A New Group Contribution Method For The Estimation Of The Surface Tension Of Non-Electrolyte Organic Compounds

Eugene Olivier

SO ‘N BIETJIE OMTRENT MYSELF
(A BIT ABOUT ME)

My first Language is Afrikaans
I live in Durban, South Africa
I studied Chemical Engineering at UKZN
and completed my degree last year

CONTENTS

IMPORTANCE OF PHYSICAL PROPERTIES

-Required for design and simulation of plant.

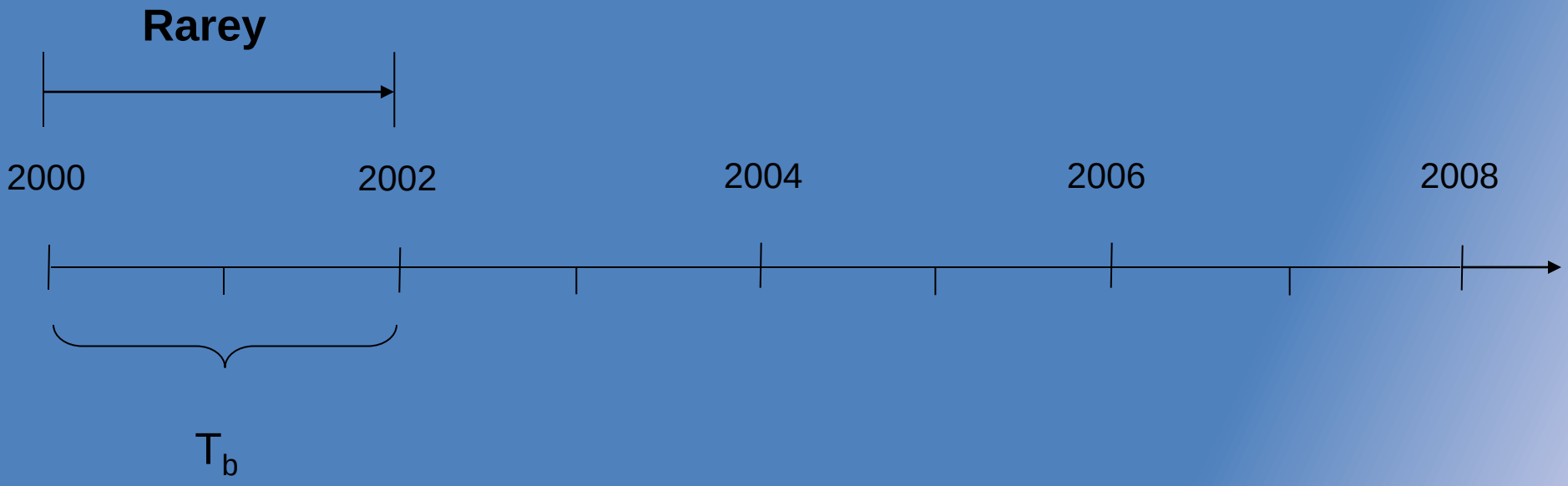
-Personal Experience:

