Perspective

Cavity and reaction field: "robust" concepts. Perspective on "Electric moments of molecules in liquids"

Onsager L (1936) J Am Chem Soc 58: 1486

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Abstract. Onsager's model to describe the behavior of molecules in liquids is put in the appropriate historical context of the evolution of chemistry. Some key aspects of the model that justify its success in the past decades are discussed, with emphasis on general features shared with many other good models we have in theoretical chemistry and that should be kept in mind for the development of further models: congruence with physical principles, simplicity and robustness. The present and future evolution of this model is briefly considered, with the aim of learning better from this example how to exploit our studies for the advancement of theoretical chemistry.

Key words: Onsager model – Solvation methods – Models in chemistry

1 The evolution of chemistry in the first decades of the century

The first readers of Lars Onsager's paper "Electric moments of molecules in liquids", published in the August 1936 issue of the *Journal of the American Chemical Society* [1], probably considered it as a further contribution to a well-established line of research developed in the preceding decades.

One of the main steps in the evolution of chemistry took place in a period of approximately 30 years, beginning with the last decade of the past century; it was essentially led by physicists. Sound experimental evidence for the atomistic description of matter and of its organization into molecular assemblies in the gas, solid, and eventually the liquid phase (1905), prompted the development of detailed models and of a conceptual comprehensive framework in which large-scale and submicroscopic aspects were harmonized, with emphasis on the real existence of the elementary building blocks, atoms and molecules, of this theory.

It was an approach to study matter considerably different from that of traditional chemistry, accustomed to using analogous concepts, but as heuristic tools, without resolute attempts to organize them into a comprehensive and "realistic" theory of matter: important exponents of the chemical community strongly sustained the view that attempts to replace the traditional chemical approach with the new one were futile, and probably misleading and dangerous.

We know now that the physical approach, with the support of new theoretical methods such as statistical thermodynamics, and with the contribution of the vigorous expansion or renovation of many experimental techniques (spectroscopies of various kinds, X-ray diffraction, etc.), organized in a new branch of science, chemical physics, "conquered" the whole realm of chemistry within a short time.

There are no objections, I think, to accepting this historical interpretation: the effort of many scientists, including among them eminent leaders such as Boltzmann, Planck, Einstein, Lorentz, and Debye, to name a few, later crowned by the new formulation of quantum mechanics, has provided the basis for a description of material systems which unifies physics and chemistry and constitutes the conceptual world in which we, theoretical chemists, are working.

2 The Onsager model

Among the various directions along which research progressed is the investigation of the properties of polar molecules. An outstanding contribution to this field was made by Debye: we quote his 1912 paper [2] and his 1929 book [3] as examples. Onsager's paper is directly related to this line of research. Debye's dipole theory [2] is quoted in the first line of the article, and then analyzed and greatly modified. Typically, no reference is made to quantum models. Everything is presented in a classical formulation, even if references to recent Pauling articles [4] indicate that quantum theory was present in the background.

There are, therefore, reasons to support my guess that among the first readers of the Onsager paper a large

number considered it a modification of the Debye formulation of molecular dipole theory for condensed systems (a theory, we remark, based on older studies of physicists, such as Mossotti [5], for example).

More attentive readers noticed other aspects of the Onsager paper. Kirkwood [6] in 1938 remarked that Onsager introduced a real cavity, conceptually quite different from the Lorentz cavity which is just a mathematical device.

The "reality" of the Onsager cavity is one of the reasons which prompted me to select this paper for this New Century Issue: this is one of the further steps in the development of "real" models using the physical approach. This is not the only reason, however, Onsager introduced new concepts, that of the reaction field and that of the cavity field, with a clear and transparent physical basis, and devised a simple model based on a few parameters with physical meaning, and easily managed computationally.

