

Lars Onsager

(1903–1976)

Biman Bagchi

Lars Onsager can be rightfully considered as one of the most influential theoretical physical chemists and theoretical physicists of the twentieth century. He is often grouped with Linus Pauling and Paul Flory, representing the three pillars of theoretical physical chemistry. The impact of Onsager's work continues to be felt to date.

Onsager was born as a Norwegian on 27 November 1903, but he spent much of his academic life in the United States of America. He was awarded the Nobel Prize in Chemistry in 1968. Onsager's pioneering contributions span a wide range, from classical electrochemistry to condensed matter physics to quantum fluids, and everywhere he introduced elegant but realistic models, which he solved exactly using mathematical techniques that he often developed himself. He is often cited, even today, as the "best calculator" that theoretical physics and theoretical chemistry has ever seen. Onsager breathed his last on 05 October 1976 in Florida, USA. Onsager was buried next to his longtime colleague, another distinguished theoretical physical chemist at Yale University, John Gamble Kirkwood, at New Haven's Grove Street Cemetery.

In one of his best-known works, Onsager presented an exact analytical solution for the thermodynamic properties of the two-dimensional (2D) Ising model [1]. This work is still considered one of the most sophisticated theoretical analyses of any problem ever carried out in science. He obtained the exact solution for the 2D Ising model in the absence of an external field. Incidentally, the three-dimensional (3D) Ising model has still not been analytically solved.

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Figure 1. Lars Onsager was awarded the Nobel Prize in Chemistry in 1968. Onsager's pioneering contributions span a wide range, from classical electrochemistry to condensed matter physics to quantum fluids.



In an Ising model, one considers a magnetic spin to be present at each lattice point. A spin interacts only with its nearest neighbours.

at each lattice point. A spin interacts only with its nearest neighbours. When two neighbouring spins point in the same direction, the total energy of the system (the Hamiltonian of the spin system) decreases by an energy J . Similarly, when the neighbouring spins are in an antiparallel configuration, the energy goes up by J . As was mentioned earlier, only the nearest neighbour interactions are counted.

This is a simple, almost a toy model of an interacting system. However, the Ising model constitutes one of the very few models of interacting systems that can be solved analytically in one and two dimensions, and these solutions are of vital importance. The one-dimensional (1D) solution was obtained by Ernst Ising in 1925 [2] as his PhD thesis. The results are uninteresting in some sense because the 1D Ising model does not exhibit any phase transition as J is increased or the temperature T is lowered – both have the same effect. However, the 2D Ising model exhibits a phase transition¹, an order-disorder (paramagnetic to ferromagnetic) transition at a critical temperature T_c in the absence of any magnetic field. It exhibits a first order phase transition in the presence of the magnetic field [3].

Onsager's solution played and continues to play a pivotal role in the theory of phase transitions. This remains the only exactly

¹See Classics Section, Scaling Laws for Ising Models Near T_c , *Resonance: Journal of Science Education*, Vol.21, No.10, pp.951–961, 2016.

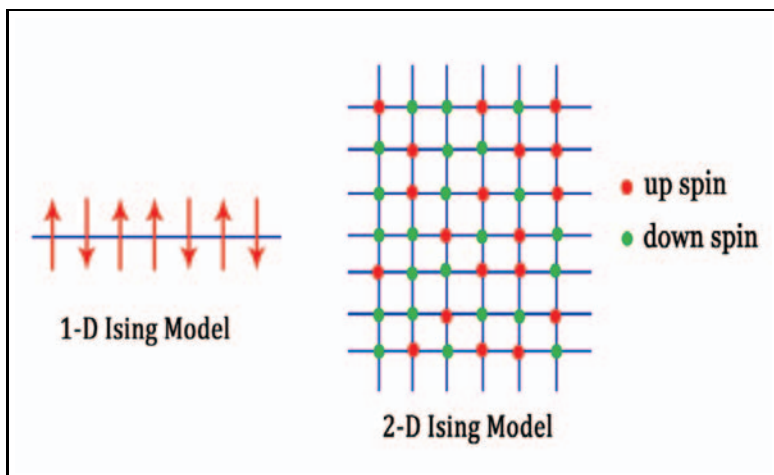


Figure 2. 1D and 2D Ising models. In the 2D model, red dots represent up spins while green dots represent down spins.