Final year design project

Biodiesel Plant

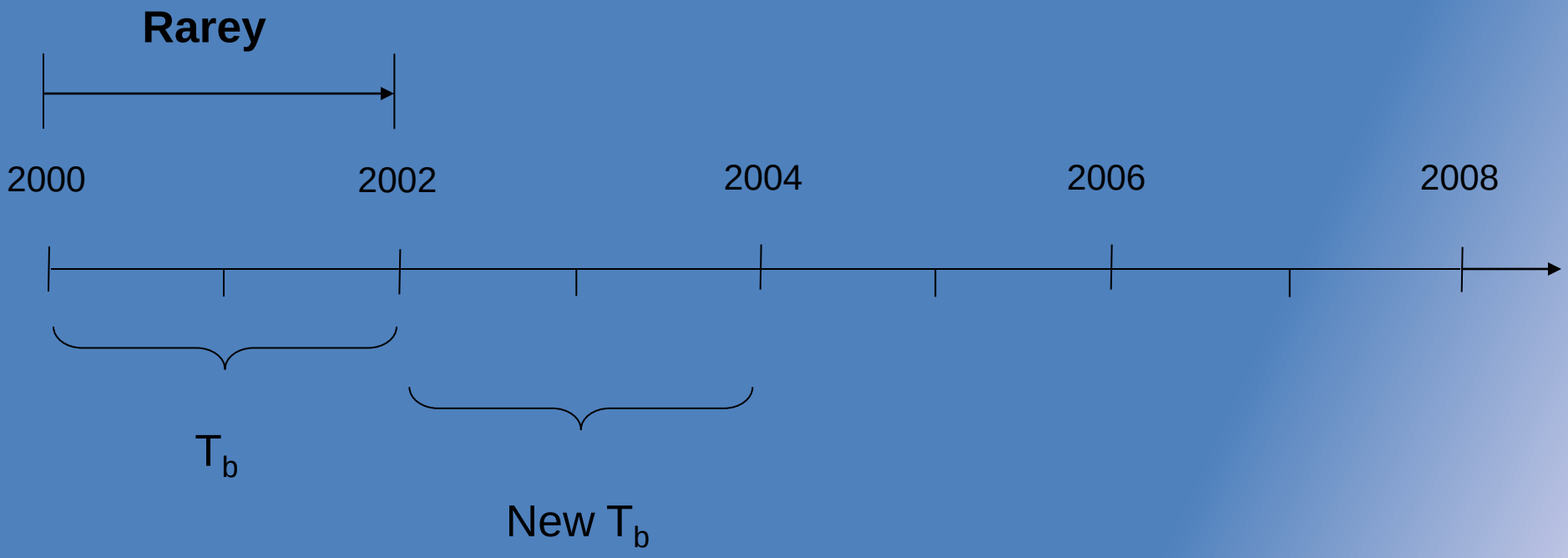
Missing Properties

PROJECT TIMELINE



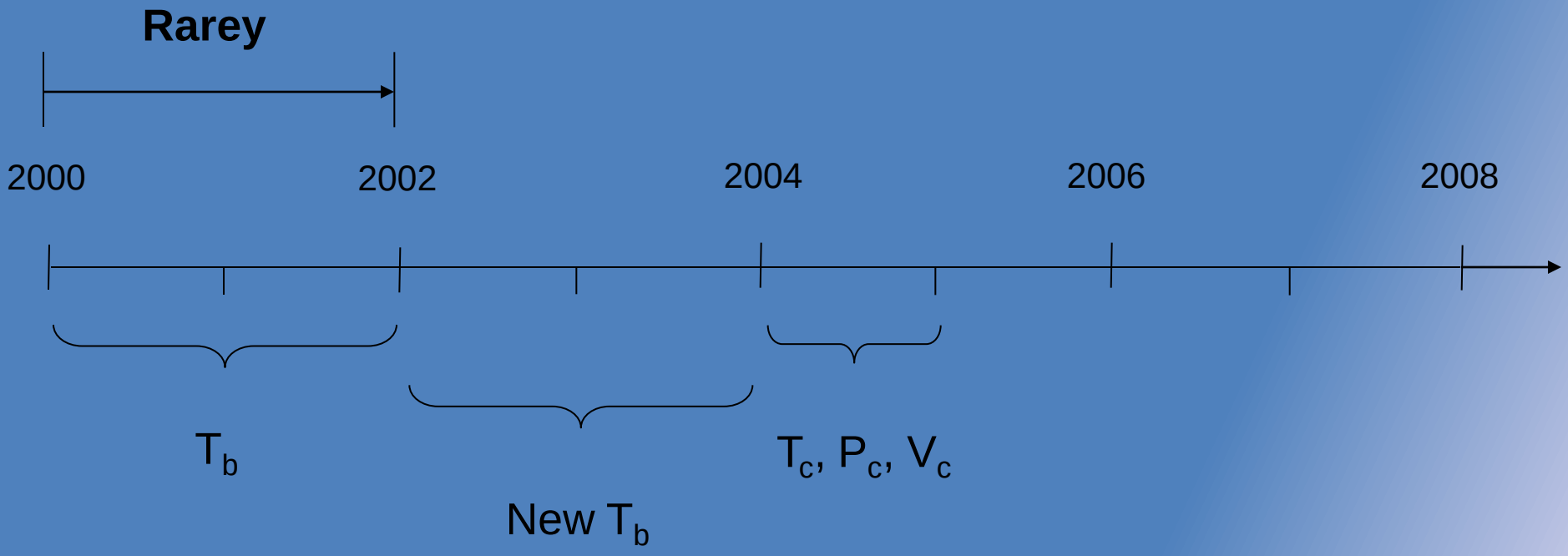
W. Cordes, J. Rarey, *A New Method for the Estimation of the **Normal Boiling Point** of Non-Electrolyte Organic Compounds*, Fluid Phase Equilibria, 201/2, 397-421 (2002).

PROJECT TIMELINE



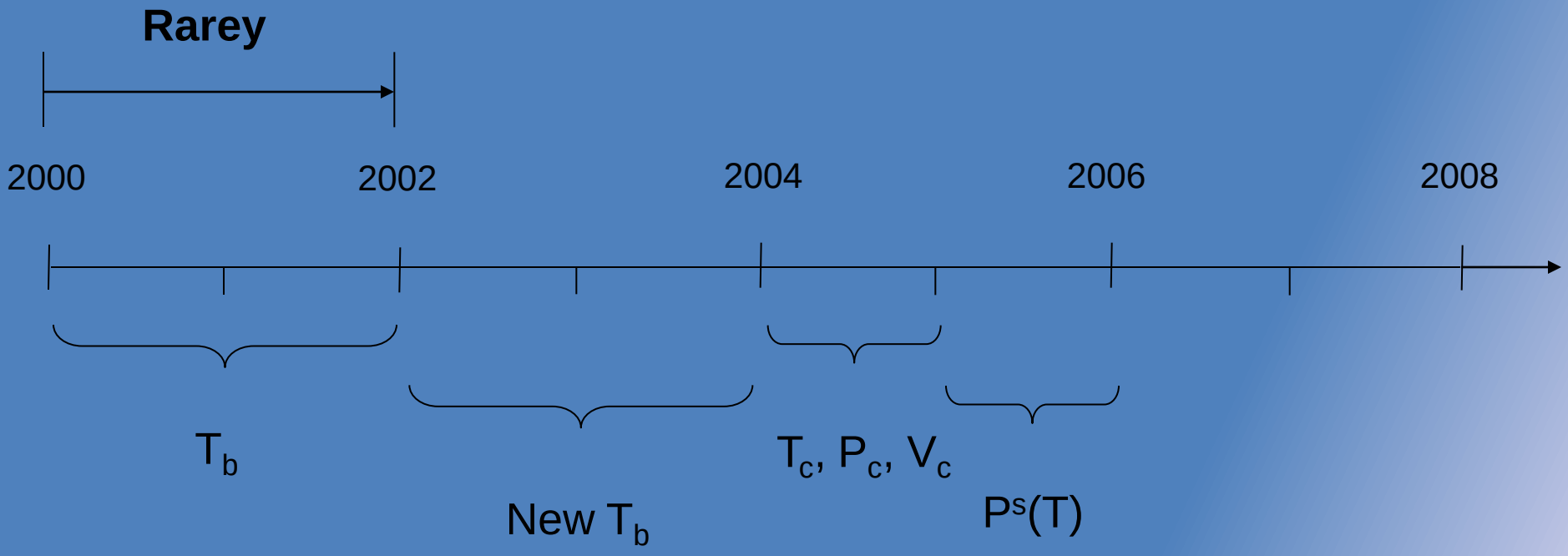
Y. Nannoolal, J. Rarey , D. Ramjugernath, W. Cordes, *Estimation of Pure Component Properties, Part 1: Estimation of the* ***Normal Boiling Point*** *of Non-Electrolyte Organic Compounds via Group Contributions and Group Interactions*, Fluid Phase Equilibria, 226, 45-63, 2005.

