

## **CREATIVITY AND RATIONALITY IN A LOCAL SCIENTIFIC CONTEXT: THE CASE OF VAN DER WAALS' $\psi$ -SURFACE.<sup>1</sup>**

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### ABSTRACT

The discovery of the  $\psi$ -surface is examined as a solution to a specific problem-situation, the thermodynamic study of binary mixtures. I try to reconstruct all the constraints van der Waals had to comply with, technical, methodological or even ontological, before rationally arriving at the specific solution as the alternative which best suited his purposes. The notion of locality of scientific practice is stressed, especially with regard to the formation of new disciplines.

### 1. *Introduction*

In order to understand the formation of disciplinary boundaries, one often has to study the particularities of local (or, according to some, research) schools. Examining, for example, the formation of physical chemistry necessarily obliges one to study the ways the discipline was viewed by the practitioners in the various local schools. The differences, methodological as well as ontological, between, say, Ostwald's group in Leipzig and Noyes' group at M.I.T., have been as decisive in defining the boundaries of physical chemistry as was their common commitment in using physics for the analysis of chemical phenomena and, more specifically, in exhausting the possibilities provided by thermodynamics for chemistry. Another example is quantum chemistry. The discourse developed by those following the approach of Heitler and London to chemical valence and the discourse developed by those following the more pragmatic approach of Pauling and Mulliken, implied a different set of constitutive criteria for quantum chemistry (Gavroglu, Simoes 1994).

In this paper, I would like to discuss the way in which the constraints of a particular local community of Dutch scientists implied a specific set of conclusive criteria for physical chemistry. It should be noted that the formulation of physical chemistry and chemical thermodynamics did not automatically lead to their adoption by the physicists or the chemists. There ensued a stage of *adapting physical chemistry and chemical thermodynamics to the exigencies of the laboratory*.

The case I examine is J.D. van der Waals' theory of mixtures and his insistence on using those aspects of Gibbs' work which would be best suited for defining an experimental program at the Physical Laboratory of the University of Leiden. My choice of van der Waals is dictated by the fact that he was one of the protagonists in articulating some of the constitutive elements of physical chemistry. Van der Waals' alter ego was the doyen of the Dutch experimentalists, Heike Kamerlingh Onnes, and the former's theory of mixtures was put to test by the latter in an experimental program spanning nearly twenty years of studying the  $\psi$ -surface.

Van der Waals' successful application of the method of the  $\psi$ -surface to the study of binary mixtures was *by no means a trivial task* and raises a variety of interesting questions. Why did van der Waals choose to use the  $\psi$ -surface for the study of binary mixtures while everyone else — including Gibbs — had declined to follow this path? Why did van der Waals use the  $\psi$ -method, and not any other thermodynamic function of Gibbs? Why had he not applied the same method, namely the  $\psi$ -line, to the study of single substances, and only applied it to the more complicated case of mixtures? How did it occur to van der Waals to use the  $\psi$ -method, or in other words, was there some *necessity* which led him, in a stronger or weaker sense, to this method? An answer to these questions may elucidate the special methodological elements of the Dutch scientist that made Gibbs' work so easy to accommodate in his own program. Moreover, these questions are directly related to the problem whether creative discoveries can be rational.

My main conclusion will be that van der Waals, though deeply committed to thermodynamics, proposed a notion whose outstanding characteristic was that its determination was independent of entropy considerations. The definition of van der Waals'  $\psi$ -surface did not involve entropy. His aim was the definition of an entity which could be of practical use to experimentalists by avoiding in the definition a direct

reference to entropy. He made specific efforts to propose a *visualizable* entity, something which was not independent of his special relations with particular *laboratory practices*.

## 2. *Some thermodynamic functions of Gibbs*

In 1873 Gibbs published two articles (Gibbs 1873a and 1873b), where he proposed some graphical methods for the representation of thermodynamic properties. His purpose was to use the concept of entropy, which was still not fully clarified, together with the Second Law of Thermodynamics in order to systematically deal with all the issues related with the equilibrium of a physical system. As he explicitly put it: "Although this principle [i.e. maximisation of entropy] has by no means escaped the attention of physicists, its importance does not appear to have been duly appreciated. Little has been done to develop the principle as a foundation for the general theory of thermodynamic equilibrium." (Gibbs 1878, p.441). The use of thermodynamic diagrams which rested upon the concept of entropy was important, not only because they facilitated the study of substances through thermodynamics, as Gibbs showed in these articles, but also because they helped clarify the concept of entropy itself. The challenging problem of the equilibrium of mixtures, the "general theory of equilibrium", was the ideal playground to test and apply these diagrams and the corresponding theoretical methods.

