



Instytut Fizyki Jądrowej
im. Henryka Niewodniczańskiego
Polskiej Akademii Nauk



Kazuya Saito

Profesor Honorowy
Instytutu Fizyki Jądrowej im. Henryka Niewodniczańskiego
Polskiej Akademii Nauk



Zbiór dokumentów związanych z procedurą nadania
tytułu

Honorowego Profesora

Instytutu Fizyki Jądrowej

im. Henryka Niewodniczańskiego

Polskiej Akademii Nauk

w Krakowie

Professorowi

Kazuya Saito

Documents related to the procedure of bestowing
the title of

Honorary Professor

of

The Henryk Niewodniczański

Institute of Nuclear Physics

Polish Academy of Sciences

in Kraków

on

Professor

Kazuya Saito

Wydano nakładem Instytutu Fizyki Jądrowej im. Henryka Niewodniczańskiego
Polskiej Akademii Nauk
Kraków 2023

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Prof. dr hab. Tadeusz Lesiak
The Director of the Institute of Nuclear Physics of Polish Academy of Sciences

Introduction

The ceremony of bestowing the Title of Honorary Professor is a great day for scientific community. Awardees are world-class scientists with achievements of fundamental importance, who, through excellent, long lasting collaboration have had an outstanding contribution to strengthening the scientific level and prestige of the institution. Such a person expands the horizons of knowledge and can be called a friend and regarded an ambassador of Polish scientists in the world.

It is a great honour for the Institute of Nuclear Physics of Polish Academy of Sciences to bestow the Title of the Honorary Professor to Professor Kazuya Saito, an outstanding specialist in the field of thermodynamic studies of molecular materials, graduated from Osaka University, the sixth imperial University in Japan. In 2004 Kazuya Saito received professorship in the Graduate School of Pure and Applied Sciences at the University of Tsukuba. The excellent calorimetric laboratory he established was visited by many young scientists from the Institute of Nuclear Physics of Polish Academy of Sciences for short or longer term scholarships. A cooperation is motivated by the reputation the Japanese scientists have due to a long tradition in adiabatic calorimetry studies of phase transitions and thermodynamic properties of condensed matter. Thermodynamic parameters depend on all degrees of freedom of the molecular system and illustrate relation between macroscopic properties and microscopic dynamics. The measurement of them is a good probe for understanding the mechanisms of phase transitions, occurring when the subtle balance between molecular structure, intermolecular interactions and molecular motions is lost. In comparison with other spectroscopic methods, the characteristic time of calorimetric measurements is the longest. These aspects of calorimetric studies are important in the context of the research in the Institute of Nuclear Physics of Polish Academy of Sciences performed by neutron, IR and dielectric spectroscopies, and by a theoretical analysis. The inclusion of adiabatic calorimetry in the investigations of properties of condensed matter allows a detection of molecular dynamics in the time scale from ps to 1000 s.

The collaboration between Professor Kazuya Saito and the scientists from the Institute of Nuclear Physics of Polish Academy of Sciences concerns a new class of glass-formers with partial long-range order. His deep understanding of the phenomena in molecular matter together with the excellent tools dedicated to experimental data analysis in the Saito Lab brought pioneering results, especially in the studies of highly ordered liquid crystal phases. The scientific projects realized within the framework of the cooperation: “Molecular motions and phase transitions in organic materials”, “Complementary studies of organic materials with partial long-range order of molecules” and “Crystallization and glass transition in liquid crystals”, were co-funded by the Japanese Society for Promotion of Science and by the Polish Academy of Sciences. The outstanding results of these joint studies provide a clear evidence of the importance of the mutual collaboration, and allow to expect further development of excellent scientific relations between the Japanese and Polish physicists and chemists interested in properties of molecular condensed matter.

We thank Professor Kazuya Saito for his tremendous cooperation with the Institute of Nuclear Physics of Polish Academy of Sciences and magnificent contributions to the thermodynamic studies of molecular condensed matter.

We are honoured to have him join the prestigious group of outstanding scientists awarded with the Title of the Honorary Professor of the Henryk Niewodniczański Institute of Nuclear Physics of Polish Academy of Sciences.



INSTYTUT FIZYKI JĄDROWEJ
im. Henryka Niewodniczańskiego
POLSKIEJ AKADEMII NAUK

Uchwała nr 59/2022
z dnia 16 maja 2022 r.

Rady Naukowej Instytutu Fizyki Jądrowej im. Henryka Niewodniczańskiego
Polskiej Akademii Nauk w Krakowie
w sprawie wszczęcia postępowania o nadanie tytułu Honorowego Profesora
Instytutu Fizyki Jądrowej im. Henryka Niewodniczańskiego
Polskiej Akademii Nauk prof. Kazuya Saito

Na podstawie §18 ust. 2 pkt. 14 Statutu Instytutu Fizyki Jądrowej im. Henryka Niewodniczańskiego Polskiej Akademii Nauk, Regulaminu nadania tytułu Honorowego Profesora Instytutu Fizyki Jądrowej im. Henryka Niewodniczańskiego Polskiej Akademii Nauk w Krakowie z dnia 14 listopada 2005 r., Rada Naukowa Instytutu Fizyki Jądrowej im. Henryka Niewodniczańskiego Polskiej Akademii Nauk uchwala co następuje:

§ 1

Wszczyna postępowanie o nadanie tytułu Honorowego Profesora Instytutu Fizyki Jądrowej im. Henryka Niewodniczańskiego Polskiej Akademii Nauk **profesorowi Kazuya Saito**.

§ 2

Członkiem Komisji, profesorem – specjalistą, została wybrana prof. dr hab. Maria Massalska-Arodź.

§ 3

Uchwała wchodzi w życie z dniem podjęcia.

PRZEWODNICZĄCY RADY NAUKOWEJ
Instytutu Fizyki Jądrowej
im. H. Niewodniczańskiego
Polskiej Akademii Nauk
Antoni Szczurek
Prof. dr hab. Antoni Szczurek



INSTYTUT FIZYKI JĄDROWEJ
im. Henryka Niewodniczańskiego
POLSKIEJ AKADEMII NAUK

Uchwała nr 69/2022

z dnia 13 czerwca 2022 r.