PROJECT TIMELINE



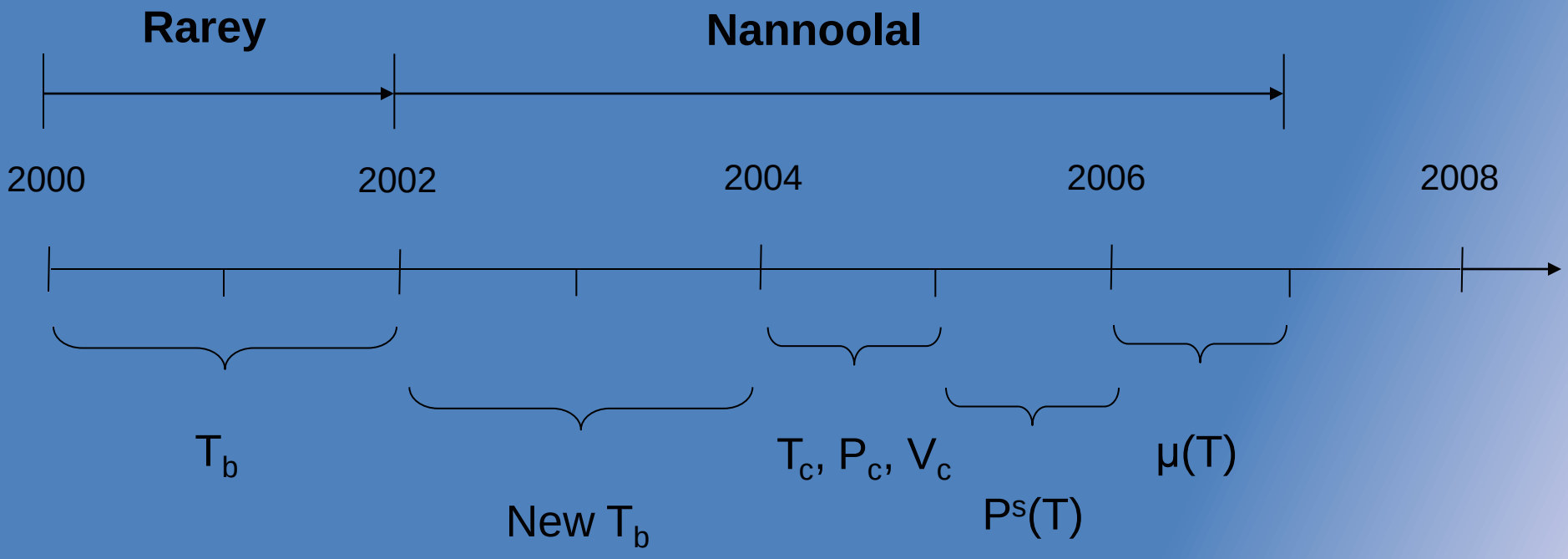
Nannoolal, Y., Rarey, J., Ramjugernath, D., Estimation of Pure Component Properties Part 2: Estimation of **Critical Data** by Group Contribution., *Fluid Phase Equilib.*, 252 (2007) 1.

PROJECT TIMELINE



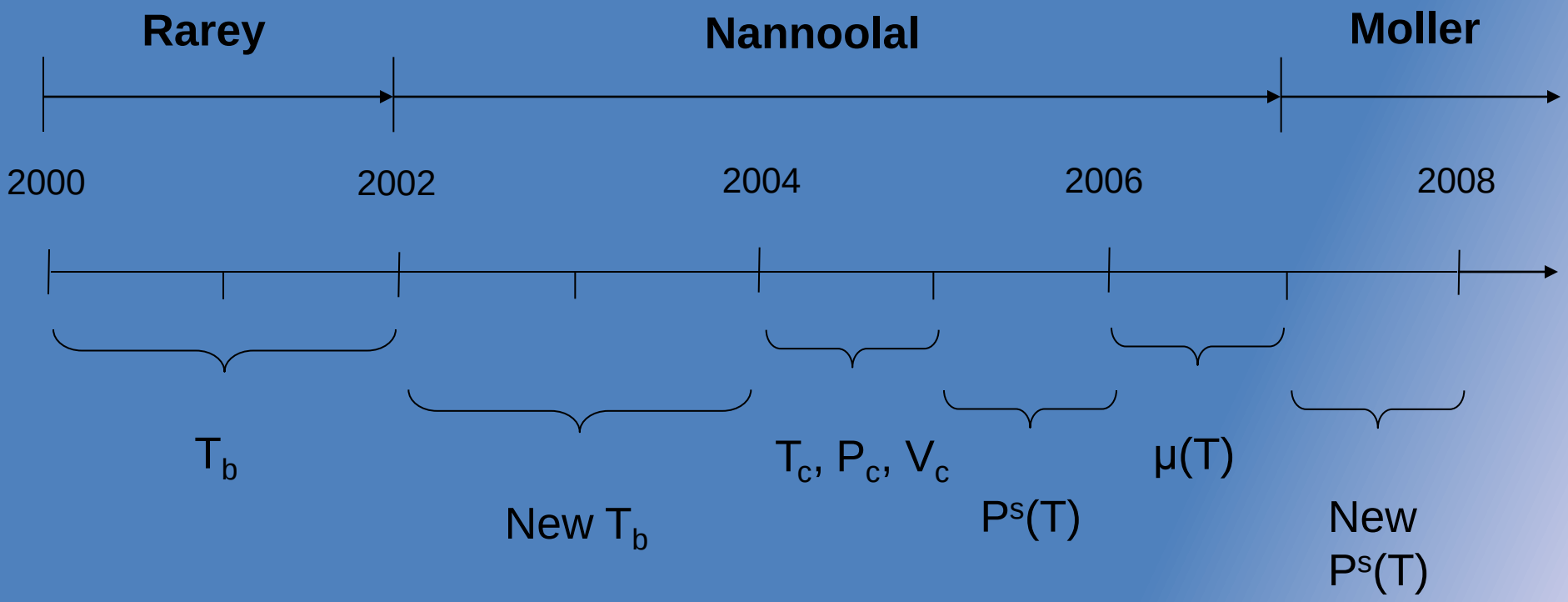
Nannoolal, Y., Rarey, J., Ramjugernath, D., Estimation of Pure Component Properties Part 3: Estimation of the **Vapour Pressure** of Non-Electrolyte Organic Compounds via Group Contributions and Group Interactions., *Fluid Phase Equilib.* , 269 (2008) 117.