After presenting some useful two-dimensional diagrams in the first article, in his second article Gibbs went on to introduce a treatment of the thermodynamic properties of a substance in terms of a surface, a three-dimensional representation of energy  $\epsilon$  as a function of entropy  $\eta$  and volume  $v$ .<sup>2</sup> One of the major features of this  $\epsilon$ -surface is that the coexisting phases are depicted as points on the surface which possess a common tangent plane. In a third major article, published in two parts in 1875-77 (Gibbs 1875/77), Gibbs introduced certain fundamental *thermodynamic functions*, namely the free energy  $\psi$ , the enthalpy  $\chi$  and the chemical potential  $\zeta$  (or  $\mu$  for a single substance), which were defined not only for a single substance but also for mixtures of different constituents. Together with the  $\epsilon$ -method of his previous article, whose definition was also extended to cover mixtures, the thermodynamic functions yield a set of methods which could in principle be used *interchangeably* to study all the

problems of the equilibrium of heterogeneous substances.

However, it is not the case that Gibbs actually studied mixtures graphically making use of *all* his thermodynamic functions. He quickly realised that this was not even possible in some cases, in the sense that, for instance, the  $\epsilon$ -method would demand a *four-dimensional* representation, even for the simplest case of a binary mixture, and thus a graphical representation would lose any practical function (Gibbs stated this explicitly; see Gibbs 1875/77, p.175). Of all his thermodynamic functions, he chose to describe (*and not actually draw*) the graphical representation of the  $\zeta$ -surface for a single substance, and to give some hints for the application of the  $\zeta$ -method for the case of mixtures of two or three substances. It is worth noticing, though, that the graphical treatment of the  $\psi$ - and  $\chi$ -methods was completely ignored in the rest of his article.<sup>3</sup>

| Gibbs' thermodynamic functions |                                |                                 |                                  |                                   |
|--------------------------------|--------------------------------|---------------------------------|----------------------------------|-----------------------------------|
| magnitude                      | energy $\epsilon$              | free energy $\psi$              | enthalpy $\chi$                  | potential $\zeta$                 |
| function of:                   | volume $V$ ,<br>entropy $\eta$ | temperature $T$ ,<br>volume $V$ | entropy $\eta$ ,<br>pressure $p$ | temperature $T$ ,<br>pressure $p$ |

Table I

### 3. Van der Waals' earlier work

We should begin our reconstruction of van der Waals' (re)discovery of the  $\psi$ -method with a reference to his earlier work on the equation of state of a single substance. This equation yielded the pressure of a fluid as a function of its temperature and volume, when the substance was in a single phase, either liquid or gaseous. In the case, however, that there was a coexistence of the two phases, van der Waals' equation of state had to be assisted by a specific criterion, proposed by Maxwell and Clausius, in order to be able to predict the constant pressure of the coexisting phases. This criterion, which employs some thermodynamic argument, is known as the 'equal area construction'. But although it seems quite easy as a geometrical method, finding the constant pressure of coexistence involves complicated algebra. (For a discussion of van der Waals' early work on the equation of state see Gavroglu 1990). It is evident from

his subsequent work and writings, that van der Waals was not fully satisfied with the application of Maxwell's method to his theory, and his reasons, we can assume, were both methodological and ontological. More specifically, van der Waals' theoretical agenda aimed at eliminating from his equations parameters expressing the *specificity of the different substances*. This he accomplished in two distinct ways. First he disregarded the differences between the liquid and the gaseous states and considered them identical, since they were composed of the same molecules (ontological claim), and, secondly, he disregarded the differences between different substances, since they were composed of similar molecules as regards the properties under investigation (methodological position).

In his search for a solution to the problem of the coexisting phases which would comply with his ontological and methodological commitments, van der Waals discovered his Law of the Corresponding States. This law yielded a method to study the coexisting phases satisfactorily. The interesting thing here, is that in the same article of 1880 (it appeared as 12th chapter in the translations of his thesis; e.g. van der Waals 1899, pp. 134-161) where van der Waals presented his Law of the Corresponding States, and just before he did so, he tried to solve the problem of the coexisting phases with the aid of Gibbs'  $\epsilon$ -method. Gibbs' rule for coexistence, the common tangent plane on the  $\epsilon$ -surface, can be translated into algebraic language as:

$$(1) \quad \begin{aligned} (\partial\epsilon/\partial V_1)_\eta &= (\partial\epsilon/\partial V_2)_\eta \\ (\partial\epsilon/\partial\eta_1)_V &= (\partial\epsilon/\partial\eta_2)_V \\ \epsilon_1 - \eta_1(\partial\epsilon/\partial\eta_1)_V - V_1(\partial\epsilon/\partial V_1)_\eta &= \epsilon_2 - \eta_2(\partial\epsilon/\partial\eta_2)_V - V_2(\partial\epsilon/\partial V_2)_\eta \end{aligned}$$

Van der Waals did not arrive at a satisfactory solution with this method, however, since he "quickly found out that the use of this surface as a help did not make the calculations any simpler, since introduction of approximations leads to the same way of handling the problem as the way that follows from the law of Clausius and Maxwell". Van der Waals went on to add that "the boring calculations and the complicated resulting equation" kept him from publishing his results (van der Waals 1899, p.136).