**Rady Naukowej Instytutu Fizyki Jądrowej im. Henryka Niewodniczańskiego
Polskiej Akademii Nauk w Krakowie**
**w sprawie wyboru jednostek naukowych do których zostanie przesłany
do zaopiniowania wniosek o nadanie tytułu Honorowego Profesora
Instytutu Fizyki Jądrowej im. Henryka Niewodniczańskiego PAN
prof. Kazuya Saito**

Na podstawie §18 ust. 2 pkt. 14 Statutu Instytutu Fizyki Jądrowej im. Henryka Niewodniczańskiego Polskiej Akademii Nauk, Regulaminu nadania tytułu Honorowego Profesora Instytutu Fizyki Jądrowej im. Henryka Niewodniczańskiego Polskiej Akademii Nauk w Krakowie z dnia 14 listopada 2005 r., Rada Naukowa Instytutu Fizyki Jądrowej im. Henryka Niewodniczańskiego Polskiej Akademii Nauk uchwała co następuje:

§ 1

Postanawia by wniosek o nadanie tytułu Honorowego Profesora Instytutu Fizyki Jądrowej im. Henryka Niewodniczańskiego PAN **profesorowi Kazuya Saito** przesłano do zaopiniowania:

- Radzie Naukowej Instytutu Fizyki im. Augusta Chełkowskiego Uniwersytetu Śląskiego w Katowicach;
- Radzie Naukowej Instytutu Chemii Fizycznej Polskiej Akademii Nauk.

§ 2

Uchwała wchodzi w życie z dniem podjęcia.

PRZEWODNICZĄCY RADY NAUKOWEJ
Instytutu Fizyki Jądrowej
im. H. Niewodniczańskiego
Polskiej Akademii Nauk

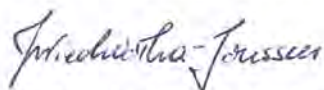
Antoni Szczurek
Prof. dr hab. Antoni Szczurek

Uchwała nr 1/311/2022
Rady Naukowej Instytutu Chemii Fizycznej PAN
z dn. 7 lipca 2022 r.

w sprawie opinii o dorobku naukowym, osiągnięciach i zasługach Profesora Kazuya Saito

Rada Naukowa Instytutu Chemii Fizycznej PAN przyjmuje opinię o dorobku naukowym, osiągnięciach i zasługach Profesora Kazuya Saito w postępowaniu o nadanie tytułu Honorowego Profesora Instytutu Fizyki Jądrowej im. H. Niewodniczańskiego PAN Profesorowi Kazuya Saito, przedstawioną w *Załączniku nr 1 do uchwały*.

Sekretarz Rady Naukowej



Prof. dr hab. Joanna Niedziółka-Jönsson

Przewodniczący Rady Naukowej



Prof. dr hab. Aleksander Jabłoński

Rekomendacja dla Profesora Kazuya Saito w związku o wszczęcie procedury nadania tytułu Honorowego Profesora Instytutu Fizyki Jądrowej im. Henryka Niewodniczańskiego Polskiej Akademii Nauk

Tytuły honorowe w nauce przyznawane w Polsce należą się wybitnym uczonym z całego świata, którzy część swojego naukowego życia poświęcili na współpracy z Polskimi naukowcami przyczyniając się do rozwoju naszego kraju.

Z ogromnym entuzjazmem przygotowałem swoją rekomendację dla wielkiego przyjaciela Polaków profesora Kazuya Saito. Profesor w sposób ciągły współpracuje z Polską od ponad 20 lat. Wielu pracowników Instytutu miało okazję odwiedzić Jego laboratoria i wspólnie z nim prowadzić badania. O Jego szacunku dla naukowców pracujących w Instytucie świadczy fakt wysyłania swoich japońskich współpracowników do Polski w celu prowadzenia wspólnych badań oraz Jego udział w naukowych spotkaniach organizowanych w Polsce.

Profesor Saito jest uznanym specjalistą, który z pomiarów termodynamicznych potrafi odczytać zmiany struktury materii skondensowanej: ciekłych kryształów, cieczy jonowych etc. Biegłość w analizie zmian entropii układu pod wpływem zmian struktury pozwoliła Mu na zgłębienie zasad rządzących przejściami fazowymi, kinetyką procesów krystalizacji i zeszklenia oraz dynamiką molekularną i dynamiką sieci w mezo-fazach, kryształach organicznych i cieczach jonowych. Badał tak odległe zjawiska jak przewodnictwo w strukturach organicznych, powierzchnie Fermiego w metalach, izomery fullerenów, upakowanie molekuł w strukturach żyroidalnych, czy pojemność cieplną polimerów. Jedna z Jego prac ukazała się w Nature i zgromadziła prawie 700 cytowań.

Nie mam wątpliwości, że profesor Kazuya Saito należy do znakomitych naukowców pracujących na styku termodynamiki, miękkiej materii i chemii materiałowej. Jest także wielkim przyjacielem Instytutu i Polaków. Jako Honorowy Profesor Instytutu stanie się ambasadorem Polskich naukowców w Japonii.

Signed by /
Podpisano przez:

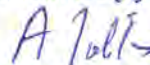


Robert Hołyst

Date / Data:
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Profesor dr hab. Robert Hołyst
Kierownik zakładu miękkiej materii
Instytutu Chemii Fizycznej PAN

Przewodniczący Rady Naukowej



Prof. dr hab. Aleksander Jabłoński



Chorzów, dnia 15 września 2022 roku

Uchwała nr 30/2022

Po zapoznaniu się z dostarczoną dokumentacją Rada Naukowa Instytutu Fizyki Uniwersytetu Śląskiego w Katowicach popiera kandydaturę prof. Kazuya Saito do tytułu Honorowego Profesora Instytutu Fizyki Jądrowej im. H. Niewodniczańskiego PAN w Krakowie.

Uzasadnienie:

Prof. Kazuya Saito jest światowej klasy fizykiem eksperymentalnym specjalizującym się w zakresie fizyki materii skondensowanej. Ma na swoim koncie wiele ważnych osiągnięć naukowych. Ponadto intensywnie współpracuje z Oddziałem Fizyki Materii Skondensowanej IFJ PAN wywierając duży wpływ na rozwój naukowy jego pracowników. To wszystko czyni go doskonałym kandydatem do tytułu Honorowego Profesora Instytutu Fizyki Jądrowej im. H. Niewodniczańskiego PAN w Krakowie.

Prof. Kazuya Saito przez wiele lat związany był z Uniwersytetem Osaka, gdzie realizował swoją pracę doktorską, którą obronił w 1986r. Po doktoracie, przez 9 lat był profesorem w Tokyo Metropolitan University, po czym powrócił do badań na macierzystą uczelnię do Osaki. Od kwietnia 2004 roku jego działalność naukowa jest umiejscowiona w Samodzielnym Laboratorium badań fizyko-chemicznych, które utworzył w Uniwersytecie w Tsukubie, gdzie uzyskał tytuł profesorski.

