Scattering on Liquid-Liquid Interfaces

Int. Workshop, June 22-24 2007
Conference Center Klinten, Rodvig, Denmark

An international workshop on the topic of scattering from liquid-liquid interfaces by x-rays and neutrons will be organized from June 22-24 2007 at the Conference Center Klinten near Rodvig Denmark. The workshop aims to discuss among leading scientists in the field the opportunities and needs to study liquid-liquid interfaces with neutrons. An overview of the current work on liquid-liquid interfaces will be given, current instrument options and future developments will be outlined and a plan for co-operation in the future use of neutrons to investigate liquid-liquid interfaces will be developed.

Invited speakers:

John Ankner	SNS, Oak Ridge, USA
Jean Daillant	CEA, Saclay, France
Giovanna Fragneto	ILL, France
Alain Gibaud	Universite du Maine, Le Mans, France
Oleg Konovalov	ESRF, Grenoble, France
Mark Schlossman	University of Illinois at Chicago, USA
Robert Thomas	University of Oxford, UK
Metin Tolan	University of Dortmund, Germany
John Webster	ISIS, Chilton, UK
Ali Zharbaksh	Queen Mary, University of London, UK

Deadlines:

Abstract submission:	April 20. 2007
Registration:	April 30. 2007

Venue: Conference Center Klinten, Rodvig, Denmark
Workshop fee: **350 EUR**

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Contacts: Thomas Gutberlet, PSI, thomas.gutberlet@psi.ch
Adrian Rennie, Uppsala University, Adrian.Rennie@fysik.uu.se

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Workshop on Scattering from Liquid-Liquid Interfaces

Title of workshop:	Scattering from Liquid-Liquid Interfaces
Starting date:	22/06/2007
Ending date:	24/06/2007
Location:	Conference Center Klinten
	Søndervej 8, 4673 Rødvig
	Phone: +45 5650 6800, fax: +45 5650 6473, e-mail: info@klinten.dk
Co-organizers:	T.Gutberlet (PSI), A. Rennie (Uppsala University)

Workshop program

June 22 2007

14:00 Welcome

14:10 Metin Tolan, University of Dortmund, Germany
Adsorption of thin liquid films on fluid and solid interfaces

X-ray reflectivity studies of thin liquid films adsorbed on liquid and solid substrates are presented. It will be shown to what extend microscopic information about the film structure and interaction potentials can be extracted which are not accessible with other methods. As model systems isobutane on glycerol and CO_2 on silicon habe been investigated. The measured surface roughness for isobutane films on glycerol is smaller than expected from the harmonic approximation of the interaction potential. Expressions for the surface roughness in slightly anharmonic potentials are given and compared with the data. Very good agreement between the modified theory and the x-ray data is achieved. In contrast to this system it is shown that adsorbed CO_2 films on silicon substrates may conain a structure which is almost solid like.

14:50 Jyotsana Lal, ANL
Dynamics at surfaces and interfaces in polymer bilayer films.

We report a further development of X-ray photon correlation spectroscopy (XPCS) in order to probe capillary wave dynamics at a buried polymer interface of a bilayer. The bi-layer was chosen so that the critical angle for total external reflection for the top layer is smaller than that for the bottom layer. When x-rays are incident below the critical angle of the top layer only the structure and dynamics of the top layer are probed. When x-rays are incident above the critical angle of the top layer but below that of the bottom layer, a standing wave is set up. The phase of this standing wave can be adjusted to have a maxima at the polymer-polymer interface and simultaneously a node at the polymer-air interface. Consequently, one can isolate the static scattering and XPCS from the buried layer. Results on a system consisting of a 100 nm polystyrene (PS) film on top of an 100 nm polybromostyrene (PBrS) film, supported on a Si substrate will be reported. The dynamics are consistent with a low-viscosity mixed layer between the PS and PBrS and coupling of the capillary wave fluctuations between this layer and the PS.