solvable non-trivial Hamiltonian model of an interacting system (not counting the solution in the presence of the magnetic field). The most important use of the Onsager's exact solution of the 2D Ising model is the value of the critical exponent that it provides [4]. The solution showed that the mean-field theory was wrong (as was expected and further expounded later). The exact solution served as the essential test that all numerical methods applied to various problems (mostly in three dimensions) had to pass. Even after almost 75 years, the appeal and importance of Onsager's solution have not decreased a bit. The reason is that all the phase transitions are actually quite similar to each other, especially near the critical temperature. This universality has made the exact solution of Onsager even more useful.

The second, or rather, equally famous work of Onsager is in the area of non-equilibrium statistical mechanics. In a seminal paper published in 1931, he established important reciprocal relations for irreversible processes that essentially gave birth to non-equilibrium thermodynamics [5, 6]. Let us look at the importance of this work. In order to begin any study on time-dependent phenomena, we need to establish a relationship between the imposed force (\mathbf{X}) and the resultant flux (\mathbf{J}). In nature, it is observed that near equilibrium systems, fluxes are linearly proportional to the imposed force [7]. Examples of such forces are the temperature

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gradient across a system, concentration gradient and the electric potential gradient in an electrolyte solution. This linearity means that we can write an equation of the form $\mathbf{J} = \mathbf{L}\mathbf{X}$ where \mathbf{L} is a matrix that contains coefficients that quantify the response. If we consider \mathbf{J} as a vector of dimension n , then \mathbf{J} is an $n \times n$ matrix. Let us provide a concrete, almost everyday example of \mathbf{J} , \mathbf{L} and \mathbf{X} . When we set up a temperature gradient across a metal plate that contains a junction of two metals with different conductivities, we find that the system also generates a voltage difference between the two ends. This voltage difference can be used to light a lamp, for example. This is known as the Seebeck effect [3]. This is actually quite amazing. Many of us have seen this in museums. That is, “a temperature difference not only gives rise to thermal conduction – the transport of heat from higher temperature to lower temperature – but also a voltage difference”. This is an example of cross-relation. Similarly, when we send an electric current across a junction of two different metals, heat is generated. Thus, an electrical potential gradient and the flow of electric current gives rise to a temperature gradient between two conductors. This is called the Peltier effect [8]. Thus, in addition to pure terms, like thermal conduction in the Seebeck effect and electrical conduction in the Peltier effect, we also have reciprocal cross-effects. Such phenomena are crucial as they are present almost everywhere.

Onsager proved that these reciprocal cross-terms are equal, that is $L_{ij} = L_{ji}$ (popularly known as Onsager reciprocal relationship). This was an enormously important result that paved the way for the development of non-equilibrium statistical mechanics, as already mentioned. These relations were ultimately explained by time correlation function formalism, which is the heart of linear response theory.

Onsager’s results on reciprocal cross-terms was an enormously important result that paved the way for the development of non-equilibrium statistical mechanics.

Onsager’s paper of 1931 was a significant milestone for two more reasons. It introduced the principle of ‘microscopic reversibility’ that states that at equilibrium, each step must be individually balanced in population change. This is sometimes also referred to as the ‘principle of detailed balance’. Microscopic reversibility