Godny podziwu jest zakres zainteresowań naukowych Prof. Kazuya Saito, obejmuje on zarówno wszelkie aspekty fizyczne dotyczące faz ciekłokrystalicznych, jak również dynamikę molekularną oraz własności termiczne, elektryczne i magnetyczne niskowymiarowych przewodników organicznych. Nie do przecenienia jest także jego rola w badaniu zjawiska formowania fazy szklistej oraz kinetyki krystalizacji. Wkład w każdy z tych obszarów badawczych jest udokumentowany



UNIWERSYTET ŚLĄSKI

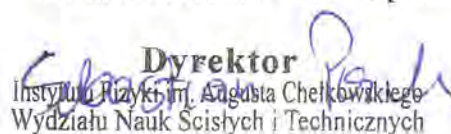
INSTYTUT FIZYKI
IM. AUGUSTA CHELKOWSKIEGO

licznymi pracami naukowymi opublikowanymi w czasopismach o wysokim czynnikiem wpływu, które są często cytowane przez innych badaczy. Prof. Kazuya Saito jest autorem książki *Chemical Physics of Molecular Condensed Matter*, wydanej w 2020 r. przez wydawnictwo Springer oraz czterech rozdziałów kompendium techniki kalorymetrycznej pt. *Comprehensive Handbook of Calorimetry and Thermal Analysis* wydanego przez John Wiley and Sons Ltd. W 2004 roku. Jego sumaryczny dorobek publikacyjny obejmuje blisko 300 artykułów naukowych. Jest także cenionym nauczycielem akademickim, wypromował 37 magistrów i 7 doktorów.

Profesor Kazuya Saito odegrał ważną rolę w kształtowaniu profilu naukowego wielu czasopism naukowych o cyrkulacji międzynarodowej jak *Journal of Thermal Analysis and Calorimetry*, *The Journal of Chemical Thermodynamics*, *Bulletin of the Chemical Society of Japan*, czy *Journal of the Physical Society of Japan*, pełniąc w nich odpowiedzialne funkcje. Ze względu na aktywną działalność naukową oraz wybitne osiągnięcia naukowe Profesora Saito doceniano powierzając mu wysokie funkcje w towarzystwach naukowych, uhonorowano też nagrodą James J. Christensen Memorial Award podczas konferencji CALCON w 2011 roku.

Przewodniczący Rady

Dr hab. Sebastian Pawlus, prof. UŚ


Dyrektor
Instytutu Fizyki im. Augusta Chelkowskiego
Wydziału Nauk Ścisłych i Technicznych

dr hab. Sebastian Pawlus, prof. UŚ



**INSTYTUT FIZYKI JĄDROWEJ
im. Henryka Niewodniczańskiego
POLSKIEJ AKADEMII NAUK**

**Uchwała nr 120/2022
z dnia 14 listopada 2022 r.**

**Rady Naukowej Instytutu Fizyki Jądrowej im. Henryka Niewodniczańskiego
Polskiej Akademii Nauk w Krakowie
w sprawie nadania tytułu Honorowego Profesora
Instytutu Fizyki Jądrowej im. Henryka Niewodniczańskiego Polskiej Akademii Nauk
prof. Kazuya Saito**

Na podstawie §18 ust. 2 pkt. 14 Statutu Instytutu Fizyki Jądrowej im. Henryka Niewodniczańskiego Polskiej Akademii Nauk, Regulaminu nadania tytułu Honorowego Profesora Instytutu Fizyki Jądrowej im. Henryka Niewodniczańskiego Polskiej Akademii Nauk w Krakowie z dnia 14 listopada 2005 r., Rada Naukowa Instytutu Fizyki Jądrowej im. Henryka Niewodniczańskiego Polskiej Akademii Nauk uchwała co następuje:

§ 1

Nadaje tytuł Honorowego Profesora Instytutu Fizyki Jądrowej im. Henryka Niewodniczańskiego Polskiej Akademii Nauk **profesorowi Kazuya Saito**.

§ 2

Uchwała wchodzi w życie z dniem podjęcia.

PRZEWODNICZĄCY RADY NAUKOWEJ
Instytutu Fizyki Jądrowej
im. H. Niewodniczańskiego
Polskiej Akademii Nauk


Prof. dr hab. Antoni Szczurek

Laudation
at Ceremony of Bestowing the Title of Honorary Professor
of the Henryk Niewodniczański Institute of Nuclear Physics
of Polish Academy of Sciences
upon Professor Kazuya Saito

Ladies and Gentlemen, Members of Scientific Council of the Institute of Nuclear Physics of Polish Academy of Sciences, Distinguished Guests, Colleagues and Friends, Dear Kazuya, Dear Honorary Professor

Today I have the honor and pleasure to introduce and commend the personality and achievements of our distinguished guest Professor Kazuya Saito. Let me start with a bit of history: It was in January 2000 that professor Kazuya Saito visited our Institute for the first time. His visit was the result of the long-lasting scientific friendship between professor Jerzy Janik and professor Michio Sorai the Director of the Research Center of Molecular Thermodynamics at Osaka University, the Honorary Professor of our Institute since 2006. Their first meeting took place fifty years ago at Liquid Crystal Conference in Bangalore. They discussed then about a metastable crystalline phase found in our Institute, which in fact occurred to be a new form of glass with long-range order of some degrees of freedom. The basis for the collaboration of the Japanese and Polish groups, altogether involving about 50 scientists, was a common interest in thermodynamic studies of phase transitions in molecular condensed matter. It was perfectly well known that in Japan, thermodynamics is traditionally of the top world level meaning for us, the goal to live up to such a high standard. Our best specialist in calorimetry, the late professor Jacek Mayer visited Osaka University several times in the period between 1994 and 2001. Later, two of us, Professor Tadeusz Wasiutyński and me, were invited as the visiting professors there in 2002 and 2003. It was a valuable experience for us to see how Kazuya was forming the group of his scientific pupils, how they spent together a lot of time, having lunches every day in the campus canteen and celebrating special occasions during dinners in restaurants. Scientific discussions were conducted sometimes while walking in the surrounding countryside of Osaka. His students had the habit of taking guests from abroad to public concerts, where their leader was playing flute with an orchestra. We had the opportunity to accompany Kazuya in building his authority and establishing a friendly “master-pupils” relationship, where his sense of humor and his positive attitude to work were important factors.