15:10 T. Takiue, Kyushu Uni.
Adsorbed Films of Alkanol and Fluoroalkanol Mixtures at the Hexane/Water Interface Studied by Synchrotron X-ray Reflectivity

During the past decade, surface sensitive spectroscopic or optical techniques such as ellipsometry, sum-frequency spectroscopy, neutron and X-ray scattering, XAFS etc. have been developed and applied mainly to the air/water interface to probe the structure of adsorbed films on microscopic length scales. Recently, Schlossman et al. have applied synchrotron X-ray reflectivity (XR) to oil/water interfaces and have started to examine the structure of these interfaces. In this study, the adsorbed film of mixed alkanol (C20OH : 1-Eicosanol) - fluoroalkanol (TFC10OH : 1,1,2,2-Tetrahydroheptadecafluorodecanol) system at the hexane/water interface was investigated by means of interfacial tension and XR measurements. We found: (1) interfacial coverage changes very steeply at phase transition points, (2) two different condensed monolayer phases are similar to the condensed phases of each of their corresponding single surfactant systems, (3) the expanded phase is in an inhomogeneous state consisting of monolayer domains and (4) the adsorbed film close to the transition points is in an inhomogeneous state. Here we will show some findings obtained by applying both techniques to the mixed alkanol – fluoroalkanol system.

15:30 coffee break

16:00 Jean Daillant, CEA, Saclay, France
Scattering from nanoparticles at the oil/water interface

Chemically synthesized nanoparticles with a metal core surrounded by a dielectric ligand shell have received a lot of interest in recent years because of their unique electrical, magnetic and optical properties [1]. Another very promising use of nanoparticles is to exploit their similarities with surfactant molecules to stabilize emulsions [2]. An important difference between surfactants and particles is the much stronger adsorption of the particles at the interface and therefore a much higher stability of the emulsion. Most of the studies in the past were focused on micron-sized particles, which are irreversibly adsorbed at the interface. Reducing the particle size to the nm scale, the energy of attachment decreases, and eventually becomes comparable to the thermal energy. In this case, thermal fluctuations can be enough to exchange nanoparticles between interface and bulk, which opens the possibility of "self-healing", where defects will be removed. We have synthesised 2.5nm gold nanoparticles coated with different ligands in order to tune the surface energy which allow the formation of stable emulsions. The organization of the nanoparticles at the interface has been investigated by electron microscopy and AFM. The same nanoparticles have also been investigated at macroscopic oil/water interfaces in a Langmuir trough. Their organisation has been characterised by x-ray reflectivity and grazing incidence x-ray diffraction at the ESRF ID10B. After a presentation of the experimental method, I will discuss the structure of the nanoparticle film as a function of surface pressure. Reversible buckling occurs at high pressure which can be correlated to the isotherm measurements.

[1] S. Sun, C. B. Murray, D. Weller, L. Folks and A. Moser, Science 279, 1989 (2000).
[2] R. Aveyard, B. P. Binks and J. H. Clint, Advances in Colloid and Interface Science, 100-102, (2003), 503.

16:40 John Webster, ISIS, Chilton, UK
Neutron Reflection From Liquid-Liquid Interfaces

The Interfacial width of hexadecane/water has been studied using neutron reflectometry on the SURF reflectometer at ISIS. These data along with the experimental method and analysis will be presented. In addition work on diblock copolymers at the same interface will be shown together with a view on the opportunities presented by the new INTER reflectometer on target station 2 at ISIS.

17:20 A. Vorobiev, ESRF
Structure of the interface between ferrofluids and non-magnetic liquids obtained by the synchrotron radiation scattering

Ferrofluid is a fluid material with properties tailored on the nanometer level. It consist of single domain magnetic particles with a typical size of 10 nm dispersed in a liquid carrier [1,2]. Because of their superparamagnetic susceptibility, they can conveniently be positioned and safely fixed by external magnetic fields. This insures wide application of ferrofluids in different devices and technological processes [3]. Some of the most recent and advanced applications, e.g. targeted drug delivery inside of the human body, require special stability of ferrofluid that implies understanding of the processes occurring at the interface between ferrofluid and another non-magnetic liquid.
We used grazing incident scattering of synchrotron radiation to study the structure and time evolution of surfacted ferrofluid brought into contact with a thick layer of immiscible non-magnetic liquid. Particularly, two types of interfaces were studied: (a) interface between water-based ferrofluid and light oil; (b) interface between oil-based ferrofluid and water. Reflectivity and diffraction experiments were performed on ID10B beamline (ESRF, Grenoble) owing to possibility of the beam tilt and availability of the photon energy of 22 keV.

[1] R. E. Rosensweig, *Ferrohydrodynamics* (Cambridge University Press, Cambridge, England, 1985).
[2] E. Blums, A. Cebers, and M. M. Maiorov, *Magnetic Fluids* (de Gruyter, Berlin, 1997).
[3] B. M. Berkovsky, V. F. Medvedev, and M. S. Krakov, *Magnetic Fluids; Engineering Applications* (Oxford University Press, Oxford, 1993).