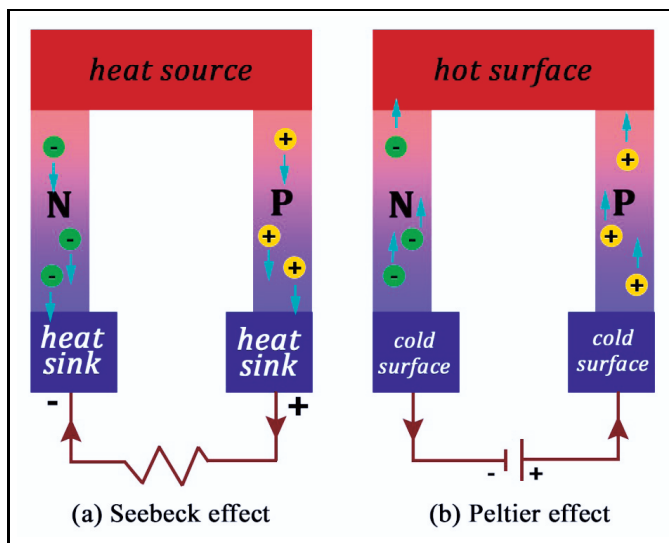


Figure 3. (a) Seebeck effect – electric current is generated between a hot and a cold surface; (b) Peltier effect – application of potential gradient between two surfaces generates a temperature gradient.

puts constraints on rate constants and is widely used in the study of chemical and biological reactions. The second significant concept that evolved from the 1932 paper was the rate of entropy production. This concept ultimately led to Prigogine’s formulation of the principle of the minimum value of the rate of entropy production at a steady state maintained at far from equilibrium [7]. Although Prigogine received Nobel Prize for this work, it has remained controversial.

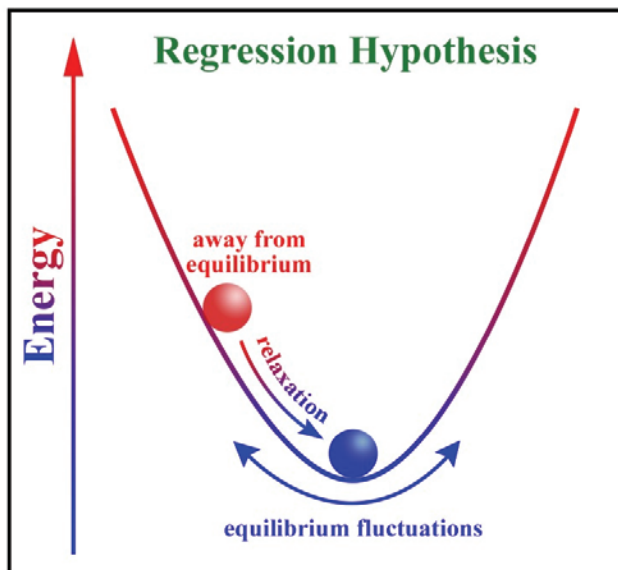
Another fundamental concept that can be traced back to Onsager’s 1931 paper is ‘Onsager’s regression hypothesis’. This hypothesis states that for a small perturbation from equilibrium, the system returns to equilibrium at the same rate as a fluctuation does at equilibrium. The hypothesis can be explained in the following way.

Figure 4 shows an energy landscape that represents a system both at equilibrium and away from equilibrium. Equilibrium fluctuation is represented by the normalized time correlation function $f(t)$.

$$f(t) = \frac{\langle \delta X(0) \delta X(t) \rangle}{\langle (\delta X(0))^2 \rangle}. \quad (1)$$

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Figure 4. Representation of a system in equilibrium (blue) and away from equilibrium (red) on an arbitrary energy landscape. Onsager's regression hypothesis connects equilibrium fluctuations to the relaxation from a non-equilibrium state.