Our projects with Professor Saito as a leader were designed for young adjuncts and PhD students. They formally started under the agreement on scientific cooperation between the Polish Academy of Sciences and the Japanese Society for the Promotion of Science. We are proud that our program involved 7 Japanese scientists, presenting their results in our Institute and visiting, with their Polish colleagues, other scientific centers in Poland as well as historical and cultural objects. For many of them, it was the first contact with Europe. At the University of Tsukuba, the same number of our colleagues were on scholarships lasting from two weeks up to two years, performing there valuable thermodynamic studies under the Professor's expert

eye. The research concerned phase transitions and structure studied by complementary methods in various liquid crystalline compounds synthesized in Warsaw Military Academy and the Chemical Faculty of the University of Wrocław. The members of Saito's laboratory and those of our Division of Condensed Matter Physics are the authors of nearly 20 well-cited joint papers, often with significant conclusions. It is worth mentioning that it was a great opportunity for our young scientists to observe Japanese work and scientific cooperation models as well as technical culture, they acquired from the very beginning, for example, visiting the well-thought-out Science Museum.

Let me now briefly outline the rich scientific career of Kazuya Saito, the outstanding world-known scientist working at the intersection of thermodynamics, soft matter and material chemistry. He is a Doctor of Science, graduated from Osaka University in 1986. Since 2004 he is a professor in the Graduate School of Pure and Applied Sciences at the University of Tsukuba and in 2018–2021 he has been the Dean of the Faculty of Pure and Applied Sciences. As a young doctor of chemistry, he was an assistant at the Tokyo Institute of Technology, a research associate at Tokyo Metropolitan University, and then an associate professor at Osaka University. Kazuya Saito was also a guest professor at the Open University of Japan. Since his first scientific paper in 1983, he has published all together about 300 papers with nearly 5000 citations (without self-citations). In most of the papers, he was a leading author. Many achievements of Professor Saito and his group are regarded as pioneering. To show a wide diversity of topics studied by professor Kazuya Saito let me mention the titles of his two papers, the one published in *Nature* under the title “Nuclear magnetic resonance characterization of isomers of C₇₈, C₈₂ and C₈₄ fullerenes”, which collected 700 citations, and the second one published this year in the prestigious journal of *Soft Matter* under the title “Aggregation structure of chiral cubic liquid crystals revealed by X-ray diffraction utilizing a new algorithm” which clarified a long-standing puzzle of a chiral structure spontaneously formed by achiral rodlike molecules. Professor Saito presented the results of his studies in more than 110 invited talks at international conferences, several of them in Poland. He promoted 7 doctors and nearly 40 master theses were prepared under his supervision. The community of physicists and chemists dealing with condensed matter honored professor Kazuya Saito with many distinctions. Let me mention three significant academic awards given by the Japanese Liquid Crystal Society, the Japan Society of Calorimetry and Thermal Analysis, and the prestigious James J. Christiansen Memorial Award of The Calorimetry Conference. Professor Saito was the Director of the International Association of Chemical Thermodynamics, the President of the Japan Society of Calorimetry and Thermal Analysis, and a member of the Advisory Board of The Calorimetry Conference (since 2002) and of the *Journal of Chemical Thermodynamics* (since 2017). Some specialist journals owe a great deal to his knowledge, experience, and various skills and talents during his time as their editor. He is the Chairman of the International Conference on Chemical Thermodynamics, which is planned for this year. Professor Kazuya Saito is the author of important books: “Gibbs energy and Helmholtz energy” published by the Royal Society of Chemistry, and “Comprehensive Handbook of Calorimetry and Thermal Analysis” published by John Wiley and Sons Ltd. His monograph, “Chemical Physics of Molecular Condensed Matter,” published by Springer in 2020, is a unique book presenting the scientific knowledge from the last decade for various selected systems, where the molecular

structure is a decisive factor for features of material. In references of this book, one can find 30 Polish authors of the cited papers, and half of them are from our Institute. The highest level of the scientific achievements of Professor Saito was acknowledged by the scientists from two Polish centers: the Institute of Physical Chemistry of the Polish Academy of Sciences and the Institute of Physics of the Silesian University consulted in our procedure of conferring the title of Honorary Professor. The supporting letters are signed by Professors Robert Hołyst, Aleksander Jabłoński, and Sebastian Pawlus.

The spectacular scientific activity of Professor Saito concerns mostly thermodynamic studies of condensed phase materials. He is one of those scientists who understand the complexity of processes and phenomena in condensed matter physics. His 40-year studies of various molecular systems such as liquid crystals, molecular magnets and spin systems, ionic liquids, low dimensional organic conductors, fulleren isomers, and polymers to name but a few were performed on the best technical level with a deep knowledge of mechanisms of molecular dynamics and phase transitions and of the nature of vitrification and crystallization. For us, the most important are his basic researches full of novel ideas on highly ordered liquid crystalline materials. Based on thermodynamic studies, he has shown the essential role of molecular chains, being the reservoir of configurational entropy, in the stabilization of the phases with various liquid crystal ordering degrees. Entropy changes in the phase transitions are related to the activation of subsequent molecular motions on heating the substance. His next concept of the “quasi-binary picture of liquid crystal order,” assuming microscopic segregation of layers of rigid cores from those of flexible chains of molecules, starts to be acknowledged in the literature. This model elucidates the correlation between molecular layers implying crystal-like three-dimensional structures in some liquid crystal phases. Interestingly, it removes in some sense a distinction between two types of liquid crystals: those created through changes in temperature and those forming in the dissolving process, which enables a unified understanding of thermotropic and lyotropic liquid crystals. In turn, studying the possibilities of heat storage in metal complexes, Saito found that it is molecular flexibility which controls the ease of supercooling of liquid state and nucleation-growth process during cold crystallization. In multi-component systems with iron and nickel, some bistability and tristability phenomena with dual spin-state conversion were discovered in response to lowering and increasing the temperature. These discoveries, as well as many others, are based on the virtuoso use of adiabatic calorimetry methods through high-precision measurements by unique laboratory-made instruments dedicated to special physical problems. That brings the precise values of thermodynamic parameters, worked out thoroughly by specialists thanks to a perfect workshop of experimental data analysis in the laboratory Professor Saito established in the Graduate School of Pure and Applied Sciences at the University of Tsukuba. In models, papers, and presentations of our Honorary Professor one can trace the Japanese appreciation of perfection, discipline and beauty together with a natural ease in the visualization of difficult patterns.