17:40 T. Gutberlet, PSI
X-ray reflectivity study of the adsorption of azacrown ethers and palmitic acid at the hexane-water interface

Azacrown ethers substituted with different alkyl chain length (decyl, palmitoyl, dodecyl) and palmitic acid have been investigated at the aqueous-organic hexane-water interface by means of x-ray reflectivity. These systems are of interest in Permeation Liquid Membrane techniques to separate aqueous solutions by a hydrophobic membrane to select chemical species. The x-ray reflectivity measurements reveal the presence of a dense interfacial layer at the hexane-water interface. The longer alkyl chain substituted azacrown ethers show a diminished interfacial roughness. Here, the experimental set-up and results will be presented in detail and discussed.

18:00 dinner

June 23 2007

09:00 Giovanna Fragneto, ILL, France
FIGARO: a reflectometer for the study of fluid interfaces

FIGARO (Fluid Interfaces Grazing Angles ReflectOmeter) will be a high flux, flexible resolution, time-of-flight reflectometer with a vertical scattering plane, to be commissioned at the ILL spring 2008. It will be used for studies of thin films at air/liquid and liquid/liquid interfaces mainly in the realms of soft matter and biology. Applications involve the study of the interaction of proteins with lipid monolayers, surface behaviour of surfactants, polymers and other amphiphiles at liquid/air and liquid/liquid interfaces. Unique features of the instrument include the simultaneous use of a Brewster Angle Microscope during the reflectivity measurements and the possibility to strike the interface from above and below in a wide q-range. With an incoming beam of wavelengths comprised between 2Å and 30Å, it will be possible to attain a q-range from ~0.002 $Å^{-1}$ to ~ 0.32$Å^{-1}$ by using two incoming angles of 0.7˚ and 3˚.
A system of four choppers independently rotating in pairs will allow the choice of 6 different wavelength resolutions, ranging from 1.2 to 10%. Choppers are followed by two guide sections covered with supermirrors of m=4 deflecting downwards and upwards to allow incoming angles of the neutron beam between ±0.3 and ±4˚. Angles are not fixed and therefore a wide choice of selected q-ranges is allowed. For liquid/liquid interfaces it is important that the incoming beam can approach the interface from above or below the horizon as one liquid phase may be far more easily penetrable than the other.
A two dimensional multitube detector will be positioned at 3m from the sample. This detector will allow measurements of specular and off-specular reflectivity as well as GISANS

09:40 John Ankner, SNS, Oak Ridge, USA
Prospects for Reflectivity Studies of Liquids at the SNS

Following several months of commissioning, the Liquids Reflectometer at the Spallation Neutron Source can assert some claim to its designation as a reflectometer. In the coming months, we plan to justify our “liquids” designation as well. Thus far, we have carried out extensive beamline characterization, developed alignment protocols and instrument-control software, and built our first generation of solid/air and solid/liquid sample cells. We have in addition commissioned our beamline wet laboratory and initiated research projects on polymer films and brushes, as well as Langmuir-Blodgett- and Langmuir-Schaeffer-deposited films. This summer, we host our first official users, perform our first liquid/air measurements, and install a robotic sample handling system. We will present highlights of this activity and look ahead to future prospects and projects.

10:20 coffee break

10:50 Ali Zharbaksh, Queen Mary, University of London, UK
The structural studies of amphipiles adsorbed at a liquid-liquid interface using neutron reflectometry

We report the application of neutron reflectometery for the structural study at the interface between oil and an aqueous solution. The effect of counter ion size and charge (SO_4^{2-} and Br^-) on the structure, at the oil-water interface, of trimethyl tetradecyl ammonium sulphate/Bromide (C_{14}TAS / C_{14}TAB) will be discussed. The amphiphile distribution profiles for Adsorption of water-soluble, zwitterionic *n*-hexadecylphosphorylcholine (C_{16}PC) and also phospholipids amphiphiles at the oil water interface determined by simultaneous fitting of the reflectivity data at several grazing angles and contrasts will also be presented. In addition to the bare interfacial width between two immiscible electrolyte solutions and the effect of added salt on the interface.