Van der Waals' pronouncement about the boring calculations seems at least peculiar in retrospect. This is so in particular when one takes into consideration the ways van der Waals, later on, chose to implement the

$\psi$ -surface as well as the corresponding work at Leiden, where such 'boring' calculations and complicated expressions were everyday practice, as were also geometrical representations of tangential planes on *actual plaster models* of surfaces, and even more complicated constructions. But this judgement is in itself important, as it lays emphasis on the following point: we understand that van der Waals was prepared to sacrifice mathematical rigour for the sake of avoiding undue complication. One then wonders why van der Waals articulated his method with the use of the  $\psi$ -surface, notwithstanding the fact that he could neither claim to have used a mathematically simple case nor to have attained a more rigorous treatment. Was there, in the meantime, another methodological criterion which determined his choices? Were there any external factors which may have obliged him to re-think his methodological commitments?

#### 4. *Van der Waals' first attempt to deal with mixtures*

For a number of reasons van der Waals was obliged to turn to the study of mixtures. There was a suspicion that some deviations from the predictions of van der Waals' equation of state in the behaviour of substances, was due to the influence of admixtures. As long as a complete theoretical account for mixing was lacking, van der Waals' insistence on calling upon the influence of admixtures could be accused of being an *ad hoc* move to save his theory. On the ontological level, there was the belief that the molecules of the liquid and the gaseous state were ontologically different, and the followers of this belief also tried to explain the 'anomalous' behaviour in terms of mixing of the "liquidons" and the "gasons" (on the relevant controversies, see Levelt Sengers 1979).

It is worth noting that van der Waals' first attempt to deal with mixtures, in his 1880 article, was not an attempt to construct an equation of state for them, as for pure substances, but discussed the coexistence of phases in mixtures. If nothing else, this was an indication of his belief, that the problem of coexistence was the fundamental problem for mixtures. He drew some interesting conclusions on the behaviour of binary mixtures, and these were mainly in the form of semi-empirical laws and qualitative arguments.

5. *The complete theory of mixtures*

Van der Waals' complete theory for binary mixtures was presented to the Academy of Sciences of Amsterdam on the 23rd of February 1889, "at the insistence of my friend Kamerlingh Onnes" (van der Waals 1910, p.262), and first appeared in the *Archives Néerlandaises* for 1890 under the title *Théorie moléculaire d'une substance composée de deux matières différentes*. In this article of 1890, van der Waals drew an explicit distinction between two parts in the study of mixtures, exactly as he had done in the case of single substances: the first was the equation of state, and the second was the problem of the coexisting phases. His strong belief in the validity of the kinetic theory, his ontological commitment to the real existence of molecules and his methodology of treating molecules as if their volume and attraction were the only features which mattered in the formulation of a theory, led him *directly* to an equation of state for mixtures which was 'identical' to the one for single substances, where only the expression for the constants  $a$  and  $b$  varied with composition  $x$ :

$$(2) \quad (p + a_x/V^2)(V - b_x) = RT$$

and

$$(3) \quad \begin{aligned} a_x &= a_1x^2 + 2a_{1,2}x(1-x) + a_2(1-x)^2 \\ b_x &= b_1x^2 + 2b_{1,2}x(1-x) + b_2(1-x)^2 \end{aligned}$$

where  $a_{1,2}$  and  $b_{1,2}$  express the mutual attraction between the different molecules of the two substances, and the influence of the presence of different molecules upon the mean free path, respectively.

With the first problem being solved, van der Waals moved on to the problem of contriving rules for the coexistence of different phases in the case of mixtures. He was quite uneasy about the Maxwell-Clausius method, and he was quite convinced that this method cannot be applied to mixtures. He suggested, however, that "one can resolve the question here in another way, by making use of the thermodynamic potential  $\mu$ " (van der Waals 1900, p.4). For  $\mu$ , one of Gibbs' thermodynamic functions, one has the relation:

$$(4) \quad d\mu = Vdp - \eta dT$$

where  $\eta$  is the entropy. Van der Waals proceeded to solve the problem of the coexisting phases for single substances with the help of  $\mu$ . The solution can be briefly described as follows: if we regard temperature as a constant then we can represent the relation between  $\mu$  and  $p$  graphically on a  $\mu$ - $p$  diagram. Taking the equation of state in account (for a single substance, of course), the general course of this curve, for temperatures below the critical, is like in Fig.1. At the double-point  $e$  two equal values of  $\mu$  refer to the same value of  $p$ , and this point represents the point of phase-coexistence between liquid and gas.

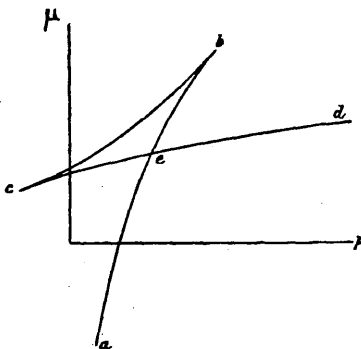


Fig.1

And, then, there was something rather unexpected. Van der Waals concluded with the remark that this method can be extended and applied to mixtures, but he did not proceed to complete such an application (van der Waals 1900, p.5):

This construction can be extended for the case of two mixed substances. However this can be handled also in another way which I think I should prefer.