Dear Kazuya, I would like to express our admiration for your outstanding scientific achievements and magnificent contribution to the development of thermodynamic studies of molecular condensed matter. Please accept our appreciation of everything you have done for us, of your merits in strengthening the level of scientific studies in the Division of Condensed

Matter Physics. I am sure that friendliness and the partnership nature of our cooperation were the sources of progress in the common projects for both sides. Your visits here and the scholarships of our students and postdocs in your Lab fostered their scientific development and often introduced a new look at our own results obtained by methods complementary to the thermodynamic ones. Your active membership in the Scientific Committee of our conference “Multiscale phenomena in molecular condensed matter” helps to refine its scientific level. We appreciate deeply your experience and talent in experimentation and the masterful interpretation of experimental data focused on the relation of macroscopic features with microscopic structure and interactions. You are showing us a proper pattern how to cultivate successfully research and to find satisfaction from the scientific way of life. Of special value is your great ability to set the right perspectives on research goals, to confront theoretical concepts with their application to real molecular objects, and to make the complexity of material structures and physical phenomena easier to understand. Your excellent talks and discussions help us to see clearly the importance of intermolecular interactions, anharmonicity, entropy factor, and molecular shape in the aspect of phase transitions and phase stability. You have shown us in fact the importance of molecular crystals themselves from the fundamental and applicational point of view. We have really learned a great deal by studying your papers and tracing your reasoning in the description of new types of molecular order. We would like to thank you for all these fruitful years of cooperation.

Dear Kazuya, please do accept our very best wishes for many good years to come with exciting scientific findings and achievements. Let your cooperation with our Institute develop smoothly with a growing number of brilliant newcomers interested in molecular condensed matter studies. Optimistically, one can say that despite your huge scientific achievements we are now congratulating you on, there are still open questions in our field and there is still much room for further material studies, as no universal rule to control polymorphism was found and, for example, crystal engineering as well as avoiding of crystallization remain still a challenge

Prof. dr hab. Maria Massalska-Arodz

Kraków, 18th May 2023

*Faksymile dyplomu Honorowego Profesora
Instytutu Fizyki Jądrowej im. Henryka Niewodniczańskiego PAN
wręczonego Profesorowi Kazuya Saito*



The Henryk Niewodniczański
Institute of Nuclear Physics
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In pursuance of a Resolution of
the Scientific Council of the Institute the title of

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**Professor
Kazuya Saito**

in recognition of his magnificent contributions to thermodynamic
studies of molecular condensed matter and tremendous cooperation
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Kraków, on the XXX twenty-sixth day of May two thousand twenty three

Intramolecular Structural Degrees of Freedom as an Essential Actor in Molecular Condensed Matter

Kazuya SAITO*

Abstract

This short text summarizes several research subjects I have been involved in on aggregation structures and physical properties of molecular systems in roughly chronological order. The main emphasis of the research subject has been the possibility and effect of internal structural degrees of freedom of molecules beyond their shape as a whole. Remarkably, people in the IFJ and their achievements have significantly affected my research throughout the period.

Introductory Remark

This text sketches, emphasizing the relation to the people in the IFJ, the research journey in which I have pursued the possible effect of the internal flexibility of molecules on their aggregation structures and physical properties. Because of the numerous related literature, I cite only essential papers.

Student Time at Osaka University

I started my research work as a last-year undergraduate student in chemistry under the supervision of Prof. H. Chihara at Osaka University in the spring of 1980. He explained his research theme as molecular dynamics in crystals and conducted experimental studies by calorimetry and nuclear spectroscopies, such as NMR and NQR. I was assigned to the former group, which Dr. T. Atake effectively headed. The professor gave me a research subject of the calorimetric study of structural phase transitions in the crystal of deuterated biphenyl, an organic compound, of which the molecule consists of two benzene rings connected by a single bond. Starting from this compound, I continued the study of phase transitions of *p*-polyphenyls (Fig. 1), longer linear oligomers consisting of benzene moieties, and wrote my thesis for the degree of Doctor of Science. The structural phase transition in *p*-polyphenyls accompanies a seeming change in molecular conformation between “planar” at high temperatures and alternately “twisted” [1]. In this respect, the transitions belong to a new hierarchy different from a simple description of molecular crystals as consisting of rigid molecules, broadly explaining the appearance

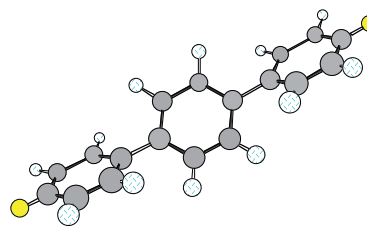


Figure 1: Molecular structure of *p*-terphenyl, the second member of *p*-polyphenyls. Two end hydrogen atoms are colored yellow.

*Department of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, JAPAN. E-mail: kazuya@chem.tsukuba.ac.jp

of plastic and liquid crystals [2–5]. I understood this newness, essential to my research afterward, only at the final stage of my thesis writing.

My first encounter with people at the IFJ happened during my graduate course. The phase transition of biphenyl, the smallest member of *p*-polyphenyl, is displacive distinctly from the order-disorder type of other members and is driven by the so-called soft mode, a lattice vibration of which the frequency points to null at the transition temperature. Since this soft mode brings molecules into the twisted conformation, I imagined an internal soft mode of the molecular twisting vibration. However, I could not materialize the idea: Since the reported works had established severe coupling between the twisting and lattice (translational) degrees of freedom in this crystal, the treatment was too demanding to me. In such a situation, I was shocked by finding a paper written by Prof. Wasiutyński and coworkers [6]. The title was “The Internal Soft-Mode Phase Transition in Solid Biphenyl.” The paper utilized the self-consistent phonon (SCP) theory to incorporate the temperature effect and successfully explained the phase transition. Thus, the authors of this paper became my heroes in a sense. Although I did not reach the SCP approach, I wrote some codes and performed lattice dynamical analyses for the inversion of heat capacities of biphenyl and *p*-terphenyl (the second member) [7]. Essentially, the inversion comes from the so-called phason excitation in incommensurately modulated biphenyl crystal.

At Tokyo Metropolitan University

After spending about one year as a post-doc at the Tokyo Institute of Technology, where Dr. Atake was an associate professor in Prof. Y. Saito’s group, I got a research associate position in a group of Prof. I. Ikemoto at the Faculty of Science, Tokyo Metropolitan University. The Ikemoto group mainly worked on the chemistry and physics of organic conductors, and I was an author of several papers reporting discoveries of new organic superconductors, accordingly. My interest in the effect of internal degrees of freedom on the physical property led me to identify the possibility of glass transitions in widely studied organic conductors. The glass transition in the superconductor with the highest transition temperature (at that time) resolved a mysterious cooling-rate dependence of superconducting properties later at Osaka University [8]. Besides, the professor was broad-minded and allowed me to continue the studies of non-conducting molecular crystals. Indeed, before I identified the glass transitions in organic conductors, I reported the glass transitions due to the freezing of intramolecular motion in crystalline *trans*-azobenzene and *trans*-stilbene [9]. The internal motion to freeze can be regarded as an elementary one in polymer dynamics.

