Maxwell's lever rule and expansion of water in freezing: two poorly understood phenomena

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Abstract

The view about condensed matter as a network with nodes identifiable as molecules and bonds as flux tubes is one of the basic predictions of TGD and obviously means a radical modification of the existing picture. In this article two old anomalies of standard physics are explained in this conceptual framework. Analytic equations of state quite generally fail in critical region for gas liquid-phase transition. Empirically the pressure in critical region depends only on temperature and is independent on molecular volume whereas equations of state predict this dependence.

Maxwell's area rule and lever rule is the proposed modification equation of state in critical region. There are two phases corresponding to liquid and gas in the same pressure and the proportions of the phases vary so that the volume varies. The lever rule used for metal allows allows to explain the mixture but requires that there are two "elements" involved. What the second "element" is in the case of liquid-gas system is poorly understood. TGD suggests the identification of the second "element" as magnetic flux tubes connecting the molecules. Their number per molecule varies and above critical number a phase transition to liquid phase would take place.

Second old problem relates to the numerous anomalies of water . The most well-known anomalies relate to the behavior near freezing point. Below 4 $\circ$C water expands rather than contracts as temperature is lowered. Also in the freezing an expansion takes place.

A general TGD based explanation for the anomalies of water would be the presence of flux tubes with both ordinary and non-standard value of Planck constant $h_{eff}/h = n$. Flux tubes associated with hydrogen bonds could have also non-standard value of Planck constant in which case the flux tube length scales like n. The reduction of n would shorten long flexible flux tubes to short and rigid ones. This would force the molecules nearer to each other but also reduce their motility of molecules. This would create empty volume leading to an increase of volume per molecule as temperature is reduced.

The energy for particles with non-standard value of Planck constant is higher than for ordinary ones. In freezing all dark flux tubes would transform to ordinary ones and the surplus energy would be liberated so that the latent heat should be anomalously high for all molecules forming hydrogen bonds. Indeed, for both water and NH_3 the latent heat is anomalously high. Hydrogen bonding is possible if molecules have atoms with lone electron pairs (electrons are not assignable to valence bonds). Lone electron pairs could form Cooper pairs at flux tube pairs assignable to hydrogen bonds and carrying the dark proton.

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1 Introduction

The view about condensed matter as a network with nodes identifiable as molecules and bonds as flux tubes is one of the basic predictions of TGD and obviously means a radical modification of the existing picture. In the sequel two old anomalies of standard physics are explained in this conceptual framework. The first anomaly was known already at the time of Maxwell. In critical region for gas liquid-phase transition van der Waals equation of state fails. Empirically the pressure in critical region depends only on temperature and is independent on molecular volume whereas van der Waals predicting cusp catastrophe type behavior predicts this dependence. This problem is quite general and plagues all analytical models based on statistical mechanics.

Maxwell's area rule and lever rule is the proposed modification of van der Waals in critical region. There are two phases corresponding to liquid and gas in the same pressure and the proportions of the phases vary so that the volume varies.

The lever rule used for metal allows allows to explain the mixture but requires that there are two "elements" involved. What the second "element" is in the case of liquid-gas system is poorly understood. TGD suggests the identification of the second "element" as magnetic flux tubes connecting the molecules. Their number per molecule varies and above critical number a phase transition to liquid phase would take place.

Second old problem relates to the numerous anomalies of water (see `http://www1.lsbu.ac.uk/water/`). I have discussed these anomalies from TGD viewpoint in [K1]. The most well-known anomalies relate to the behavior near freezing point. Below 4 ◦C water expands rather than contracts as temperature is lowered. Also in the freezing an expansion takes place.

A general TGD based explanation for the anomalies of water would be the presence of also dark phases with non-standard value of Planck constant $h_{eff}/h = n$ [K4]. Combining this idea with the above proposal this would mean that flux tubes associated with hydrogen bonds can have also non-standard value of Planck constant in which case the flux tube length scales like n. The reduction of n would shorten long flexible flux tubes to short and rigid ones. This reduce the motility of molecules and also force them nearer to each other. This would create empty volume and lead to an increase of volume per molecule as temperature is lowered.