## 6. The problems with the $\epsilon$ - and the $\mu$ -method

Why all this fuss about  $\mu$ , just to solve the *already solved* problem for single substances? This is a central question, especially since van der



Waals did not use  $\mu$  for mixtures. And what is, then, the meaning of this obscure reassurance that the latter could actually be done, but that he *did not prefer* it himself? Van der Waals' point in presenting a solution for single substances using the thermodynamic potential  $\mu$  in this context, was primarily to present an application of Gibbs' thermodynamic functions. This was an application as powerful and general, as the ones he had in mind when he wrote, a couple of pages before he started discussing  $\mu$ , as a comment about the deduction of the conditions of coexistence from considerations of the mechanical theory of heat, that (van der Waals 1900, p.2):

Of course, one could deduce the condition which must be satisfied at coexistence of the liquid and the gaseous state of a substance from the kinetic theory as well, but this deduction does not show the characteristic of evidence and generality, which is a feature of the thermodynamic approach.

Now, the Maxwell-Clausius method was also, in a way, an outcome of this thermodynamic approach; however it was not as *straightforward and as easily representable* as this method with  $\mu$  and the corresponding Fig.1, at least in the sense that with the "equal area construction" one has to *count* the equal areas after plotting the isotherm, whereas with the  $\mu$ -method one has just to *plot* and then *observe* the point of intersection. But this is still not the whole story, because I have not answered why van der Waals preferred  $\mu$  among all the possible thermodynamic functions defined by Gibbs. This question becomes especially difficult to avoid if we recall that it was actually with another thermodynamic magnitude, namely energy  $\epsilon$  as a function of volume and entropy, that van der Waals first attempted to solve the problem, without completing his treatment.

I propose the following reconstruction: van der Waals started with  $\epsilon = f(V, \eta)$ , which was rather complicated as a graphical construction, as well as an algebraic method (tangent planes on a three-dimensional surface and solution of some complicated differential equations). Along the way he was able to find his law of corresponding states, which helped him solve the problem of coexistence in a general manner. This still had the disadvantage that it was not a very straightforward process, if one needed to find *just one specific* point of equilibrium, and that even the resulting general mathematical formula was not a simple one. Then, when

van der Waals returned to the same problem again and insisted on using one of Gibbs' functions, he sought one which would be more easy to handle than  $\epsilon$ , which he thought was the potential function  $\mu$ .

But why didn't van der Waals actually apply the  $\mu$ -method to mixtures, although he claimed he could? When van der Waals claimed that the considerations about  $\mu$  were also valid for mixtures, this is to be understood as "valid up to a certain extend". Because, even though, it is true that if  $\mu_1$  and  $\mu_2$  are the thermodynamic potentials of the first and of the second component respectively and  $x$  is the composition then there follow some relations between these and the pressure of coexisting phases, it is not true that these relations are as easy to *visualise* and *represent* as in the case for single substances of Fig.1. And certainly a graphical representation would demand one more axis of co-ordinates, namely the axis of  $x$ , yielding, therefore, a *three-dimensional representation*. Now the point  $e$  in Fig.1, which represents different phases in equilibrium, is a kind of 'knot' in the two-dimensional figure. What would this 'knot', as well as the part  $ebce$ , look like in three dimensions? Whatever it would look like, it certainly would not be easily *constructible*, and therefore all the simplicity and applicability of this method which rested upon the simplicity of Fig.1 would have been undermined.<sup>4</sup>

Extending the  $\epsilon$ -method to mixtures would not have been practical either. He would have had to express energy as a function not only of volume and entropy, but of constitution  $x$  as well, or  $\epsilon = f(V, \eta, x)$ . But this would have meant that a graphical representation would need four dimensions, and this of course was not *visualizable*. It was not so much the case that the algebraic differential equations would have become much more complicated than eq.(1) for a single substance, but it was rather the case that the  $\epsilon$ -method for mixtures *as a graphical representation would have lost any practical significance*.

Given that the Maxwell-Clausius method when applied to mixtures was rather incongruous, together with the fact that it was impossible to render the  $\epsilon$ -method *visualizable*, I argue that van der Waals sought a thermodynamic potential which would have a two-dimensional representation for a single substance, so that its expansion to binary mixtures would demand three dimensions, a number just enough to have a *visualizable* representation. In this respect,  $\mu$  was not just any thermodynamic potential, but it had the pleasant and promising property to be two-dimensional for a single substance. Van der Waals probably discovered the  $\mu$ -

method in his effort to find a thermodynamic potential appropriate for mixtures, and of course he presented it in the same context. This may explain why this method, which was only appropriate for single substances, appeared just where a method for mixtures was expected. The fact that it turned out that the  $\mu$ -method was quite complicated — not even graphically constructible — for mixtures, did not appear to be a sufficiently strong reason for van der Waals to ignore this alternative, especially since, in principle, it could have led to a way of resolving the problem.