PROJECT TIMELINE



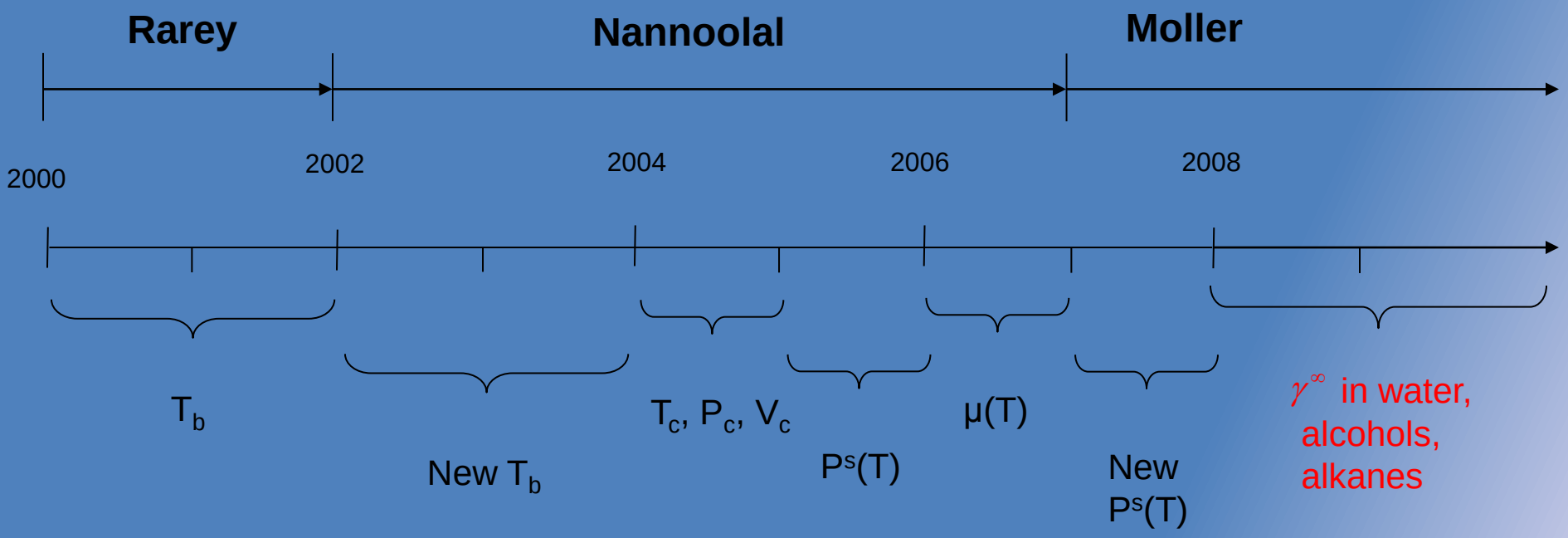
Nannoolal, Y., Rarey, J., Ramjugernath, D., Estimation of Pure Component Properties Part 4: Estimation of the **Liquid Viscosity** of Non-Electrolyte Organic Compounds via Group Contributions and Group Interactions., *Fluid Phase Equilib*. , 281 (2009) 97.

PROJECT TIMELINE



Moller, B., Rarey, J., Ramjugernath, D., Estimation of the **Vapour Pressure** of Non-Electrolyte Organic Compounds via Group Contributions and Group Interactions., *J. Mol. Liq.* , 143 (2008) 52.

PROJECT TIMELINE



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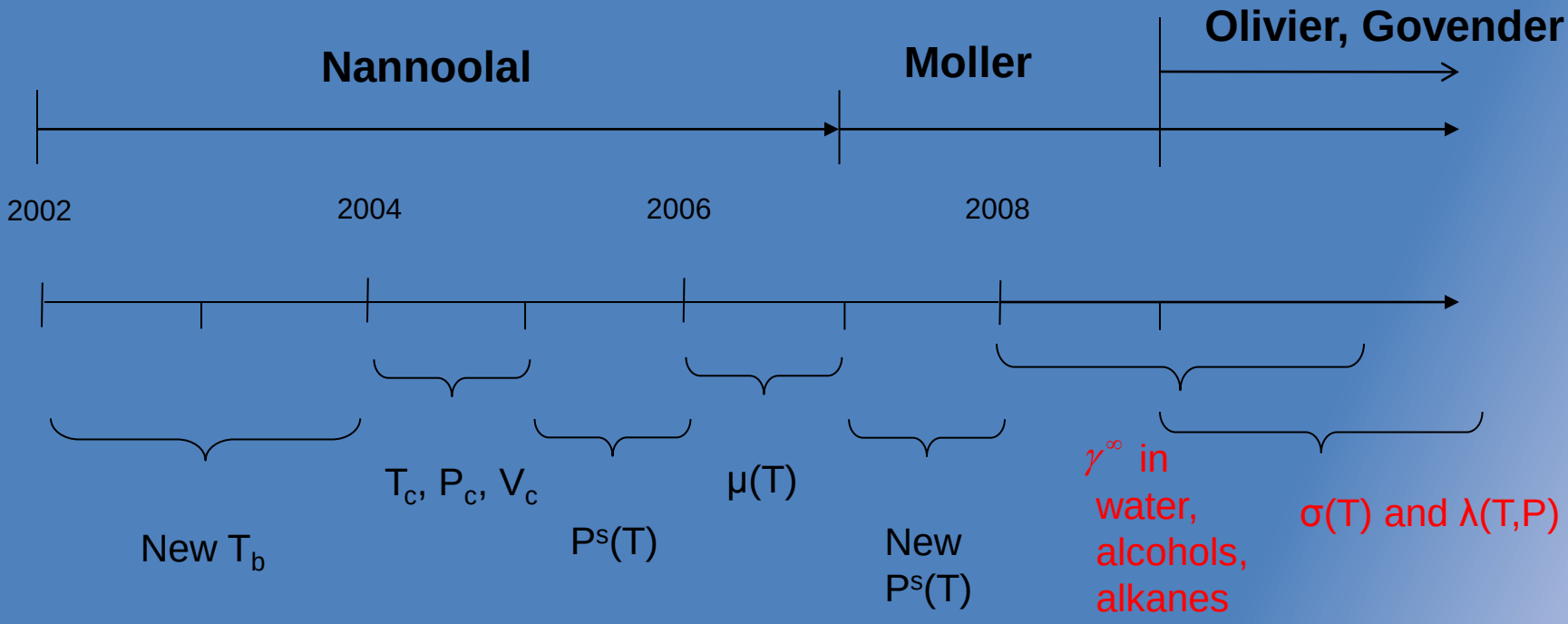
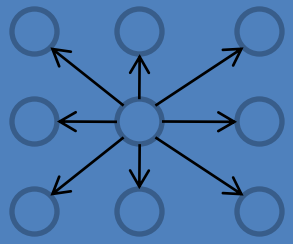
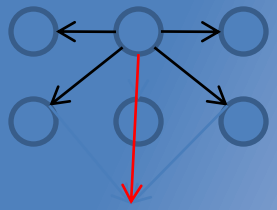


