

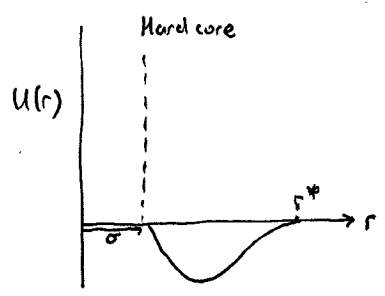
12. PHASE TRANSITIONS AND BROKEN SYMMETRY.

PELITI CH. 5
PATHRIA CH. 12
COLEMAN CH. 11.

Phase Transitions

- CHANGES OF STATE, CONDENSATION
- DEVELOPMENT OF BROKEN SYMMETRY.

1. CONDENSATION



$$H = \sum \frac{p_j^2}{2m} + \sum_{i < j} u(\vec{r}_i - \vec{r}_j)$$

$$Q_N(V, T) = \frac{1}{N!} \int \prod_{j=1}^N \frac{d^3 p_j d^3 r_j}{h^3} e^{-\beta H}$$

WHAT PROPERTIES DOES THIS PREDICT?

$$\bullet \quad -\frac{A}{Nk_B T} = \frac{1}{N} \ln Q_N(V, T) = f(V, T) \equiv \frac{-\mu}{k_B T} \quad N \rightarrow \infty$$

$$P = -\frac{\partial A}{\partial V} = k_B T \frac{\partial f}{\partial V} \geq 0.$$

$$\bullet \quad \frac{\partial P}{\partial V} = k_B T \frac{\partial^2 f}{\partial V^2} \leq 0 \quad \text{always (negative / zero.)}$$

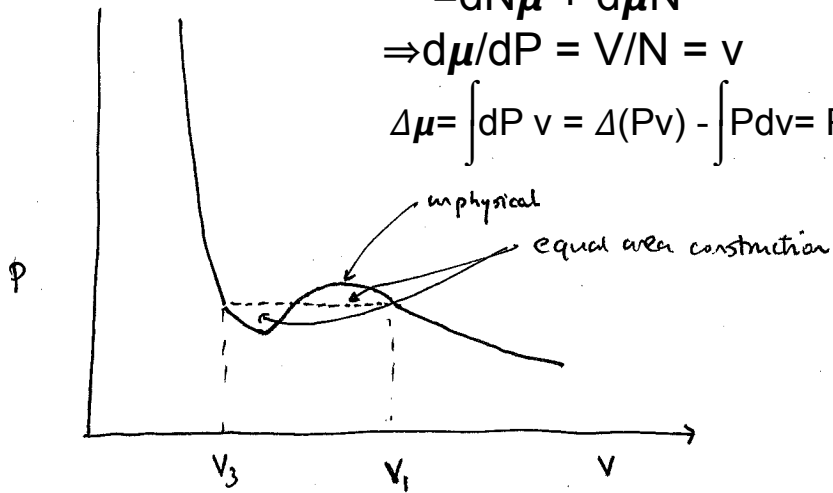
$\frac{dP}{dV} = 0 \Leftrightarrow$ infinitely compressible.
 \equiv TWO PHASES

$$dG = \mu dN + V dP - S dT$$

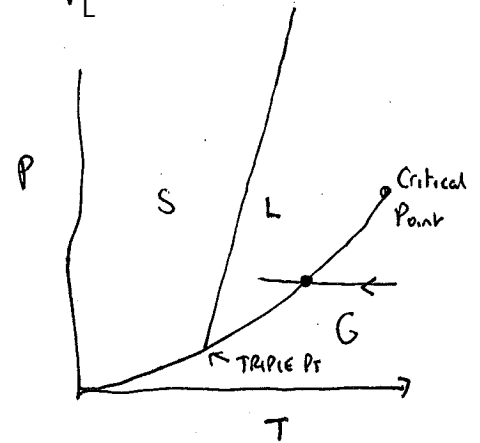
$$= dN \mu + d\mu N$$

$$\Rightarrow d\mu/dP = V/N = v$$

$$\Delta\mu = \int dP v = \Delta(Pv) - \int P dv = P\Delta v - \int P dV = - \int \Delta P dv$$



$$\Delta\mu = - \int_{v_L}^{v_G} \Delta P dv = 0.$$



v_1^{-1} & v_3^{-1} are the densities of the low/high density phase.

Approximate methods which assume uniform density give regions where

$\frac{dP}{dv} > 0$. These are unphysical, unstable solutions.

- Singularities in $P(v, T)$ are a result of taking the thermodynamic limit

$$P_N = \left[k_B T \frac{\partial \ln Q}{\partial V} \right] \quad \text{is free from singularities}$$

$$P(v, T) = \lim_{N \rightarrow \infty} P_N(v, T) \quad \text{has singularities.}$$

12.2 Van der Waals Gas

Maxwell was so excited about Van der Waals Thesis that he taught it w/while to learn Dutch. VdW 1873. JCM 1874. (Nature)

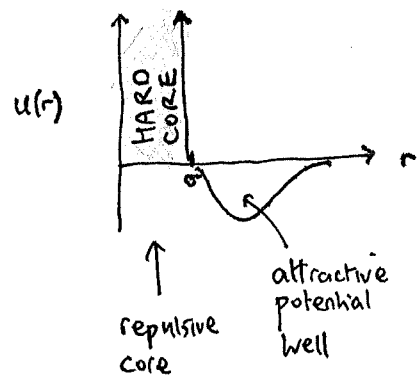
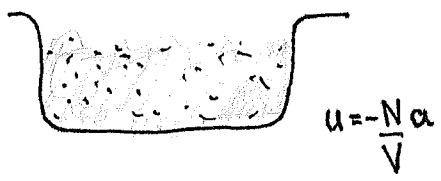
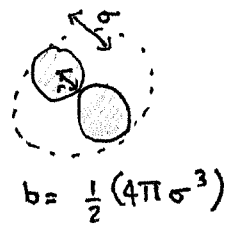
$$PV = Nk_B T \iff A = -Nk_B T \ln \left(\frac{V/N}{\lambda_T^3} e \right)$$

Ideal Gas.