To deal with mixtures, van der Waals demanded that the thermodynamic function to be used should be graphically constructible in three dimensions, otherwise both  $\epsilon$  and  $\mu$  could have done the job. A second, and maybe more significant constraint, was that the thermodynamic conditions, which would yield the points of equilibrium between different phases, should also be visualizable upon the same diagram, as for instance the conditions of equilibrium for Gibbs'  $\epsilon$ -method are depicted as a common tangent plane. If this were not the case, then the whole effort of constructing a diagram would be in vain, since it would be of no practical importance. *And it was practical importance that van der Waals was interested in otherwise he would have just given a number of relations and equations, which if solved, would give the points of phase-coexistence.* This second constraint forbids us to use, for instance, three-dimensional representations of, say  $\epsilon = f(V, \eta, x)$  as a function of only  $V$  and  $\eta$ , with  $x$  as a parameter — that is surfaces of  $\epsilon = f(V, \eta)$  for different values of  $x$ . (Notice that this was the general solution that Gibbs had proposed). Such a choice would have been acceptable, it was a solution which would have obeyed the criteria of constructibility and visualizability, but it would have also been quite messy to try to find the interesting points in a geometrical manner on different diagrams. There is, though, a way out; that is, there exists a mathematical way of reducing the number of parameters a thermodynamic function depends on. Here are the details:

If we have a magnitude  $z$  as a function of two others,  $x$  and  $y$ ,  $z = f(x, y)$ , and we are interested in the following magnitudes:

$$(5) \quad (\partial z / \partial x)_y, \quad (\partial z / \partial y)_x, \quad z - x(\partial z / \partial x)_y - y(\partial z / \partial y)_x$$

(which of course are the ones van der Waals was interested in, as is

evident from eq.(1)), then there is a simple linear transformation  $z \rightarrow w$  which makes  $w$  a function of  $x$  only, if we choose  $w = z - ay$ , and  $a = (\partial z / \partial y)_x$ , because then  $(\partial w / \partial y)_x = (\partial z / \partial y)_x - a = 0$ , if  $a$  is considered constant with regard to  $y$ . Then the rest of the magnitudes we are interested in, from eq.(5), become:

$$(6) \quad \begin{aligned} (\partial z / \partial x)_y &= (\partial w / \partial x)_y = (dw / dx) \\ z - x(\partial z / \partial x)_y - y(\partial z / \partial y)_x &= w + ay - x(dw / dx) - ya \\ &= w - x(dw / dx) \end{aligned}$$

and thus  $w$  is a function of  $x$  only, at constant  $a$ , and the form of the magnitudes we were interested in did not change.

This means that if we apply the same procedure to  $\epsilon = f(V, \eta)$ , we could eliminate one of the parameters  $V$  or  $\eta$ , to get a function representable in two dimensions! Concerning the linear transformation  $\epsilon \rightarrow \chi$  or  $\epsilon \rightarrow \psi$ , one has two options: either one eliminates  $V$  with the transformation  $\chi = \epsilon - aV$ , where  $a = (\partial \epsilon / \partial V)_\eta = -p$ , or one eliminates  $\eta$  with the transformation  $\psi = \epsilon - a\eta$ , where  $a = (\partial \epsilon / \partial \eta)_V = T$ . The first choice would yield some  $\chi = \epsilon + pV$ , as a function of entropy  $\chi = f(\eta)$  at constant pressure, whereas the second would yield:

$$(7) \quad \psi = \epsilon - T\eta$$

with  $\psi$  as a function of volume alone at constant temperature, something which would meet van der Waals' practical objectives, *since volume is directly measurable while entropy is not*. The conditions of eq.(1) for  $\epsilon$  would, then, give the following conditions for  $\psi$ :

$$(8) \quad \begin{aligned} (d\psi / dV_1) &= (d\psi / dV_2) \\ \psi_1 - V_1(d\psi / dV_1) &= \psi_2 - V_2(d\psi / dV_2) \end{aligned}$$

as eq.(6) implies. This is exactly the  $\psi$ -method van der Waals proposed in his 1900 (p. 6):

The function  $\psi = \epsilon - T\eta$ , that is the free energy, possesses the property, if it is regarded at constant temperature and as variable with  $V$ , that it reveals the two phases which can coexist, through the pair of points of contact with a double-tangent.

accompanying his words with Fig.2.