There is a story related to the IFJ in this period. I and a student, Y. Yamamura, now an associate professor in my group, tried to control the twist phase transition by a chemical modification of the molecule under the scope of a unified theory of displacive and order-disorder phase transition developed in the dielectrics community [10]. The highlight is to modify the order-disorder nature of the phase transition of the *p*-terphenyl crystal (Fig. 1). The substitution of hydrogen atoms at the two molecular ends with fluorine atoms did not alter the crystal structure but reduced the transition temperature to ca. 2/3 of the original one [11]. Notably, the low-temperature phase was incommensurately modulated. Here, another paper by Prof. Wasiutyński was important [12]. The paper studied the pressure effects on the phase transitions in biphenyl and *p*-terphenyl and predicted the appearance of an incommensurate phase in *p*-terphenyl. Since fluorine substitution and exerting pressure similarly stabilize the planar conformation, the paper explained the observation. The hero became more incredible than before to me. Placing the twist transitions in *p*-polyphenyls under a unified view [10, 13] enabled us to visit the impurity effect. It simply resembles the mean-field behavior for the order-disorder transition of *p*-terphenyl [14], whereas it is somewhat counterintuitive for the displacive one of biphenyl [15]. A more different impurity from the mother crystal exerts less effect and *vice versa*. We

pointed out the similarity to the localization of vibration.

After we wrote, in a community circular [11], a short account that pointed out at least two types of roles played by internal degrees of freedom in structural phase transitions in molecular crystals, referring to our work on another compound, a letter came to me from Prof. Wasityński. This letter was the first contact with people in IFJ, except for simple reprint requests, which I have no complete record to check. However, at that time, I never expected how the IFJ would be essential in my research.

At Osaka University

A phone call from Prof. M. Sorai, who was granted the Honorary Professor of the IFJ in 2006, triggered my move as an associate professor to the Microcalorimetry Research Center, Faculty of Science, Osaka University, in 1995. He worked in broad fields using calorimetry, including spin crossover phenomena and thermotropic liquid crystals. He had been involved in collaborative research with Prof. J. Janik’s group, which became supported by the intergovernmental agreement between Japan and Poland after 1999. This fact brought me into a new stage of my relationship with the IFJ.

Prof. Sorai did not request any specific research subjects in his group but asked to assist students in working on liquid crystals [16]. The students tackled exotic liquid crystalline phases called the “cubic” phases, and I joined the project. Thus, my research on liquid crystals started subjecting somewhat irregular targets but has continued until now, as I will mention later. When I joined the team, a few series of adiabatic calorimetry, which yields heat capacity for not only liquid crystalline phases but also crystals at low temperatures (ca. 10 K), were complete. Although the calorimetric results indicated the disorder of alkyl groups attached at the molecular end is significant in any liquid crystalline phases, consistent with Prof. Sorai’s finding for other compounds, we needed different ways to proceed. Since some cubic phases possessed the same space group ($Ia\bar{3}d$) as the cubic phase in lyotropics, we started to assess how similar to (or distinct from) the cubic phases in lyotropic systems are in our systems. Considering the severe disorder of the alkyl groups, we hypothesized that they behaved as solvents in the lyotropics. We drew the phase diagram of the binary system with the liquid alkane of a long chain (tetradecane) and compared it with the diagram of neat systems against the chain length. The diagrams resembled each other unless the mother compound had a too-short chain. This finding led us to the concept of a quasi-binary (QB) picture of thermotropics [17]. The other issue we concentrated on was the inverted phase sequence against temperature in two cubic mesogens: SmC phase \rightarrow cubic phase in one series and cubic phase \rightarrow SmC phase in the other series. The chain length dependence of the entropy of transition between them indicated the following: The chain disorder is more severe in the cubic phases than the SmC phase, whereas the core arrangement has better order in the former. The resultant sign of the entropic competition between them governed the phase sequence (Fig. 2) because thermodynamics requests entropy to increase with temperature monotonously [16].

The struggle to resolve the inverted phase sequence led me to recognize the importance of the alkyl groups in many (yet not all) liquid crystals and our ability to enumerate the conformational disorder through

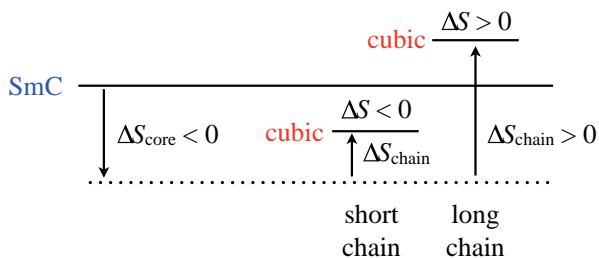


Figure 2: Entropic competition between molecular cores and alkyl chains explains the inverted phase sequence in short ($\Delta S = \Delta S_{\text{chain}} + \Delta S_{\text{core}} < 0$) and long ($\Delta S > 0$) chain compounds. The alkyl groups serve as the entropy reservoir.

analyzing the chain-length dependence of entropy (ΔS -analysis [18]). Many standard textbooks use illustrations depicting cylinders or ellipsoids to explain liquid crystals (see Fig. 4a). Thus, the potential importance of alkyl groups residing in most actual mesogenic molecules has been treated too little. In this respect, I emphasize that Prof. Janik was one of the first researchers to conduct experimental works on the internal dynamics of alkyl groups in liquid crystals [19].

Under the framework of the intergovernmental support of joint research, Prof. Sorai hosted the late Dr. J. Mayer. We conducted experiments on spin-reorientation phenomena in rare-earth orthoferrites, yielding some joint publications. Even after this support ended, Research Center for Molecular Thermodynamics reorganized from Microcalorimetry Research Center in 1999, and its successor has held a payable position for visiting foreign professors. Before my move to the present place, Prof. Wasiutyński, my hero, and Prof. M. Massalska-Arodź spent their time in the Research Center. Many people stayed at the Center afterward.