There is no need to summarize Onsager's paper. The essential point is given by his model of a molecule M within a cavity of appropriate shape encircled by the molecules of the polar solvent. If the liquid is not subjected to external fields, there will be a field of local origin, called a reaction field, $\mathbf{R}$, which depends on the displacements of the surrounding molecules produced by the permanent multipoles of M and which at the same time modifies the molecular charge distribution via the polarization functions of M. In the presence of an external field, $\mathbf{E}$, there will be a cavity field, $\mathbf{G}$, related to $\mathbf{E}$ and to the shape of the cavity. In conclusion, the field acting on M will be $\mathbf{G} + \mathbf{R}$, the first term only contributing to the orienting force-couple in the case of the presence of an external field.

This general formulation is reduced to a simple form. The molecule is represented by a permanent point dipole μ, and by a polarizability, α, the cavity has a spherical shape with radius a, and the surrounding molecules are reduced to a continuum dielectric medium with fixed dielectric constant.

Onsager is well aware of the limitations thus introduced within his model. He discusses problems about the appropriate choice of the cavity radius and of its dependence on thermal volume changes; he also considers the generalization of the model to other cavity shapes: both subjects are treated briefly but with illuminating remarks about reciprocity and symmetry relations holding in the model. In his article Onsager examines other aspects of the physical problem, such as the effects of hydrogen bonds and the changes in the model on passing from pure polar solvents to mixed polar–nonpolar solvents and finally to nonpolar solvents, and the limitations introduced by considering the medium as a linear continuum dielectric, neglecting aspects related to dielectric saturation or compression, as well as aspects related to the discrete structure of the medium.

These remarks reveal that there was an extended and detailed analysis of the properties of liquid systems in general, under the formulation of the model and its applications to demonstrate the nonexistence of spurious Curie points (which was his starting point) and to present an improved theory for the dielectric constants of pure liquids and solutions (which constitutes the main body of the article).

This accurate analysis is accompanied by a rigorous formal elaboration of the model to which I shall return later. A few years before Onsager, Bell [7] presented a model consisting of a dipole, μ, within a spherical cavity immersed in a continuous uniform dielectric medium. This model is quite similar to the Onsager one, but is summarily treated and with some errors; now it is completely forgotten, and is only quoted in extensive reviews of the subject.

3 The success of the Onsager model

Onsager model has not been forgotten. It has been widely used, and is still in use. One of the reasons for this popularity is its very simple mathematical expression. The simplicity of the model is another point to which I shall return later. We have to recall that in 1936, and for many years after, the most sophisticated computational tool available in our laboratories was the slide rule: to use Onsager's formulas a slide rule is not necessary: the back of an envelope and a pencil are sufficient.

Easily obtaining the result is not sufficient to assure the popularity of a formulation. In the Onsager case a reason for the success is the physical "robustness" of the model. It may be modified with little effort and adapted to many different problems. Among these I quote its extension to describe solvent shifts in electronic spectra and to estimate dipole moments of molecules in their excited states. The chemical spectroscopic literature is full of applications of the Onsager model, both in the past (I quote here as examples the texts I have in my room, Refs. [8–10]) as well as at present. The popularity of this model has led to a phenomenon which occurs in several similar cases. There are few quotations of the original Onsager paper in this literature: as the model's so often applied, there is no reason to quote its source. As a sort of compensation there is the adjective "onsagerian", which has found use in some specialized literature.

The model is still in use, and I quote here a recent remark as a bridge to pass from the examination of some aspects of the Onsager paper to more general considerations. Lombardi [11] recently remarked that there are important discrepancies between the dipole moments of molecules in their excited state obtained via solvatochromic shifts, as is normal practice, with respect to the more precise values derived from Stark effect measurements. Solvatochromic values are currently obtained by applying Onsager's formula, adapted in the 1950s to the problem of solvatochromic shifts, but without other changes with respect to the original model. This is another point I must stress: the intrinsic, or maximum, accuracy of the results given by a model.

The chemical elaboration of models derived from the "realistic" physical approach has always been accompanied by the search for higher accuracy. Chemistry is the science of subtle differences among similar systems, a problem not so important in physics. I give here an example I use with my students: in physics there is not much

difference between methanol and ethanol; in chemistry we rely very much on their differences. These differences are substantial when we are looking, for example, at the very different chemical effects produced by the ingestion of small quantities of the two substances in living bodies.