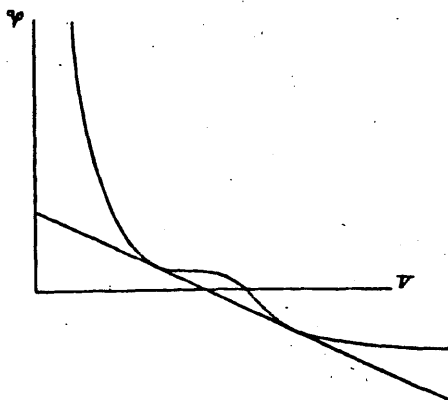


Fig.2

The fact that this method is two-dimensional and without 'knots' makes it possible to have a *constructible extension in three dimensions, in the case of mixtures*. Let us continue to quote van der Waals (van der Waals 1900, p.6):

Now we want to introduce three axes, the one of  $V$ , of  $x$  and of  $\psi$ . If one constructs the values of  $\psi$  for all values of  $V$  and all the ones of  $x$ , which lie between 0 and 1, so one gets a surface which plays the same role for a mixture of two substances as the curve  $\psi$  for a single one. Instead of a tangent on two points of the curve one gets here a tangent plane, which has two points of contact to the surface.

This is the method of the  $\psi$ -surface for mixtures, which, it must be emphasised, can reveal the coexisting phases of a mixture, at a given temperature, in the *same manner* which was employed in Gibbs'  $\epsilon$ -method, namely with a common tangent plane. It must be stressed that this renders the coexisting phases *visualizable* on the  $\psi$ -surface, and also that this quite straightforward geometrical method can be applied on a constructed model, given the simple form of the  $\psi$ -surface. This was actually done in both Amsterdam and Leiden. Van der Waals constructed a wooden model of the  $\psi$ -surface for reasons of exhibiting its general properties

and Kamerlingh Onnes, based on experimental results, constructed a large number of plaster models (as in Fig.3), upon which he would roll a pane-glass covered with lamp-black in order to find out the coexisting phases. This fact reveals one of the most important features which gave the  $\psi$ -surface its high esteem in Leiden: that it could be used for *heuristic purposes*, that the *constructed model* of the  $\psi$ -surface could actually be used to *predict* the behaviour of mixtures.

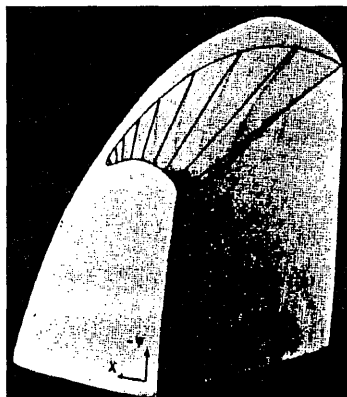


Fig.3

Given the fact that the exact numerical solution of an equation like eq.(8) was impossible at the time, and that exact laws and semi-empirical formulas for the behaviour of mixtures were unavailable, the need of alternative, graphical methods for studying mixtures gained in importance. The question is then raised, why one needed *three-dimensional* methods, why the traditional two-dimensional diagrams were insufficient. To answer this question, one should notice that the situation with mixtures is much more demanding than for single substances: the nature of condensation phenomena in mixtures is much more complicated, there are many more factors to be taken into consideration and there are more magnitudes to be determined. As was quickly realised, one can work on a two-dimensional diagram for a specific case, but condensation phenomena can only be studied on a graph of more dimensions. The fact that  $\psi$  could exhibit the whole behaviour of the phenomena offered the opportunity to have *indications about the possible characteristics of the laws*

for mixtures. Furthermore, and this is an issue which was of extreme importance to the experimentalists, *the use of a three-dimensional surface was a means to reduce the number of necessary measurements and experiments*. For instance, one could study the behaviour of a mixture for only a given set of values for the constitution, say  $x = 0, 0.25, 0.5, 0.75$  and 1, and then construct the  $\psi$ -surface by *extrapolating* from these measurements. This would facilitate the prediction of the behaviour of the mixture for many other values of the constitution, or at least *direct the experimentalist* to the important regions, to the regions, that is, where interesting phenomena take place. The ability to predict, by both methods, suited the theoretician van der Waals as well as the experimentalist Kamerlingh Onnes. The capacity to construct models of the  $\psi$ -surface and to make theoretical and experimental predictions with their aid marked Leiden's physics culture.

### 7. Van der Waals' methodological commitments

Our interpretation of van der Waals' preference for  $\psi$ , rests on the examination of all the alternatives he could have employed for the study of mixtures and for various reasons he did not. In his attempt to deal with mixtures he first proposed some semi-empirical laws for the behaviour of mixtures, but he became dissatisfied with such a solution, probably because semi-empirical laws could not express his ontological views with regard to the behaviour of molecules in a mixture. Also the extension of the known method, the Maxwell construction, was not valid for mixtures, as van der Waals immediately realised.<sup>5</sup>

After van der Waals learned of Gibbs' work, he tried to use it for a theory of mixtures. Van der Waals imposed certain *methodological constraints*. *Constructibility* and *visualizability* became the dominant criteria. The  $\epsilon$ -method of Gibbs, could not play such a rôle, since its extension for mixtures would be four-dimensional. In his search for an appropriate 'reduction' by one dimension, van der Waals 'discovered' the  $\mu$ -method — guided probably by Gibbs' exposition of the (almost identical)  $\zeta$ -method. But the  $\mu$ -method did not lead to a constructible surface. There were also  $\psi$  and  $\chi$ , which had received almost no attention by Gibbs himself together with a mathematical method of reduction that could lead from  $\epsilon$  to these magnitudes, which had to do with the for-

mulation of the corresponding criterion of equilibrium (see Table I).