Quite generally, the energy for particles with non-standard value of Planck constant is higher than for ordinary ones [L1]. In freezing all dark flux tubes would transform to ordinary ones and the surplus energy would be liberated so that the latent heat should be anomalously high for all molecules forming hydrogen bonds. Indeed, for both water and NH_3 having hydrogen bonds the latent heat is anomalously high. Hydrogen bonding is possible if molecules have atoms with lone electron pairs (electrons are not assignable to valence bonds). Lone electron pairs could form Cooper pairs at flux tube pairs assignable to hydrogen bonds and carrying the dark proton. Therefore also high T_c superconductivity could be possible.

2 Maxwell's lever rule as an indication for the presence of magnetic flux tubes

Van der Waals equation of state (`http://tinyurl.com/yayjgehm`) is a simple model for two phase system used for mostly pedagogical purposes. The model is not realistic. In particular, it has difficulties in the critical region, where two phases are present. The latter difficulties are actually encountered also in the partition function approach of statistical mechanics.

2.1 Van der Waals equation of state

Consider first the van der Waals equation of state.

1. Van der Waals equation of state has variables (n, T) so that the natural thermodynamical function is free energy F. The equation is of form

$$P = (\frac{\partial F}{\partial V})_T = \frac{n}{1-nb_1}T - a_1 n^2 \quad . \tag{2.1}$$

Here one has $n = N/V$, where N is particle number and constant parameter. $(b_1 = 0, a_1 = 0)$ gives the equation of state for ideal gas. The interpretation of the parameters is discussed in `http://tinyurl.com/yayjgehm`.

2. To deduce free energy F and internal energy E one would need also the partial derivative of free energy

$$S = (\frac{\partial F}{\partial T})_V \quad , \tag{2.2}$$

so that $dF = SdT - pdV$ could be integrated. The information about entropy is not included in van der Waals.

3. The expressions of both E and F can be fixed by assuming that E is a homogenous funktion of (S, T, P, V):

$$E = TS - PV \quad . \tag{2.3}$$

This is additional assumption, which of course need not be true.

   (a) The assumption would give for the free energy per particle the expression

$$f = \frac{F}{N} = \frac{E - TS}{N} = \frac{PV}{N} = \frac{P}{n} \quad . \tag{2.4}$$

   In the case of van der Waals one obtains by using the expression for the pressure already given

$$f = \frac{P}{n} = \frac{T}{1-nb_1} - a_1 n \quad . \tag{2.5}$$

   (b) The entropy per particle is given by

$$s = \frac{S}{N} = \frac{(\frac{\partial p}{\partial T})_V}{n} = \frac{1}{1-nb_1} \quad . \tag{2.6}$$

   $s = S/N$ does not depend on temperature at all.

   (c) For single particle energy $e = E/N$ one has

$$e = \frac{TS-PV}{N} = a_1 n \quad . \tag{2.7}$$

   Also e depends on n only.

4. Van der Waals indeed allows 2 phases and they appear simultaneously in the critical region. The equation of state can be written as a condition for the vanishing of 3rd degree polynomial $P_3(n, T)$ as a function of n

$$\begin{array}{lll} P_3(n,t) = \sum_{k=0}^{3} p_k n^k = 0 & p_3 = 1 \ , & p_2 = -\frac{1}{b_1} \ , \\ p_1 = \frac{P}{a_1 b_1} + \frac{T}{a_1 b_1} \ , & p_0 = -\frac{P}{a_1 b_1} \ . & \end{array}$$

The number of the real roots for n is odd: either 3 or 1. In the critical region, which corresponds to a cusp catastrophe (see `http://tinyurl.com/ngfa9t3`) having n as behaviour variable, the number of real roots is 3, call them $n_{max} \geq n_0 \geq n_{min}$. The largest root n_{max} and smallest root n_{min} correspond to liquid and gas phases. The middle root n_0 is unstable if the polynomial equation is interpreted as a vanishing of the derivative of a fourth-order polynomial of n having p and T as control parameters. It has no physical identification.

The projection of the cusp (see `http://tinyurl.com/ngfa9t3`) to (p, T) has shape of V with curved edges. The tip of V corresponds to critical point and at the edges of V a phase transition takes place between vapour phase and critical phase or liquid phase and critical phase. Above the tip one cannot say whether the phase is gas or liquid and the continuous transformation of gas to liquid can be also regarded as poorly understood.