So, good models for chemical applications must be robust and flexible, allowing more detailed descriptions of the system and of the property under examination. Onsager's model has these positive features. In the last two decades it has been widely used with important modifications permitting more realistic descriptions of the systems, but keeping the essential points: the cavity, the reaction field, and the cavity field.

The methods now in use range from semiclassical to very sophisticated quantum mechanical descriptions of the solute, permitting the study of solutes of very different size, from a single electron to molecules composed of several thousands of atoms. The solvation methods are now applied to a very broad range of properties, from the evaluation of solvation energies to the study of reaction mechanisms to the analysis and prediction of solvent effects on molecular properties of a very complex nature, such as electro-optical and magnetic properties. For many properties the results are within the error bar of the experimental results, for others they are not far out, and complete agreement with experiment will probably be reached by further refinements in the computational formulation of the model. For many others there are no experimental results to compare with, and the model predictions are used as a first, but reliable, guess.

4 The "robustness' of the Onsager model

It is instructive to examine some points of the evolution of the Onsager model to show better its robustness.

4.1 The cavity shape

There are no intrinsic reasons in the model to keep a spherical shape for the cavity or to only extend the model to other regular cavities, such as the ellipsoids considered by Onsager. Efforts to keep a spherical shape for the cavity may lead to absurd results: see, for example, the remarks expressed by Luzhkov and Warshel [12] about its use for ion pairs. The most convenient shape is based on the van der Waals envelope of the molecule, modified by factors related to the finite size of the solvent molecules: the solvent excluding surface may be a first acceptable description. Today models adopt cavities with these irregular shapes.

4.2 The description of the solute

The point-dipole approximation used by Onsager is not essential: higher multipole moments have been progressively included in the models with spherical or ellipsoidal shapes. Important progress has been the introduction of quantum mechanical descriptions of the solute. This change created new ways of using Onsager's model.

The first is the direct calculation of polarization effects without the use of empirical values of α. Polarizability alone is not sufficient to achieve chemical accuracy; better results can be obtained by using group polarizabilities (and hyperpolarizabilities) at the cost, however, of a proliferation in the number of parameters of dubious quality. The direct quantum mechanical calculation avoids these problems and introduces a new dimension to the model. The Schrödinger equation is, in fact, no longer linear: this leads to a refinement of the model (We remark that in the Onsager formulation there was no influence on $\mathbf{R}$ of the polarizability enhancement of the solute dipole. This was introduced in 1938 by Böttcher [13], but was limited to the original dipole-only model.) and opens the way to "robust" extensions of the model to nonequilibrium problems.

Another consequence of the use of a quantum mechanical description of the solute is that we are no longer obliged to rely on multipole expansions of the solute charge distributions. They may still be used, of course, but other options are open, such as to use the quantum mechanical charge distribution directly or to derive from the quantum mechanical charge distributions other parameters, local charges, for example, explicitly defined to reproduce the solute field in the regions of interest and thus reducing computational costs.

A third important consequence is the possibility of extending the field of application of the models to all the properties of the solute, as we have already remarked. In particular, the solvatochromic shifts and the related excited-state dipole moments we mentioned can now be computed at a level attaining chemical accuracy.

4.3 Solute-solvent interactions

We have already mentioned Onsager's warnings concerning possible limitations of his model due to an incomplete description of solute–solvent interactions. All the points he considered have now been examined: it would be too long to give a resumé of the conclusions and of the studies still in progress. Suffice it to say that for all the possible limitations of the model he considered there is a positive answer based on a physically reasonable modification of the model. We add that there are solutions for other limitations Onsager has not considered, the first being related to the intrinsic quantum mechanical overlap of the solute and solvent electron distribution, on which much work has been done [14] and the second to the presence of quantum dispersion contributions to the solute–solvent interactions (the latter being inserted in the reaction-field framework by Lindner [15]).