Van der Waals' commitment to a *visualizable and constructible* solution led him to his choice of the  $\psi$ -method among the possible alternatives. (See Table II). Hence the assessment of methodological considerations in examining his choice of the specific solution cannot be neglected.

| magnitude  | function of: (single substance) | criterion of equilibrium         | to reduce number of parameters set:                                       | method of finding coexistence | extension for mixtures  |
|--|---------------------------------|----------------------------------|---|-------------------------------|---|
| energy $\epsilon$                                      | volume $V$ , entropy $\eta$     | $(\delta\epsilon)_{\eta} \geq 0$ | $[\eta = \text{const.}]$  | tangent plane                 | four-dimensional  |
| free energy $\psi$                                     | temperature $T$ , volume $V$    | $(\delta\psi)_T \geq 0$          | $T = \text{const.}$<br>(van der Waals' proposal)                          | tangent plane                 | tangent plane for $T = \text{const.}$ , function of volume and composition (directly measurable quantities) |
| enthalpy $\chi$  | entropy $\eta$ , pressure $p$   | $[(\delta\chi)_p \geq 0]$        | $[p = \text{const.}]$   | ['knots']                     | ['knots' for $p = \text{const.}$ , function also of entropy]  |
| potential $\zeta$<br>(or $\mu$ for a single substance) | temperature $T$ , pressure $p$  | $(\delta\zeta)_{T,p} \geq 0$     | $T = \text{const.}$<br>and/or<br>$p = \text{const.}$<br>(Gibbs' proposal) | 'knots'                       | 'knots' for $p = \text{const.}$<br>and/or<br>$T = \text{const.}$  |

Table II

It should also be pointed out that we have to do with the depiction of *properties* and not of *entities*; in other words, what is rendered visualizable with  $\psi$  are the thermodynamic properties of mixtures, and not any 'picture' of the arrangement of the molecules. Van der Waals' *ontolo-*



*gical commitments* and more specifically his belief in the reality of molecules was expressed in his work involving the equation of state rather than the  $\psi$ -surface. In contrast to the *ontological premises* concerning the existence of molecules which may have guided him to the specific equation of state, it was his *methodological premises* which were decisive in his choice of  $\psi$  for mixtures.

### 8. *Some general comments*

The experimental program of Heike Kamerlingh Onnes, who was the first to liquefy helium in 1908, did have an appreciable effect in influencing van der Waals to make the particular theoretical choices. *Practical applicability* was the most important outcome of constructibility and visualizability of the method; the  $\psi$ -surface could actually be constructed according to experimental measurements and be used to facilitate the experimental study of the properties of mixtures, and this was actually the case at the Cryogenic Laboratory at Leiden, under the direction of Kamerlingh Onnes. The mutual influence between Kamerlingh Onnes and van der Waals is evident in their regular correspondence, which concerned mainly technical matters and their regular bi-weekly meetings prior to or following the meetings at the Academy in Amsterdam. We should also not overlook the dedication of van der Waals' book on mixtures in 1900 to Kamerlingh Onnes, where we read: "the fortunate co-operation between theory and experiment, of which the following pages are but a token, is to be ascribed to you, in the first and decisive place" (van der Waals 1900, dedication). An experimental project was launched around in 1890 at Leiden under the title "Contributions to the knowledge of van der Waals'  $\psi$ -surface", and it lasted for about two decades. In this project, the constructibility and visualizability of the  $\psi$ -surface became one of its most celebrated features and it can be argued that the study of mixtures with the aid of the  $\psi$ -surface constituted even a *heuristic factor* in the process of the liquefaction of helium.<sup>6</sup>

$\psi$  was the theoretical *instrument* which allowed van der Waals to study the properties of substances as — in essence — *properties of their molecules*. To clarify this point, I should add that from the form of the  $\psi$ -surface, and more specifically from the generation of 'plaits' upon it, one could draw conclusions about the physico-chemical affinity of the

different mixed substances. Quantitatively, this was done by estimating, from the course of the plaits on the  $\psi$ -surface, the coefficients  $a_{12}$  and  $b_{12}$  of eq.(3); these were, of course, interpreted as expressing molecular properties. In this way, through a 'phenomenological' study of the  $\psi$ -surface, one could draw conclusions with ontological implications. This was actually done in Leiden, where it was used as a means to accomplish a more general goal: the goal of classifying substances, *according to physico-chemical criteria*. In this sense the method of the  $\psi$ -surface for studying mixtures was a *constitutive element* of Leiden's style of doing physical chemistry. The constructed moulds became *heuristic artefacts*.