At the right (left) hand side of V there is single real root n_G (n_L). $n_G < n_L$ allows the interpretation in terms of gas and liquid phases.

2.2 The problems of van der Waals

Consider now the problems of van der Waals in the critical region.

1. Van der Waals allows besides gas phase also liquid phase but the model does now work well in liquid phase. In the critical region where both gas and liquid phases are possible, the model works badly. Equation of state forces the system to a 2-dimensional surface in (n, p, T) space ($n = N/V$, also V can be used as variable since N is constant parameter).

   The standard interpretation is that both phases are present as pure phases and only their fractions vary. The intermediate phase allowed by van der Walls is not present. The empirical finding that the pressure for given temperature does not depend on V. $p(V, T) = p(T)$ condition states that the pressures of the two phases are same: this can be interpreted as equilibrium condition. It follows from van der Waals naturally for different roots n for the equation of state.

2. Already Maxwell proposed a modification of van der Waals. Area rule (for a visualization see `http://tinyurl.com/ycabjdhh`) tells how the oscillatory behaviour of $p(T, V)$ as function of V as one moves in transversal direction (in which p varies) to V along cusp from lowest sheet of cusp (n_-) to the highest sheet (n_+) by increasing V is replaced with constant behavior. In other words, the curve along cusp connecting constant T curves connecting the points at upper and lower sheet of cusp with the same value of p is replaced with a straight vertical line. The condition is that the area below the line is same as the area below the oscillatory curve of constant p.

   Lever rule (`http://tinyurl.com/ybuq7aye`) is needed to understand the proportions of the two phases. Usually the rule is applied to metal alloys. Consider two pure phases α ja β and their mixture γ. Let the fractions of phases α and β be X_α and X_β. Assume that the phases contain two "elements" A and B. Let the proportions of B be a in α, b in β and c in γ. The lever rule

   $$X_\alpha = \frac{c-b}{a-b} \tag{2.8}$$

   follows trivially from the fact that in mixed phase γ one has $c = X_\alpha a + (1 - X_\alpha b = X_\alpha(a-b) + b$.

   In critical regions a and b should vary. To me this picture however represents a problem. What the two "elements" are in the case of say water? If water molecule corresponds to A, what does B correspond to? A different state of water molecule? Or does the system contain also some other "element" than water molecule?

As a consequence of this problem the working models are numerical since analytical models cannot explain the lever rule. This problem is not only the problem of van der Waals but quite general problem of statistical models relying on partition function giving free energy F.

2.3 TGD based explanation of the lever rule

The TGD interpretation for the situation could be following.

1. In the liquid phase molecules can be connected by flux tubes. They are also possible in gas phase but their number is smaller. In particular, in vapour phase intermediate between liquid and gas also gas molecules can be connected by flux tubes to form connected networks.Only single connected network could be present in liquid phase.

   The number of flux tubes per particle can depend on the thermodynamical parameters (V,T) and is expected to be considerably smaller in gas phase in regions where one can distinguish liquid phase from vapor phase (not below the tip of V).

   In liquid state the flux tubes could be shorter than in gas phase. In liquid phase there are large connected structures - maybe only single one - whereas in gas phase these structures are smaller. At criticality they might correspond to vapour droplets. Gas phase would be different from gas phase far from criticality.

2. In critical region there are regions, which form connected networks differing with respect to the number of bonds per particle characterizing the networking. The volume of the mixed phase depends on the relative volumes of these two phases since they have widely differing densities. Large number of networked molecules gives a smaller volume. The pressures in these two kinds of regions are same in mechanical equilibrium.

3. What could be the counterparts for the two "elements" A and B? Could A correspond water molecule and B to flux tube? The portion of flux tubes would distinguish between the two phases at criticality. They are present also in gas phase unless one has $b = 0$ identically. In this case a must however vary inside critical region. For $b = 0$, perhaps realized far from the left edge of V, gas phase would have no flux tubes. In liquid phase to the right from V but not below the tip of V a would be large. At tip and below it one would have $a = b$ along some line and one can say that gas phase transforms to liquid phase. As one goes around the tip the fraction a in liquid phase becomes b for gas phase.