SURFACE TENSION

$$\sigma = \left(\frac{\partial G}{\partial A} \right)_{T,P,n} \qquad \mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j}$$

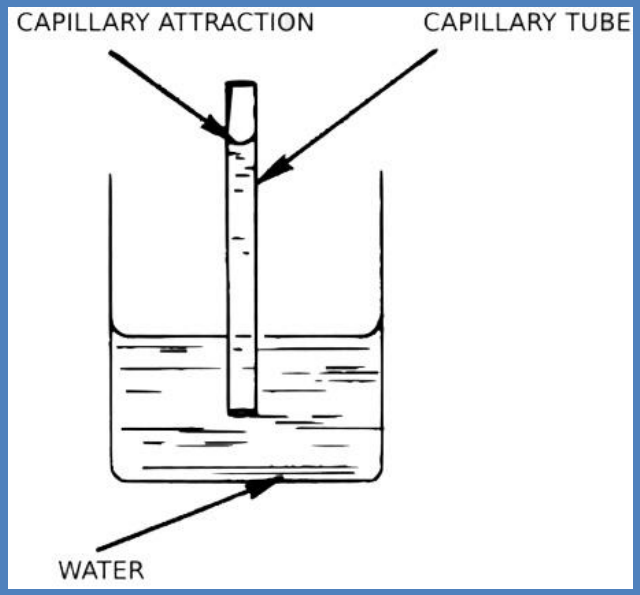


Bulk Liquid



Vapour-Liquid Interface

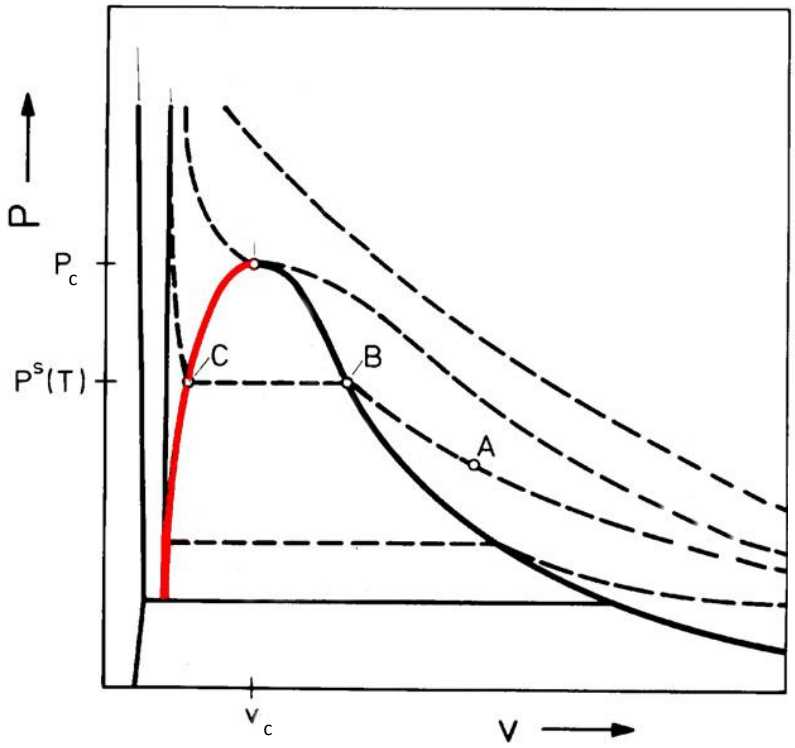
SURFACE TENSION



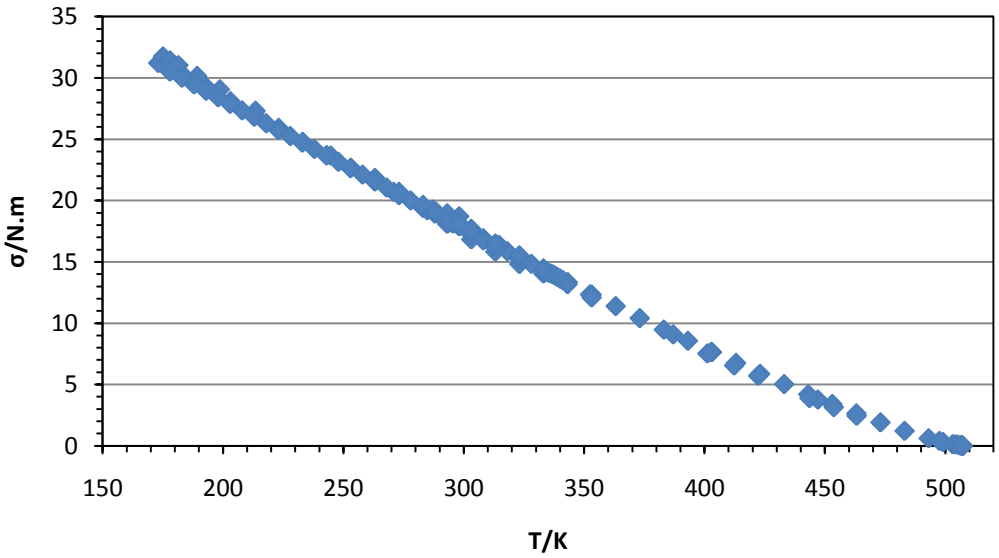
SURFACE TENSION

- Distillation
- Liquid-Liquid Extraction
- Absorption
- Adsorption
- Gas-Liquid Reactors

SURFACE TENSION



Highest value at the Triple point
Zero at the Critical Temperature



OVERVIEW OF CURRENT METHODS

- Empirical Equations
- Group Contribution
- Corresponding-States (1955-1997)
- EOS
- QSPR

EMPIRICAL EQUATIONS

- Exponential equation (Guggenheim) - $\sigma=f(T)$
- Macleod's equation - $\sigma=f(\rho_l, \rho_v)$ – Can be used with the Parachor
- Schonhorn equation - $\sigma=f(\mu_l, \mu_v)$
- Faizullin equation - $\sigma=f(\Delta H_{vap}, v_l)$

GROUP CONTRIBUTION

- Sheldon et al. (30.1 % error 66% of data)
- Conte et al.
- CSGC (Corresponding States Group Contribution)

PROS AND CONS

- Only requires molecular structure
- Only predicts surface tension at one temperature.

