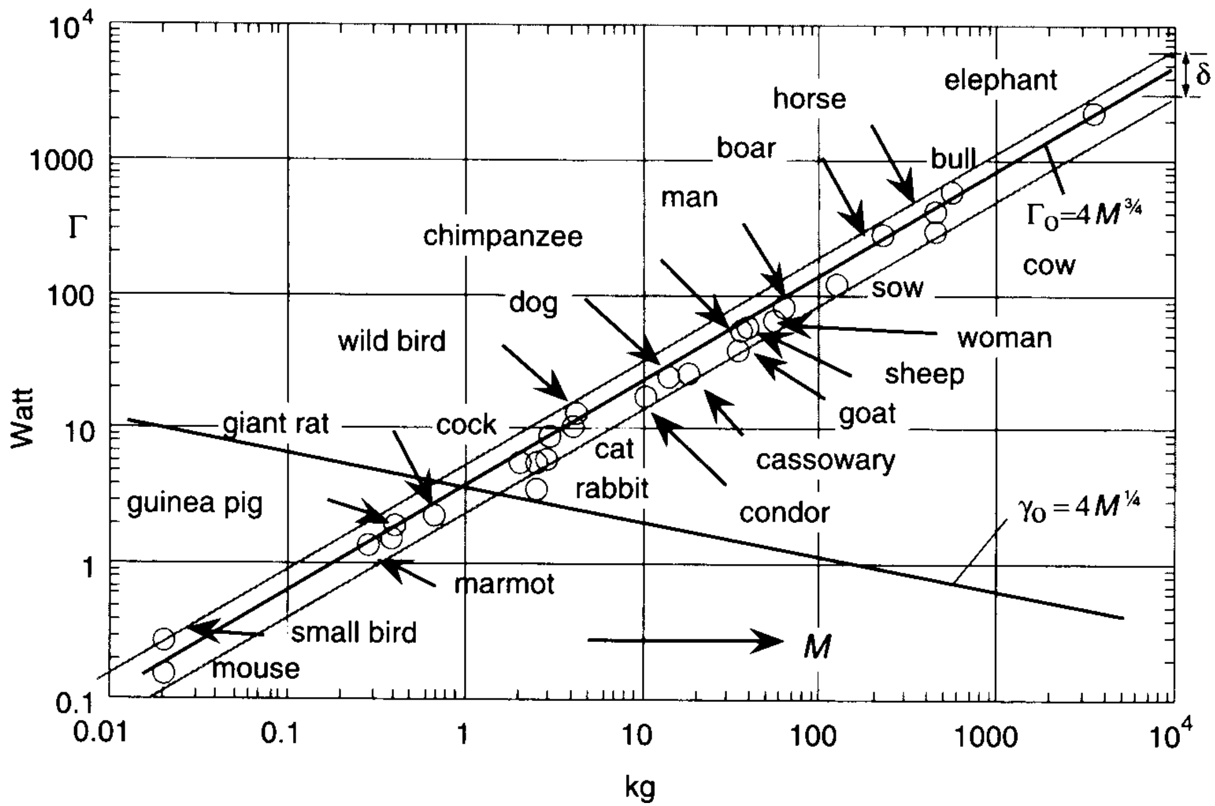


Figure A3
Metabolic rate of oxygen consumption based living systems. Mouse-Elephant-curve, B. Ahlborn, 2004. This curve also holds for bacteria (M $\cong 10^{-4}$ g).

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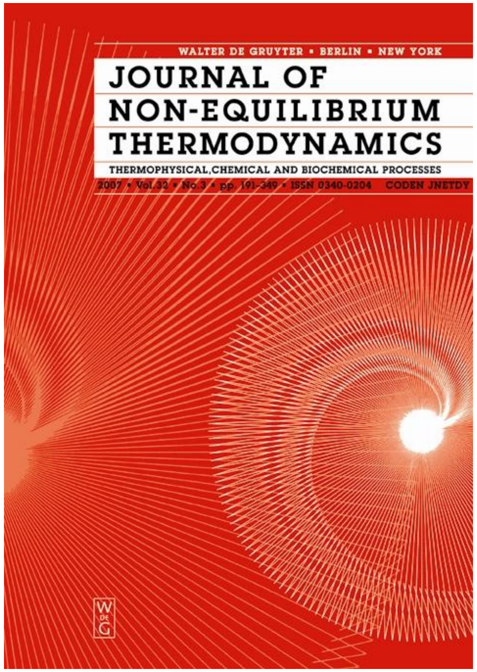


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Keep it smart and simple.
MORENE
More research needed.
Ötztaler Alpen, 5-9-2007
Similaunhütte, 3012m, (T= -10C / -30C)