11:30 Hanna Wacklin, ANSTO
PLATYPUS – The Time-of-Flight Neutron Reflectometer at Australia's New 20 MW OPAL Research Reactor

A time-of-flight neutron reflectometer (PLATYPUS) is currently being commissioned at Australia's new 20 MW OPAL research reactor at Lucas Heights, Sydney. Viewing the 25K liquid D_2 cold source, PLATYPUS has a vertical scattering plane and has been designed to study nanoscale films on solid and free liquid surfaces. In-plane structures can be studied by off-specular scattering using a 2-dimensional helium-3 detector, while scattering from magnetic materials will be examined using a polarized beam option,. One of the most exciting possibilities for this instrument is its suitability for kinetic studies (both normal and stroboscopic). This is due to the high projected flux at the sample position ($\sim 10^9$ n.cm^{-2}.s^{-1}), the use of a 4-disc variable resolution chopper system and the hi-speed area detector. The chopper system will allow us tailor the resolution of the instrument to suit the length scales of interest, without having to sacrifice angular resolution. As of April 2007 installation is almost complete, with instrument commissioning underway. In this presentation we report the current status of the instrument, as well as the design and specifications of the PLATYPUS neutron reflectometer.

11:50 D. Murakami, Kyushu Uni.
Miscibility in the adsorbed film of fluoroalkanol and cationic surfactant at hexane/water interface studied by interfacial tension and X-ray reflectivity measurements

We demonstrated previously that 1H,1H,2H,2H-perfluorodecanol ($TFC_{10}OH$) and 1-icosanol ($C_{20}OH$) are practically immiscible in the condensed film (two dimensional solid) because of the week dispersion interaction between fluorocarbon and hydrocarbon chains (J. Phys. Chem. B, 2005, 109, 1210). In this study, the miscibility of fluorocarbon alcohol, $TFC_{10}OH$ or 1H,1H,2H,2Hperfluorododecanol ($TFC_{12}OH$), and cationic surfactant, dodecyltrimethyl-ammonium bromide (DTAB) in the adsorbed film at the hexane/water interface was studied by the means of interfacial tension and X-ray reflectivity measurements. The phase diagram in the adsorbed film and the amplitude of reflectivity complementally show that binary species are miscible even in the condensed state, and furthermore that DTAB molecules are more miscible with $TFC_{10}OH$ than with $TFC_{12}OH$. These results are attributable to the strong dipole-ion

interaction between hydrophilic groups and change in the dispersion interaction between hydrophobic chains.

12:10 lunch

14:00 Mark Schlossman, University of Illinois at Chicago, USA
The Influence of Liquid Structure on Interfacial Ion Distributions

Mean field theories of ion distributions, such as the Gouy-Chapman theory that describes the distribution near a charged planar surface, ignore the molecular-scale structure in the liquid solution. The predictions of the Gouy-Chapman theory vary substantially from our x-ray reflectivity measurements of the interface between two electrolyte solutions. These structural measurements are described well by ion distributions predicted by a version of the Poisson-Boltzmann equation that explicitly includes a free energy profile for ion transfer across the interface when this profile is described by a simple analytic form or by a potential of mean force calculated from molecular dynamics simulations. These x-ray measurements from the liquid-liquid interface provide evidence for the importance of interfacial liquid structure in determining interfacial ion distributions.

14:40 Oleg Konovalov, ESRF, Grenoble, France
Studies of Phospholipids Monolayer at Liquid/Liquid Interface in Presence of an Antimicrobial Peptide

Presentation will consist of two parts. The first part will be devoted to description of the ID10B beamline at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) that makes systematic improvement of technical capabilities for studies at liquid/liquid interfaces.
In second part we will present studies of the structure and the bending rigidity of phospholipid monolayers formed at hexadecane/water interface in presence and absence of antimicrobial peptides. An application of the antimicrobial peptides (AP) as an antibiotics of new generation requires comprehensive studies of their interaction with eukaryotic and prokaryotic cell membranes. Despite the big progress in characterization of this system, its elastic properties remain unclear.
Negatively charged lipids (dipalmitoyl-phosphatidylglycerol) were used to mimic a bacterial cytoplasmic cell membrane. With zwitterionic lipids (dipalmitoyl-phosphatidylcholine) we mimicked a mammalian cell membrane. As antimicrobial peptide the peptidyl-glycylleucine-carboxyamide was chosen.
Structural characterization of the membranes was done with the X-ray Reflectivity. The Grazing Incidence Diffuse Scattering technique was applied to obtaining bending rigidity value of the systems.