At the University of Tsukuba

The first paper, co-authored with Prof. M. Massalska-Arodź, was based on the experiments during her stay in Osaka and appeared in 2004 [20]. However, our full-scale collaboration started after my promotion to a full professor at the University of Tsukuba. The first compound, 4TCB (or 4BT) [21], was a member of the mesogenic series n TCB exhibiting the SmE (or CrE) phase (Fig. 3). The SmE phase has traditionally been classified as liquid crystals and considered the closest to ordinary, i.e., ordered crystals. The precise calorimetry established its thermodynamic properties, including the residual entropy of the glassy SmE phase. Subsequent studies of the series ($2 \leq n \leq 12$) revealed the followings [22,23]: The cumulative entropy of transitions from the SmE phase to the isotropic liquid is constant irrespective of the presence of the SmA phase in between, whereas the entropy of transition from the ordered crystal to the SmE phase increases with the chain length by the same slope of the cumulative entropy of n -alkanes. The simple explanation for these findings is that the chain in the SmE phase is molten to the same degree as the liquid alkane. The same observation in another series of the SmE mesogens established the statement. The molten chains are consistent with the positron annihilation experiment [24] and manifest in a notable change in the layer spacing upon a glass transition [25,26]. Considering the most ordered nature of the SmE phase, we concluded that the chains were (almost) fully molten in any liquid crystalline phases because it is implausible that the once-disordered chain recovers its order upon heating. However, the reorder upon heating is not denied in rare cases, such as the above-mentioned inverted phase sequence. Although fundamental theories of liquid crystals have established that simple cylinders or highly-anisotropic ellipsoids can yield liquid crystalline states as thermodynamic states [5,28], the comparison of thermodynamic potentials among crystalline and liquid crystalline states with and without chain entropy indicates that its contribution to thermodynamic potential is significant, and should be essential for liquid crystalline phases to appear as thermodynamically stable phases [29]. This conclusion is consistent with rare liquid crystals without alkyl groups. Our statement is similar to Prof. Sorai’s “Chain melting prepares LC states” [27] but more mechanistic.

In parallel with the entropic study of liquid crystalline states, we have conducted a study to deepen the QB picture. Adding alkane to nematic 7CB induced the SmA phase [30], like elongating the chain (in 8CB) and mixing with a longer member. The phase diagrams could be mostly interposed if we drew them against

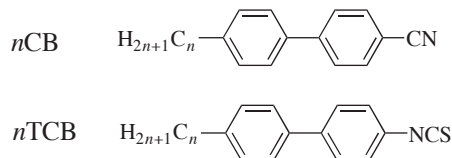


Figure 3: Molecular structures of n CB, the most famous mesogenic series historically, and n TCB, the essential subject of the collaboration.

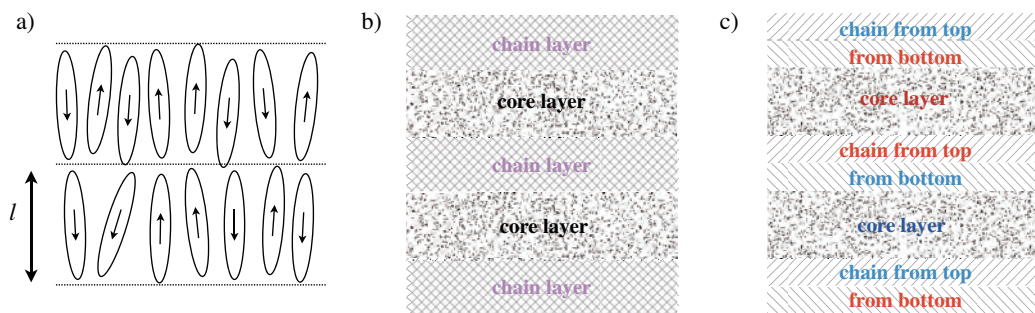


Figure 4: Evolution of understanding of orthogonal smectic phases of core-chain molecules. a) traditional illustration assuming ellipsoids for rodlike molecules; b) micro-phase separated structure; c) micro-phase separated structure with bilayered chain layers.

the averaged chain length [31], calculating which did not distinguish chains attached to the cores or free alkane. However, some details remain different from each other.

Considering the different roles of the core and chain, we wondered where they are in layered liquid crystalline phases. The layered organization would become blurred if we substituted the cylinder or ellipsoid in ordinary illustrations of smectic phases with a core-chain molecule (Fig. 4). Mixing alkane into the SmE phases of n TCB, the sample of our collaboration with the IFJ, offered vital information. Surprisingly, the unit cell, which the SmE phase possesses as the closest phase to ordinary crystals, expanded only in the interlayer direction along the long molecular axis while keeping the in-plane diffractions sharp [32]. This behavior indicates that the incorporated alkanes do not affect the spatial arrangement of cores represented by their centers of electron density. Such a situation is compatible with the micro-phase separated organization (Fig. 4b) and the invasion of alkanes only into the alkane layers. Indeed, the electron density recovered from the X-ray diffractions from the oriented samples yielded the expected form [33]. Since the aliphatic chain and aromatic cores are enthalpically disfavored, the micro-phase separated organization should be fundamental for smectic phases consisting of core-chain or chain-core-chain molecules.

Establishing the micro-phase separated organization of smectic phases enabled us to proceed further. We concentrated the orthogonal smectic phases, where on average, rodlike cores parallel the layer's normal. Although it was well established that the repeat distance of layers increases with increasing the chain length, no detailed analyses were available for its increment. Our search for reliable data over the established literature database specialized in liquid crystals revealed that the increment was classified into two groups, $1.9 \text{ \AA} (\text{CH}_2)^{-1}$ and $1.4 \text{ \AA} (\text{CH}_2)^{-1}$, if we restricted the search for mesogens reasonably similar to typical n CB and n TCB with only a single chain at a core end [34]. Based on our understanding of the fully molten chain in any liquid crystalline phases, the increment per methylene should be shorter than 1.2 \AA geometrically calculated for the all-*trans* conformation of the alkyl group. We could infer the maximum increment as 1.0 \AA from the research results on lyotropic bilayers [35]. Since the two identified increments were larger than this estimate, at least two layers of alkyl chains were necessary (Fig. 4c). The alkyl layers in these smectic phases were of bilayers coming from both sides of the layer. The increment of $1.9 \text{ \AA} (\text{CH}_2)^{-1}$ was reasonably close to twice the expected increment, implying the simple bilayer of alkyl groups directing the layer's normal. On the other hand, we had no choice except that each chain was inclined by $\arccos(1.4/1.9) \approx 43^\circ$ from the normal to rationalize the other increment, $1.4 \text{ \AA} (\text{CH}_2)^{-1}$. Interestingly, we could identify such a bent structure with chain disorder in the crystalline phase of another collaboration compound [36]. Thus, in the latter case, the chains are inclined from the normal if averaged over a short time and are normal to the layer seen over a

long time with a lateral expansion. These findings implied a new scheme was necessary as an independent dimension to describe simple layered liquid crystals. Since the averaged molecular structure is not a simple rod for the latter, it would be inconvenient for molecular diffusion normal to the layers. Indeed, some data implied that the electron density modulation inferred from higher-order diffractions is more distinct from the sinusoidal one in the former. We are studying the effects on other physical properties.