CORRESPONDING STATES

- Brock and Bird (12.2% error, 85% of data) -1955
- Zuo and Stenby
- Sastri and Rao
- Hakim et al.
- Pitzer

PROS AND CONS

- Good for simple compounds
- Not good for large compounds
- Not good for alcohols and acids
- Inputs may not be widely available

PROPOSED MODEL

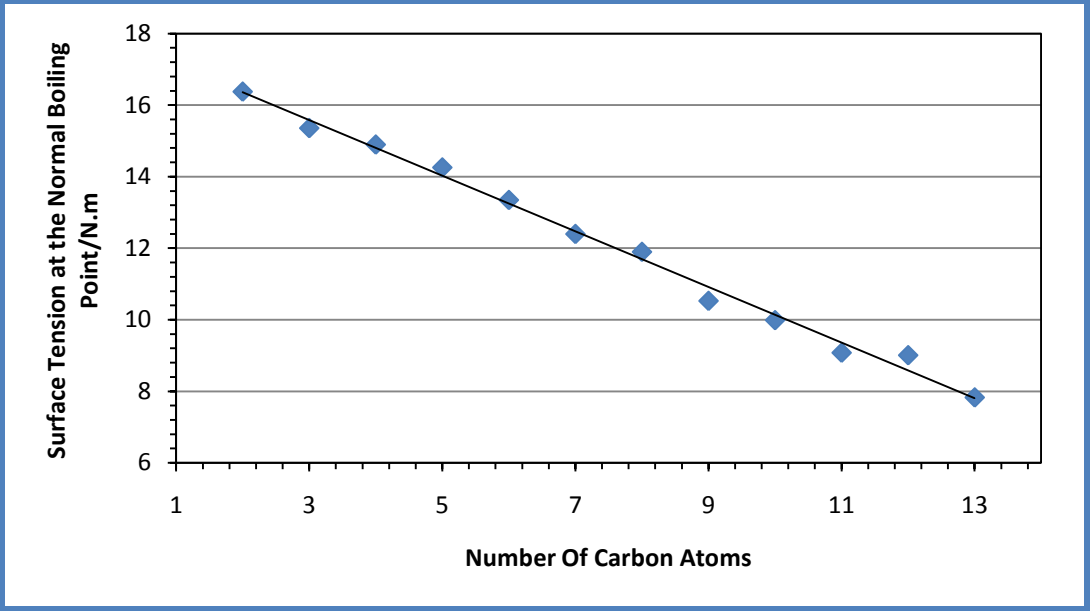
$$\sigma = \sigma_{non-polar} + \sigma_{polar}$$

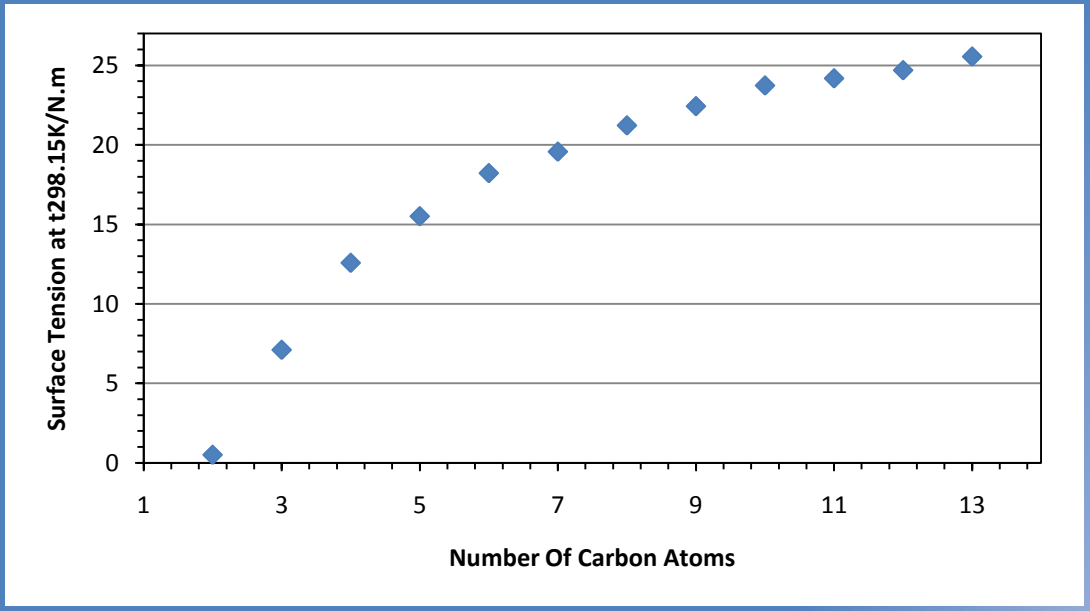
$$\sigma_{non-polar} = (a + b(1 - T / T_b))^{11/9}$$

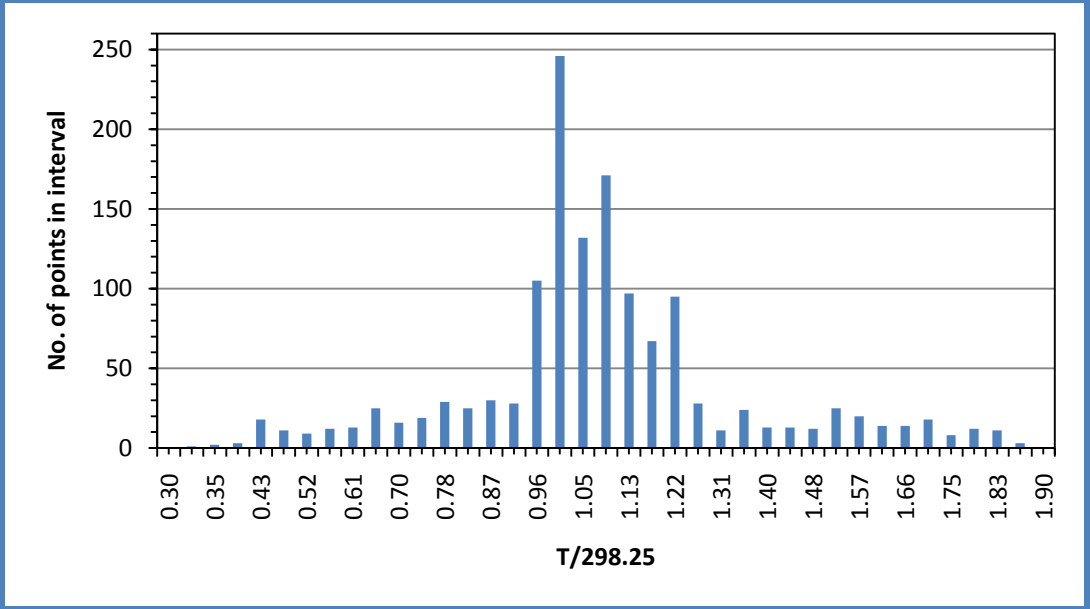
Tb chosen as reference temperature:
-Easier to model.
-Wider data range for parameter fitting.