4. What distinguishes liquid and gas phases? What suggests itself is that when the number N_b of flux tube bonds per molecule is above critical value $N_{b,crit}$, a transition to liquid phase takes place and the density is reduced to that of liquid. Below the tip of V and left to V this phase transition does not take place. To the right of the edge of we it would take place. Inside V there are both kinds of regions. What this means that the parameters a and b are new parameters characterizing the state of liquid and gas phases. This could allow better understanding of vapour phase.

5. The appearance of flux tubes could be understood in two manners.

   (a) New flux tube pairs could emerge by reconnection of flux tube loops associated with molecules.

   (b) Already existing long flux tubes (or flux tube pairs) between molecules shorten in a phase transition reducing $h_{eff} = n \times h$ to its standard value and forces the molecules connected by them to become close together. Since the phases with non-standard value of Planck constant quite generally have higher energy (for instance, bond energies are higher and atomic binding energies lower) this implies that energy is liberated in this connection process.

It seems that flux tube picture could explain the lever rule, which works but cannot be understood in thermodynamics and statistical physics. This would be seen as a direct indication for the reality of flux tubes.

3 Strangeness in the freezing of water

Water has hundreds of anomalies as one learns from the excellent web pages of Martin Chaplin (see `http://www1.lsbu.ac.uk/water/`). I have discussed these anomalies in [K1]. One of them relates to the freezing of water. Usually the volume per particle is reduced in freezing but now it increases. Second biologically enormously important anomaly is the decrease of the molecular volume instead of increase as the temperature grows form 0 °C to 4 °C.

In TGD framework the anomalies of water can be seen as a support for the existence of two phases in water: dark phase and ordinary phase. On basis of the model explaining Maxwell's rule at criticality, one can ask whether the dark and ordinary phases correspond to those for the flux tubes rather than molecules. In the case of water the flux tubes could be assigned to hydrogen bonds, which could have quite long lengths for large values of $h_{eff}/h = n$. They would be present also for other liquids. Maybe the flux tubes carrying $h_{eff}/n = n$ dark protons associated with hydrogen bonds distinguish water from other liquids.

Dark states have higher energy than ordinary ones so that the formation of dark phase requires energy. The natural assumption is that the dark phase transforms to ordinary one in the freezing of water. Long dark flux tubes would get shorter. Alternatively, dark flux loops reconnect and form short flux tube pairs between molecules assignable to hydrogen bonds. Why this should lead to an expansion of the molecular volume?

To answer this question it is useful consider first the second anomaly. Why the volume increases as one reduces temperature from 4 °C to 0 °C? As $h_{eff}/h = n$ for flux tube or reconnecting flux tubes decreases, the length of flux tube as quantal length shortens and the result could be a rather rigid short stick. There exists a proposal that these rigid flux tubes reduce the motility of water molecules belonging to the water clusters, which correspond to connected flux tube networks. Since molecules cannot move freely anymore, empty volume is generated. The outcome is an increase of the average molecular volume.

What about freezing?

1. Above boiling point water has 3.4 hydrogen bonds to its neighbors, which is nearly the maximal number 4 realized for ice (see `http://tinyurl.com/ydcedet4`). Either all existing long flux tubes would have shortened or all loops would have shortened and reconnected to flux tube pairs.

2. In freezing the dark energy is liberated so that the latent heat should be higher when a phase with a non-standard value of $h_{eff}/h = n$ is present in the liquid phase. This could explain the especially high latent heat 334 kJ/kg for water.

3. Only ammonia NH^3 (see `http://tinyurl.com/yc6zcl6o`) has comparable latent heat 332.17 kJ/kg (see `http://tinyurl.com/h3lvm43`) . Interestingly, also NH_3 molecules form hydrogen bonds and for this reason ammonium is easily miscible to water. This property might relate also to the biological importance of NH_3 and nitrogen and hydrogen containing molecules.

4. Also O and F form hydrogen bonds. More generally, any atom containing lone electron pairs, that is pairs of valence electrons, which do not belong to valence bonds, can form hydrogen bonds. A possible explanation is that the lone pair goes to a flux tube pair associated with the hydrogen bond and gives rise to a Cooper pair making possible high T_c superconductivity by the mechanism discussed in [K2, K3]. Flux tube pair would contain also the dark proton delocalized to both flux tubes.

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