Here, $X(t)$ is the time-dependent property of the system whose fluctuations are studied. When perturbed, the system moves away from the equilibrium. It relaxes back to the ground state with a change in $X(t)$ given by

$$g(t) = \frac{\Delta X(t)}{\Delta X(0)}. \quad (2)$$

According to the regression hypothesis,

$$f(t) = g(t). \quad (3)$$

That is, this hypothesis allows us to relate decay of a non-equilibrium state in terms of a fluctuation time correlation function at equilibrium. This hypothesis greatly reduces theoretical analysis because calculations at the equilibrium state are much simpler than those at the non-equilibrium state. The regression hypothesis is closely related to (and often considered the same as) the linear response theory developed by Kubo and others. Much appreciated by the community, Onsager was awarded the Nobel Prize in 1968. The Nobel community said, "The great importance of irreversible

thermodynamics becomes apparent if we realize that almost all common processes are irreversible and cannot by themselves go backwards. As examples can be mentioned – conduction of heat from a hot to a cold body and mixing or diffusion. When we dissolve a cold lump of sugar in a cup of hot tea these processes take place simultaneously.” Onsager is known for at least four more landmark works that we discuss below. Each of these works created a new area of research.

In a remarkable intellectual feat, Onsager, when he was just 25, corrected the Debye–Huückel theory² of electrolytic solutions by incorporating the electrophoretic effect that was neglected in the original formulation [9]. It is well-known to the students of electrochemistry that a moving ion experiences two types of retardation – one arises from charges on the ion atmosphere while the second one arises from the movement of the atmosphere in the opposite direction. Debye and Huückel neglected this second term, corrected by Onsager. That is why it is known as Debye–Huückel–Onsager theory.

The story goes that Onsager travelled from Norway to Zurich to meet Debye and confronted him with the assertion that Debye’s theory was wrong. Initially, Debye did not agree. But eventually, he found that Onsager’s logic was sound. So impressed was Debye that he offered him the position of an assistant researcher in his group and Onsager moved from Norway to ETH, Zurich to join Debye’s group.

Subsequently, Onsager developed the theory of concentration dependence of viscosity of an electrolyte solution which contains the interesting $(1/480)$ term that was later derived by the mode coupling theory. In this work, Onsager teamed up with his student Fuoss and the theory is known as Onsager–Fuoss theory [10].

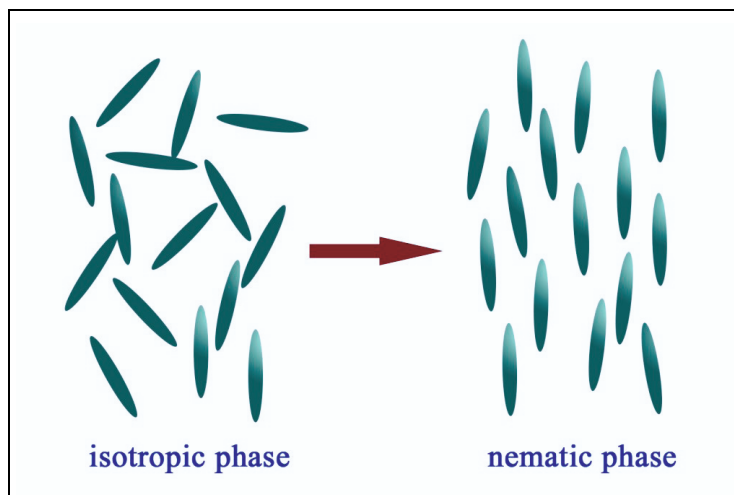
In another landmark work, Onsager developed a beautiful theory of dielectric constant of a dipolar liquid where he introduced the concept of the reaction field which finds wide use even today [11]. The expression derived by Onsager of the dielectric constant of a dipolar liquid was simple and elegant. This was subsequently

²See A K Shukla and T Prem Kumar, Peter Debye and Electrochemistry, *Resonance: Journal of Science Education*, Vol.15, No.12, pp.1068–1072, 2010.

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Figure 5. Crystallization into nematic liquid crystal phase from isotropic liquid phase.



extended by Kirkwood and is often cited as Onsager–Kirkwood theory, thus combining the names of the two outstanding theoreticians. Onsager’s theory was later extended to obtain an expression of frequency dependent dielectric function, thus completing a close connection with dynamics of dipolar liquids.

The ‘Onsager model’ of liquid crystals showed his uncanny ability to build a model that was solvable and at the same time allowed him to extract the essence of the problem. In this work, he modelled the nematogens as a system of thin long rods.