15:20 coffee break

16:00 round table

19:00 dinner

June 24 2007

09:00 Robert Thomas, University of Oxford
What can we expect to learn about surfactants at the liquid/liquid interface? Extrapolation of neutron results from solid/liquid and air/liquid results

The strengths and weaknesses in the ability of neutron reflectometry to determine the conformation of amphiphilic molecules at surfaces have now been well explored. Isotopic labelling can be used both to overcome the intrinsically low resolution of the technique and to resolve structural correlations along the surface normal in the presence of significant roughening from thermal motion. As the amphiphiles become more complicated new types of structural behaviour are starting to emerge. For example, in a series of Gemini surfactants we have found that the separation between hydrophilic and hydrophobic groups can be made to disappear depending on the chain length. The implication is that such structures will become very sensitive to changes in the media on either side of the interface. It is then interesting to speculate whether differences in such structural correlations at solid/liquid and the air/liquid interfaces can be used to guess how these molecules might behave at the liquid/liquid interface.

09:40 Bruce Law, Kansas State University
Neutron, X-ray and ellipsometric study of adsorption at liquid interfaces

In this contribution we examine the advantages of using multiple techniques, specifically, neutron reflectometry, X-ray reflectometry and ellipsometry to study adsorption phenomena at the surfaces of binary liquid mixtures near their bulk critical point. The use of multiple techniques severely limits the shape of the adsorption profile that can describe all data sets. Short length scale interfacial features are best resolved using neutron/X-ray reflectometry, whereas, large length scale interfacial features are best resolved using ellipsometry. Complex interfaces possessing surface features on many different length scales are therefore best studied using a combination of neutron/X-ray reflectometry and ellipsometry.

10:00 coffee break

11:00 resumee

12:00 end of workshop/lunch

13:00 bus transport to Copenhagen airport

List of participants:

No.	Name	Prename	Affiliation	e-mail
1	Ankner	John	SNS, Oak Ridge	anknerjf@ornl.gov
2	Arnold	Tom	DIAMOND	tom.arnold@diamond.ac.uk
3	Daillant	Jean	Orsay	jean.daillant@cea.fr
4	Fragneto	Giovanna	ILL	fragneto@ill.fr
5	Gutberlet	Thomas	PSI	thomas.gutberlet@psi.ch
6	Halbert	Candice E.	SNS	halbertce@ornl.gov
7	Koehler	Ralf	HMI	ralf.koehler@hmi.de
8	Konovalov	Oleg	ESRF	konovalo@esrf.fr
9	Lal	Jyotsana	ANL	jlal@anl.gov
10	Law	Bruce	Kansas State University	bmlaw@phys.ksu.edu
11	Major	Marton	MPI-MF	mmajor@mf.mpg.de
12	Murakami	Daiki	Kyushu University	daiki-scc@mbox.nc.kyushu-u.ac.jp
13	Rennie	Adrian	Uppsala University	Adrian.Rennie@fysik.uu.se
14	Roser	Steve	University of Bath	s.j.roser@bath.ac.uk
15	Schlossman	Mark	University Chicago	schloss@uic.edu
16	Takiue	Takanori	Kyushu University	t.takscc@mbox.nc.kyushu-u.ac.jp
17	Taylor	Diana	Oxford University	diana.taylor@chemistry.oxford.ac.uk
18	Thomas	Bob	University of Oxford	robert.thomas@chem.ox.ac.uk
19	Tolan	Metin	University Dortmund	tolan@physik.uni-dortmund.de
20	Torikai	Naoya	KENS	naoya.torikai@kek.jp
21	Vorobiev	Alexei	ESRF	alexei.vorobiev@esrf.fr
22	Wacklin	Hanna	ANSTO	hwa@ansto.gov.au
23	Webster	John	ISIS	J.R.P.Webster@rl.ac.uk
24	Wojciechowski	Kamil	TU Warsaw	kamil.wojciechowski@ch.pw.edu.pl
25	Zharbaksh	Ali	University of London	a.zarbakhsh@qmul.ac.uk

Payment:

The workshop fee is 350 Euro, which includes full accommodation at Conference Center Klinten, breakfasat, lunch and dinner during the workshop.

The workshop fee has to be paid by Bank transfer or by credit card. For payment the participants have to mention as subject for payment “Workshop Rodvig”.

Bank transfer:

Raiffeisenbank Böttstein
5314 Kleindöttingen
Account number: 63912.55
Bank code number: 80652
SWIFT code: RAIFCH22
Account holders name: Paul Scherrer Institut, CH-5232 Villigen PSI
IBAN: CH9380652000006391255

Credit card:

The following information should send to the organizers:

Amount in EUR
Credit Card Company: Visa, Eurocard/Mastercard, American Express
Card No
Exp. Date
Card Verification Value (last three numbers on the back of the card)
Cardholders name
Date
Signature

There has to be a charge of 4 %, i.e 14 EUR for each credit card transaction to be added.