During the above studies at Tsukuba, I, together with Prof. Massalska-Arodz, got a grant from the Japan Society for the Promotion of Science (JSPS) and the Polish Academy of Science (PAN) under the bilateral collaboration program in 2014-2016. This grant enabled the exchange of graduate students bilaterally and my visit together with Dr. Yamamura to the IFJ. Besides, we accepted two JSPS-supported post-docs, Drs. R. Pelka (2005-2006, currently at JFJ) and T. Rozwadowski (2018-2020, Rzeszów Polytechnic), with whom we have recently published papers [37,38].

Finally, we return to the issue of the cubic phases. Although our QB picture and supporting data implied the structure of the one phase with a space group, $Ia\bar{3}d$, would resemble lyotropic ones with the same space group, we needed another idea. The lyotropic $Ia\bar{3}d$ phase was widely accepted to involve a minimal surface known as gyroid and two-interwoven jungle gyms. The two incompatible parts reside separately. Namely, if the cores are around the edges of jungle gyms, the alkyl terminals decorate the gyroid surface. Our problem was to decide it. The Babinet principle of diffraction crystallography says that we have identical diffraction intensities from the true and complimentary electron density distributions except for the null scattering vector. Thus, this principle means we cannot solve this problem by solely analyzing the intensity data. We need outside information.

The dependence of the ratio of two strong diffractions on the chain length implied that the chains decorated the gyroid surface. Based on this information, we successfully recovered the electron density distribution utilizing the maximum entropy spirits [39]. The density clearly indicated that the rodlike cores are normal to the jungle gym bars and successively rotated to fit the symmetry requirements that the rods at the junctions are normal to the plane that the three gathering bars determine (Fig. 5). The senses of the twist (successive rotation) on two jungle gyms are opposing according to the symmetry, resulting in achiral aggregations. In fact, the gyroid phase is interrupted by another cubic phase on the phase diagram against the chain length. The electron densities revealed that this reentrance to the gyroid phase by chain elongation accompanies the thickening of the core layers. In reality, the layer is single-layered in the short-chain region and double-layered in the long-chain region. This change alters the effective volume fractions of two incompatible components, consistent with the expectation inferred from the understanding of lyotropics. The knowledge of the molecular packing in the orthogonal smectic phases implied the packing in this complicated phase along the body diagonals [40].

The cubic phase interrupting the gyroid phase on the phase diagram has been known but unrevealed long. The report of its chirality canceled all assumptions and discussions about its aggregation structure. Since chirality indicates the search space for correct phases of structure factors (Fourier components of

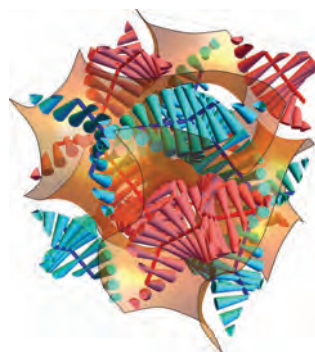


Figure 5: Idealized illustration of molecular packing in the $Ia\bar{3}d$ phase. The gyroid surface, a triply periodic minimal surface, divides the space into two, in each of which continuously rotating (twisting) molecules of an anti-spindle shape decorate a jungle gym (*srs* net). Only molecules on bars are drawn.

electron density distribution) are continuous spaces in dimension of the number of independent diffractions, we have been darkness without any symptom of light. However, we have recently reached its plausible structure [41] by utilizing a new crystallographic algorithm developed by my collaborator, Prof. Oka, at Shizuoka University [42]. Although the work is out of our collaboration with the IFJ, the story fits this text well as my final topic because molecular dynamics is vital to the algorithm. As far as I know, this algorithm is the first that positively accepts severe disorders in multi-continuous organizations frequently appearing in lyotropics. His idea while assuming significant diffractions in hands is as follows. Supposing dynamical disorder, we can assume molecules diffuse, resulting in smearing out of the electron density. This smearing suggests flattened electron density distribution. Thus, we may expect a smaller difference between the maximum and minimum in electron density for a more plausible distribution. Minimizing their difference in the Fourier-synthesized electron density is an actual calculation in iterations. Since no guarantee of converging to the correct solution exist in this iteration, another indicator is necessary. This indicator is essential in the algorithm. He identified that smooth diffusion of molecules should result in rodlike (cylindrical) or planelike (flat plane) electron density and that the isolated minimum and maximum were implausible. Since the determinant of the Hessian matrix, consisting of the second-order partial derivatives of the electron density, vanishes for cylindrical and sheetlike distribution, he anticipated that its smaller integral over appropriate space is more plausible. The algorithm worked very well for test data [42].

Applying this algorithm to the old diffraction data from this chiral cubic phase revealed a network structure as expected but with an unexpected space group $I2_13$ (Fig. 5). The structure contained two interwoven nets known as *noh* in reticular chemistry [43]. This net shares with the *srs* net of the $Ia\bar{3}d$ phase the property that all junctions of jungle gyms are three-way. We could construct a molecular packing model similar to the gyroid phase. The two nets are homochiral in vertex geometry and expected core arrangements with successive twists. Thus, unlike the gyroid case, there is no interface between counter-chiral domains. Although the achievement in the lyotropics fields [44] significantly helped the field of cubic phases in thermotropics, this result may highlight an intrinsic difference between the thermotropics of rodlike molecules and lyotropics. The study in this context is underway.

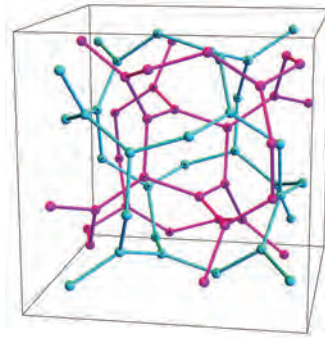


Figure 6: Interwoven *noh* nets identified in the chiral cubic liquid crystals. The unit cell contains ca. $2 \cdot 10^3$ molecules, larger about twice than the $Ia\bar{3}d$ phase. This illustration assumes the idealized nets and has no chirality, accordingly.

Concluding Remark

My research has focussed on molecular dynamics, the resultant structural organizations in general and the possibility of internal dynamics or conformational change in molecules. Molecular crystals and liquid crystals have been my main and good playground. I have not fully understood their variety, but I have identified some exciting examples. I published a book based on my experience from Springer [45]. During its preparation, my friends at the IFJ helped me considerably. The relationship with them was essential to my whole research, as described. I express my sincere thanks to them. Readers interested in this text are guided to the book before consulting the cited individual papers.

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Instytut Fizyki Jądrowej PAN
ul. Radzikowskiego 152
31-342 Kraków

www.ifj.edu.pl
e-mail: dyrektor@ifj.edu.pl
tel.: +48 12 662 80 00
fax: +48 12 662 84 58