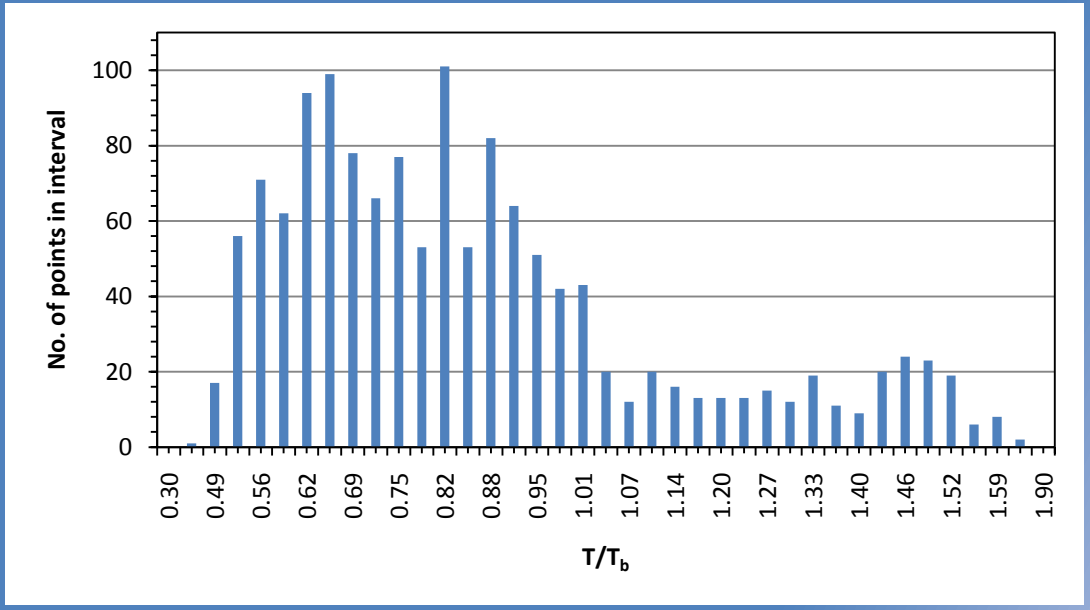
$$a = a_0 + \sum_i^m \nu_i a_i$$

$$b = b_0 + \sum_i^m \nu_i b_i$$

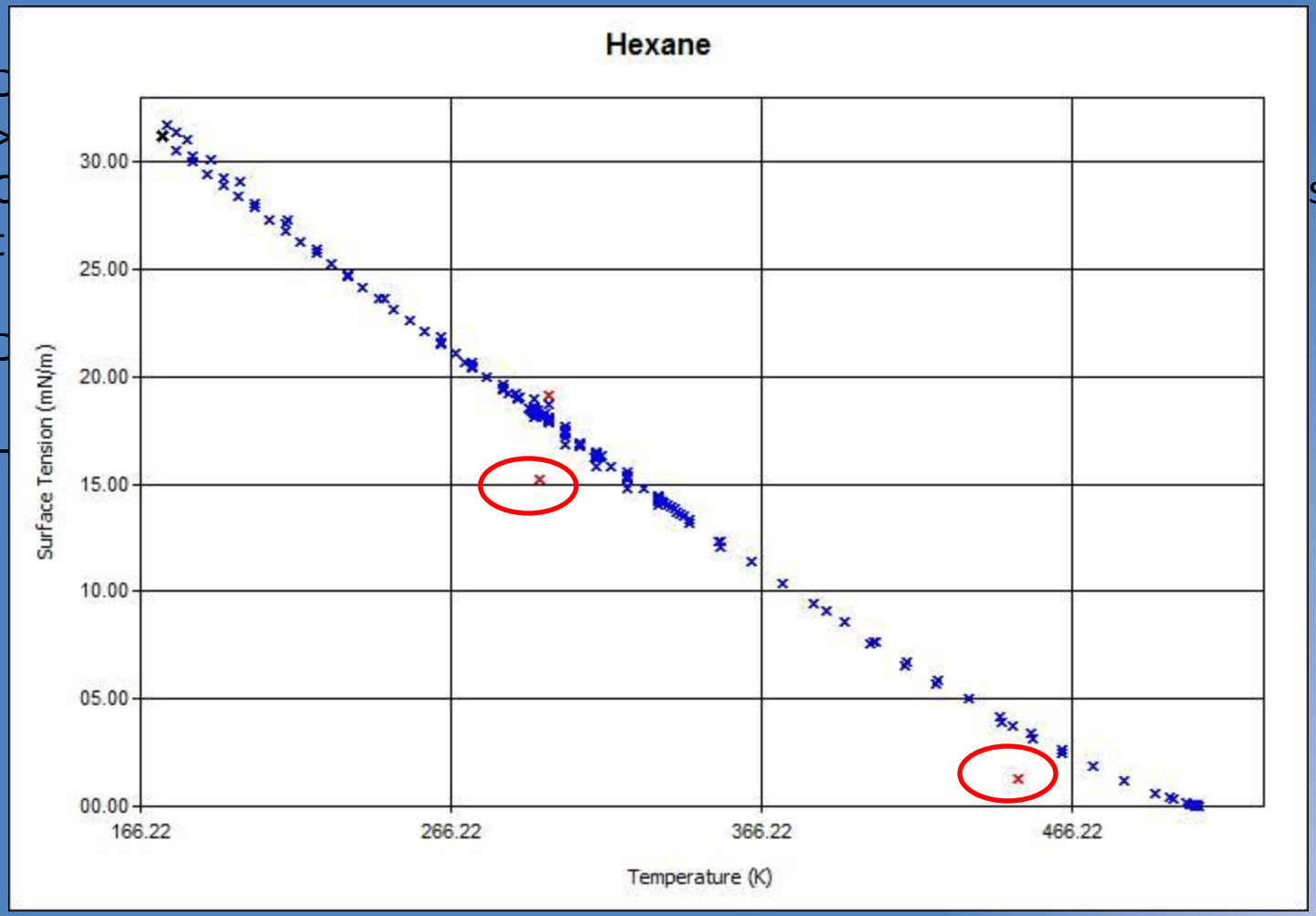

Surface Tension at the Normal Boiling Point/N.m
18
16
14
12
10
8
6
1
3
5
7
9
11
13
Number Of Carbon Atoms


Surface Tension at t298.15K/N.m
25
20
15
10
5
0
1
3
5
7
9
11
13
Number Of Carbon Atoms

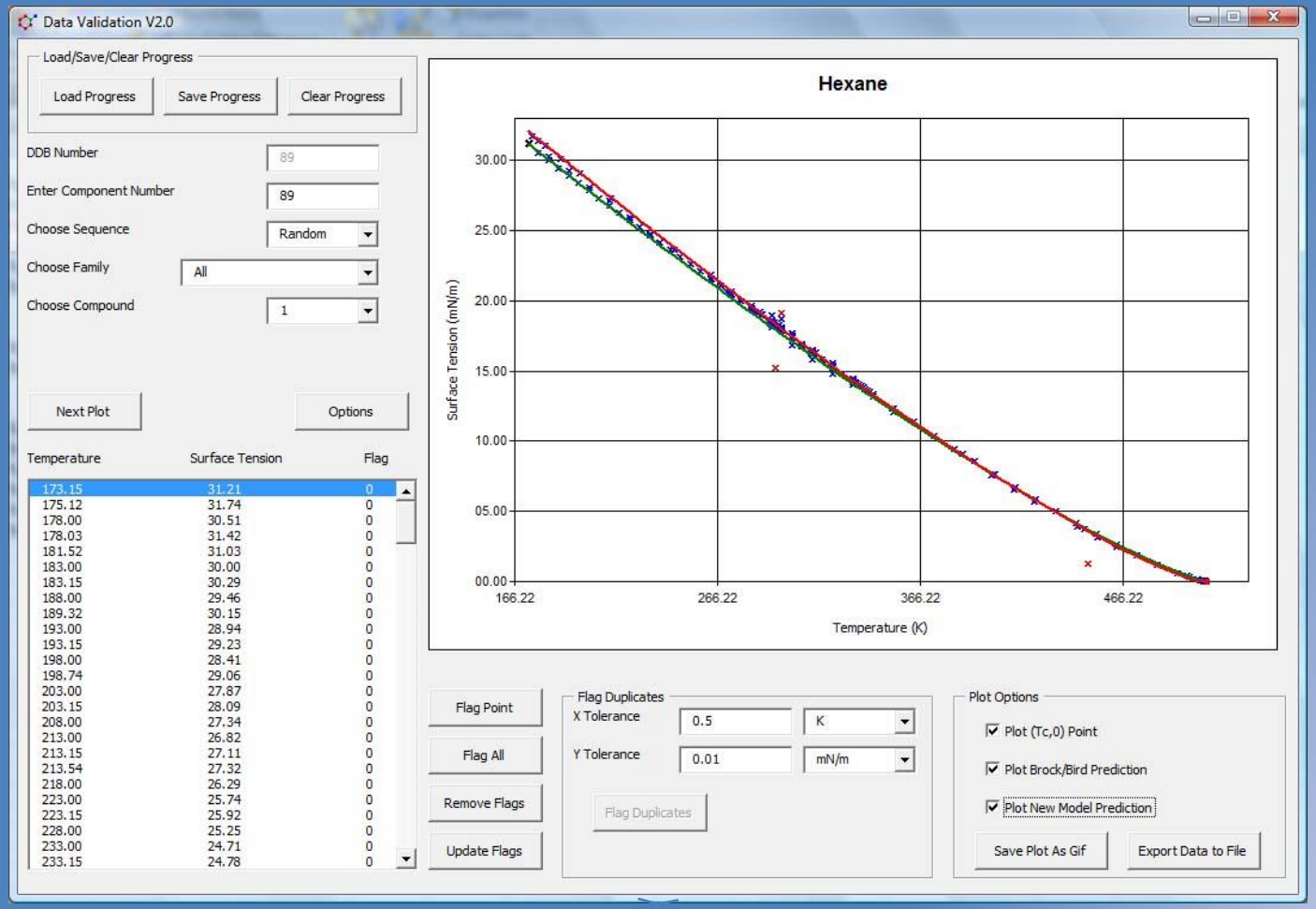

No. of points in interval
250
200
150
100
50
0
0.30
0.35
0.43
0.52
0.61
0.70
0.78
0.87
0.96
1.05
1.13
1.22
1.31
1.40
1.48
1.57
1.66
1.75
1.83
1.90
T/298.25


No. of points in interval
100
80
60
40
20
0
0.30
0.49
0.56
0.62
0.69
0.75
0.82
0.88
0.95
1.01
1.07
1.14
1.20
1.27
1.33
1.40
1.46
1.52
1.59
1.90
T/T$_b$

DATA


Hexane
Surface Tension (mN/m)
30.00
25.00
20.00
15.00
10.00
05.00
00.00
166.22
266.22
366.22
466.22
Temperature (K)

SOFTWARE



Database

SQL, DAO

Artist

FUTURE WORK

- Determine expression for non-polar part of the equation
- Regress group parameters
- Regress interaction parameters
- Assess performance using a test set.

OVERVIEW

Importance of Physical Properties

Project Timeline

Surface Tension

Current Calculation Methods

Software

Future work

ACKNOWLEDGEMENTS

Prof. Dr. J. Rarey

Prof. Dr. D. Ramjugernath

Mr. B. Moller

Mr. O. Govender

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Thank You For Listening.