Since  $\psi$  was a representation of properties, it was not necessary to be explicit about the underlying ontology. The use of the  $\psi$ -method legitimised a particular approach to the study of mixtures without requiring a commitment to the reality of molecules. Its success provided the prestige to pursue an independent approach to physical chemistry without coming into any conflict with the energeticists.  $\psi$  was a method which stemmed from the work of Gibbs, which was highly esteemed by Ostwald and the energeticists. Perhaps this is one of the reasons why van der Waals in his Nobel speech in 1908 — after Ostwald's public admission as to the reality of atoms — said for no apparent reason, that he always believed in the reality of molecules.

The Leiden group under Kamerlingh Onnes did not commit themselves to a particular ontology in an explicit manner for a long time. They studied the properties of substances and concentrated in measuring deviations from the predicted values and to proceed to a classification of substances through these deviations. This was accomplished through *physicochemical* methods and criteria. It was quite different, for instance, from Boltzmann's style, who used van der Waals' theories on the one hand, but his method was to *postulate and check* a number of different molecular models until he achieved a satisfactory *mathematical* model of the molecular forces. It was also different from the energeticists' style, who were also conducting work on the *foundations of chemistry*. The Dutch followed their own program in physical chemistry where, while there was no need *to be explicit about the ontology, a lot of emphasis was laid in proposing visualizable heuristic devices*.

In this way, we can consider the discovery of the  $\psi$ -surface by van der Waals as a solution to a specific problem-situation; as the alternative for studying the behaviour of mixtures which best suited the practical,

theoretical and ontological constraints of the local scientific community of physicists at the Netherlands around the turn of the century.  $\psi$ , viewed in this way, was not only the outcome of a rational creative process, but also an expression of a local 'style' of doing physical chemistry, a constitutive element of the local scientific discourse.

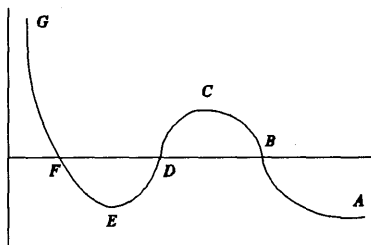
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### NOTES

1. The present paper, in an earlier version, formed my part of a joint paper together with Prof. Kostas Gavroglu, which was presented at the workshop on *The Uses of Entropy*, organised by the Dibner Institute for the History of Science and Technology, M.I.T. on April 15-16, 1994.
2. In the present paper I preferred to use for the thermodynamic magnitudes and functions the original symbols that both Gibbs and van der Waals used in their articles and treatments.
3. Some of the reasons for Gibbs choosing  $\zeta$  can be traced to some relevant points in the work of James Thomson, but the point to be stressed is that Gibbs never presented a graphical treatment of mixtures which rested on  $\psi$ ; the same applies to J.C. Maxwell, who also tried (unsuccessfully) to find a thermodynamic surface for the graphical study of the properties of mixtures (see Garber 1969).
4. Gibbs description of the  $\zeta$ -method *for a single substance* had some similar properties, namely that the coexisting phases were situated on a line where two 'sheets' of the surface crossed each other. This situation is qualitatively depicted in a figure that the reader can locate in Kamerlingh Onnes and Keesoms *Encyclopaedie* article (Kamerlingh Onnes & Keesom 1912, p. 832). We should note that this figure is a *drawing*, and not a *construction*; the form of the surface prohibits its full construction. Actually, one *can* construct the parts of the  $\zeta$ -surface which present no 'knots' *if one knows beforehand the lines along which these 'sheets' cut*. This would mean, however, that the surface itself has lost its *heuristic* value: one cannot *predict* with it the points of coexistence; these have to be known beforehand. An interesting point in itself is that *nowhere* in Kamerlingh Onnes' and Keesom's *Encyclopaedie* article, where practically *every* graphical method — significant or not — was thoroughly presented, do we have *even an indication* of how a  $\mu$ -surface for mixtures would look like. This suggests that a graphical representation of  $\mu$  for mixtures was inconceivable at

that time.

5. Maxwell's proof of the equal area construction was actually not complete, in the sense that his argument proved that areas BCD and DEF (see figure) must be equal, but it did not prove that the boiling-line FDB should be horizontal or even straight; actually, any line with negative inclination would do. The fact that the boiling-line for a single substance was horizontal and straight, which in Maxwell's proof appeared as an *ad hoc* premise only suggested by Andrews' experiments, was justified by Gibbs' phase rule, which demanded that for a single substance the isotherm and the isobar line became identical during phase coexistence. This was not the case with mixtures, however, where there were more degrees of freedom and the line FDB was therefore not straight any more.
6. This is what I argue for in the 7th chapter of my doctoral thesis at the National Technical University of Athens, "Van der Waals, Kamerlingh Onnes and the liquefaction of Helium: the local context of an experimental achievement" (to appear, in Greek).



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