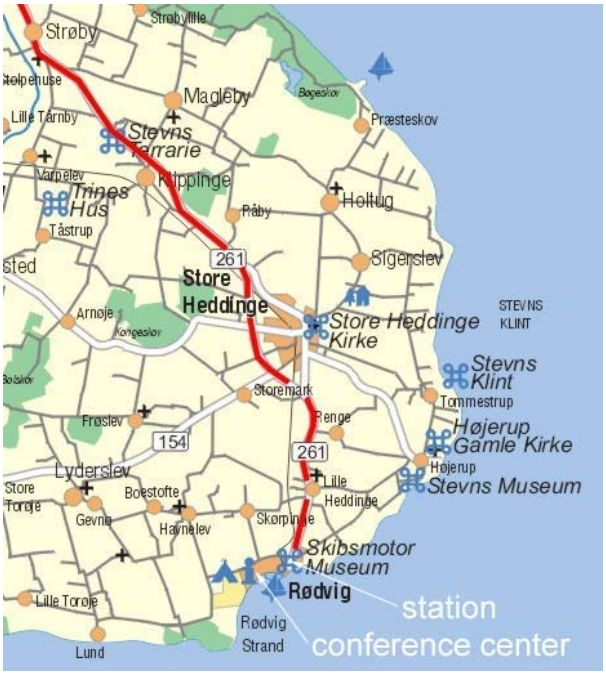
Location:

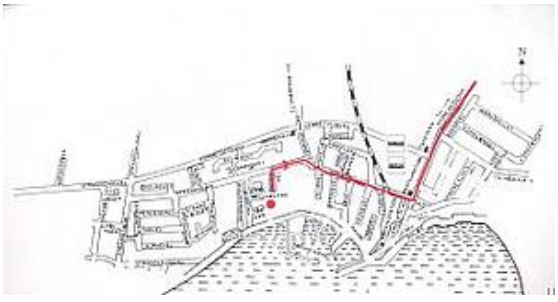
The workshop will take place at Conference Center Klinten in Rodvig, Denmark.

Conference Center Klinten
Søndervej 8,
4673 Rødvig
Denmark

Phone: +45 5650 6800
Fax: +45 5650 6473
e-mail: info@klinten.dk
http://www.klinten.dk/forside/

Rodvig is about 65 km south from Copenhagen and can be reach by public transportation from Copenhagen airport via Koge. The trip takes about 2 hours. You may find out the best transportation via the Rejseplanen web side at **www.rejseplanen.dk**. Starting from Copenhagen airport to Rodvig station. The usual route is from Copenhagen airport to Copenhagen main station, change trains to go from Copenhagen main station to Koge station, change trains at Koge station to Rodvig station. From there it is about 500 m to walk to the Conference Center Klinten in the Sondervej 8 street.





How to reach Klinten

An option by train from Copenhagen airport to Klinten on Friday morning are given below. You may find other options at **www.rejseplanen.dk**

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Station/Stop		Time		Date:	Duration	Chg.	Means of transportation
from:	Kastrup Lufthavn st	dep	09:20	22.06.07	2:15	3	
to:	Rødvig st	arr	11:35	22.06.07			
from:	Kastrup Lufthavn st	dep	09:56	22.06.07	1:49	2	
to:	Rødvig st	arr	11:45	22.06.07			
from:	Kastrup Lufthavn st	dep	10:56	22.06.07	1:49	2	
to:	Rødvig st	arr	12:45	22.06.07			

Your travel plan	Time		Date:	Platform*	Comments
Take **RE 11537** from **Kastrup Lufthavn st** towards **Helsingør st** to **København H**.	dep	09:56	22.06.07		
Arrival **København H**	arr	10:09	22.06.07		
Walk from **København H** to **København H (S-tog)**. Allow about **6 min.** to get there.			22.06.07		
Take S-train **E** from **København H (S-tog)** towards **Køge st (S-tog)** to **Køge st (S-tog)**.	dep	10:16	22.06.07		
Arrival **Køge st (S-tog)**	arr	10:54	22.06.07		
Walk from **Køge st (S-tog)** to **Køge st**. Allow about **4 min.** to get there.			22.06.07		
Take **PP Tog** from **Køge st** towards **Rødvig st** to **Rødvig st**.	dep	11:07	22.06.07		
Arrival **Rødvig st**	arr	11:45	22.06.07		
Total travel time: 1:49					