In this short summary of recent extensions of the Onsager model to illustrate its robustness I have not given recent references. It is not my intention to review here modern continuum solvation methods. Interested readers are referred to a rather comprehensive review covering the pertinent literature from the beginning to recent times [16].

This said about the robustness of the model, I now consider the other points I stressed in the preceding discussion.

1. *The simplicity of the mathematical formulation*. This has already been discussed. In passing to the modern formulations of the model this kind of simplicity has been lost. We have to consider, however, what simplicity now means. We are no longer in the time of the slide rule, and computers are pervasive. Simplicity means codes easy to use, well documented, not requiring skilled operators and complex computer structures, and especially models clearly related to the physical features of the problem.

2. *Reality of the model*. This is a different way of formulating the request that the model should be clearly connected with the physical principles and with the specific physical properties of the system. Good models share this characteristic: other models may be used, but their range of application is limited and is subject to the assumption set out in their formulation. They are not robust models.

3. *Rigorous formal elaboration of the model*. In the Onsager case it has paid off. In extensions made by many researchers, the Onsager lesson of rigor has been conserved in many realizations of the model. The rigor does not exclude the development and use of approximate expressions: theoretical and computational chemistry provides many examples of approximate formulations of robust theories; quantum chemistry is based on approximate realizations of a robust model. Approximate formulations must be accompanied by benchmark studies having as a goal the determination of the intrinsic accuracy of the model. This remark is valid for all the models we use in theoretical chemistry, but in particular for continuum solvation methods which introduce a drastic simplification of the real systems they model.

4. *New concepts*. This last point is the most important. The impact of a model is determined by the quality of the new concepts it introduces: points 1–3 are just additional conditions. Onsager's model has introduced new concepts. More than 60 years have shown their validity and their capability of surviving the revolutionary changes in our methods to describe matter. We have paid attention in the preceding discussion to concepts of the cavity and of the reaction field: also the concept of the internal field, essential to connect microscopic to macroscopic behavior of matter has recently been introduced into the accurate quantum mechanical realizations of the model.

5 About the future

Onsager's model shall continue to be exploited in the new century, and I am confident that further development of this approach shall result in important contributions to the struggle of theoretical chemistry to provide interpretations to the enthusing progress of chemistry more and more aimed to define and to study complex systems. I am also confident that theoretical and computational chemistry will also be able to provide more concrete contributions to the advancement of our discipline by modeling new systems with specific properties, by suggesting new experiments, in a continuous joint effort with other specialists.

The status and role of the Onsager model is not unique, of course. Looking at the provisional list of contributions to the New Century Issue, I notice many other robust models which introduced new concepts. This listing is surely not complete; in addition other proposals of new concepts are buried in the literature because of lack in the proper development of the model. However, we have not to congratulate ourselves on the number of models we have been able to develop or to lament for what we have missed: we have to look to the future.

My last remarks concern this point. The new century coincides with 70 years of application of quantum theories to chemistry. Two generations of theoreticians have spent their scientific lives applying quantum mechanics to chemistry. There are no doubts about their successes or about the necessity of continuing along this way. For the future we cannot, however, limit ourselves to a refinement of our methods and codes. We need new concepts, new models, new methods, and new strategies. The new concepts we are searching for are not limited to the realm of the physical approach to molecular systems, but also concern mathematics, information theory, and other scientific disciplines. Methods and strategies should introduce a more integrated use of the considerable body of knowledge we have, and that is continuously growing.

I do not have the space (nor the intellectual strength) to develop these remarks into a more coherent and detailed research programme. Substantial progress in science can be achieved with the aid of general planning, we have had several examples in our past and recent history, but is often derived from an ingenious look at the problems arising in the study of a specific subject. This second way of introducing innovation is apparently more casual and more modest, but is potentially rich with results.

I urge the readers of this issue to develop every opportunity they have to do it. Science strongly needs these efforts.

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