His amazing diversity of fundamental contributions remained a topic of discussion among the community. The ‘Onsager model’ of liquid crystals showed his uncanny ability to build a model that was solvable and at the same time allowed him to extract the essence of the problem. In this work, he modelled the nematogens as a system of thin long rods [12]. He then proceeded to obtain the second Virial coefficient of this system and showed that in the limit of long rods, below a certain temperature, the second Virial coefficient of the system could become negative, signalling the onset of orientational order.

Onsager also introduced the concept of quantum vortices that proved useful in various quantum phenomena [13]. Quantum vortices are excitations that play an important role in superfluid transitions. This idea was further developed by Richard Feynman, and the relevant theorem of quantization of vortex is embodied in a theorem known as the Onsager–Feynman circulation theorem. The concept of quantized vortex found use in type II supercon-

ductors.

Onsager had a difficult time at various US universities. He was a poor teacher and was not given tenure both at Johns Hopkins and Brown University. At Brown, his course was known as ‘sadistical mechanics’. At Brown, the Chairman wanted to keep him but was not successful as it was a time of fund cutting due to the great depression in the USA, and his poor teaching record did not help the matter either.

My own thesis adviser at Brown University, Julian H. Gibbs, overlapped about a year with Onsager at Cambridge where Gibbs was a Guggenheim Fellow. Gibbs told me that Onsager used to talk a lot with him because they two were the only Americans in theoretical physical chemistry at Cambridge. Gibbs told me that Onsager was incredibly smart with science, and was quite a jolly and warm guy. Gibbs found Onsager’s approach so high level that he had to struggle to keep up with him. I need to remind the reader that Julian Gibbs himself was outstanding, and his theories of glass transition (Adam–Gibbs, Gibbs–DiMarzio) among others, are well-known.

My mentor Robert (Bob) Zwanzig overlapped with Onsager at the Yale University during the early 1950s when Zwanzig was a postdoc with John Kirkwood and Onsager was a famous Chair Professor. Zwanzig told me several stories that I better chronicle here for posterity.

I start with a famous quote by Onsager that I heard from Zwanzig, “Never build your muscle and then go hunt for a problem. Build your muscle while solving the problem. That is the key to good research.” Many found this an extremely useful advice.

Once Zwanzig’s wife, Frances, was knitting while sitting at a table, and Onsager was passing by. He stopped and told Frances “I see you use European style, not American.” According to Zwanzig, Frances was just amazed that Onsager knew this difference when only a few women knew how to use European needle.

My third story is again from Bob. He told me that his lasting

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– Lars Onsager

image of Onsager was in a departmental party when Lars was sitting in a front chair and happily playing on his accordion a merry tune, oblivious of the rest. Bob told Onsager was good in that too!

Lars Onsager's legacy continues to live on, through his innumerable admirers and followers, and as one of the finest theoretical physical chemist that was ever born.

One cannot but feel amazed (and belittled) by the abilities of Lars Onsager! Towards the end of his life, Onsager became a better teacher, but death cut short the life of such an illustrious man. He died alone at his Florida residence in 1976. But Lars Onsager's legacy continues to live on, through his innumerable admirers and followers, and as one of the finest theoretical physical chemist that was ever born.

I end this write-up with an anecdote that happened just a few months before Onsager's death, at the Banff Conference (in Canada) on radiation chemistry in 1976. Towards the end, Onsager became interested in radiation chemistry and biophysics. At the conference, papers were presented on solvation of a nascent electron created photochemically and measured spectroscopically. While the process of solvation was debated, Onsager suddenly made the comment that the "solvation structure will be formed from outside in." This statement became famous as 'Onsager's inverse snowball picture'. This is indeed found to be true later by detailed calculations. Many of the distinguished participants, of course, realized why Onsager could be right. One of them turned to his neighbour and commented, "the old man still has it." Well, Lars Onsager always had 'them'.

Acknowledgement

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Suggested Reading

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