- Intrinsic volume of gas $V \rightarrow V - bN$.
- Interaction between them causes a pressure reduction.

$$a = -\frac{1}{2} \int d^3r U(r)$$

ATTRACTIVE



$$u = u_H + u_W$$

$$Z = \frac{1}{N! \lambda_T^{3N}} \int d^3r_1 \dots d^3r_N \exp \left[- \sum_{i < j} (u(r_i - r_j) \beta) \right]$$

$$u(r) = u_{\text{hardCore}}(r) + u_{\text{well}}(r) = u_H + u_W$$

$$Z_0 = \int d^3r_1 \dots d^3r_N e^{-\beta u_H}$$

$$\tilde{Z} = Z_0 \left(\frac{\tilde{Z}}{Z_0} \right) = Z_0 \left\langle e^{-\beta \sum_{i < j} u_W(r_i - r_j)} \right\rangle_{u_H}$$

$$Z = \frac{1}{N! \lambda_T^{3N}} Z_0 \left\langle \exp - \beta/2 \int d^3x_1 d^3x_2 \rho(x_1) u_w(x_1 - x_2) \rho(x_2) \right\rangle$$

$$Z_0 = V(V-v)(V-2v) \dots (V-(N-1)v)$$

$$= \exp \left[\sum_{j=0}^{N-1} \ln(V-jv) \right] = \exp \left[N \ln V - \sum_{j=0}^{N-1} \frac{v_0}{V} j \right]$$

$$= \exp \left[N \left(\ln V - (N-1) \frac{v_0}{2V} \right) \right]$$

$$\approx \exp \left[N \ln \left(V - \frac{Nv_0}{2} \right) \right] = (V - Nb)^N \quad b = \frac{v_0}{2} = \frac{2\pi\sigma^3}{3}$$

$$\langle e^{-\beta u} \rangle \approx 1 - \beta \langle u \rangle$$

$$\langle u \rangle = \frac{1}{2} \int d^3r_1 d^3r_2 \rho(r_1) \rho(r_2) u(r_1 - r_2) = \frac{V}{2} \left(\frac{N}{V} \right)^2 \int_{r>\sigma} d^3r u_w(r)$$

$$= -N \left(\frac{N}{V} \right) a$$

$$Z = \frac{q^N}{N! \lambda_T^{3N}}$$

$$q = (V - Nb) \left(1 + \frac{N^2 a}{V k_B T} \right)$$

$$A = -k_B T \ln Z = -Nk_B T \ln \left[\left(\frac{V-Nb}{N\lambda_T^3} \right) e \right] - \frac{N^2 a}{V}$$

$$P = -\frac{\partial A}{\partial V} = \frac{Nk_B T}{(V-Nb)} - \frac{N^2 a}{V^2}$$

$$\left(P + \left(\frac{N}{V} \right)^2 a \right) (V-Nb) = Nk_B T.$$

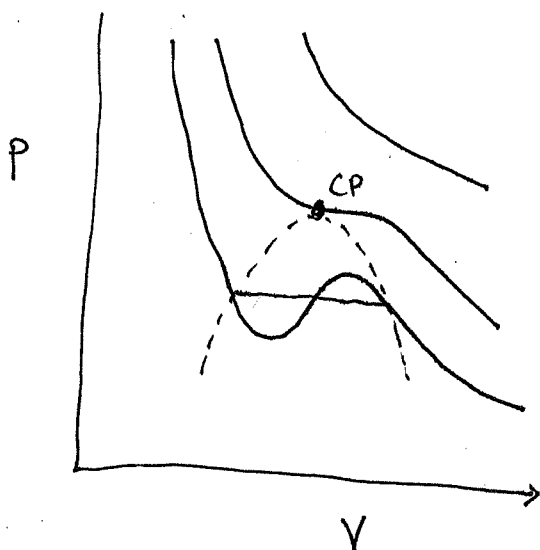
$$v = V/N$$

$$\left(P + \frac{a}{v^2} \right) (v-b) = k_B T$$

a/v^2 = pressure reduction. b = reduced volume.

Van der Waals
Equation of State. 1873.

James Clerk Maxwell, 1874



$$P = -\frac{a}{v^2} + \frac{k_B T}{v-b}$$

$$0 = \frac{\partial P}{\partial v} = \frac{\partial^2 P}{\partial v^2}$$

$$v_c = 3b, \quad k_B T_c = \frac{8a}{27b}, \quad P_c = \frac{a}{27b^2}$$

$$P_r = \frac{P}{P_c} \quad V_r = \frac{V}{V_c} \quad T_r = \frac{T}{T_c}$$

$$\left(P_r + \frac{3}{V_r^2} \right) (3V_r - 1) = 8T_r$$

• Same for all gases obeying vdW.

$$\text{Put } V_r = 1 + \delta \quad T_r = 1 + t \quad P_r = 1 \quad t = \left(\frac{T}{T_c} - 1 \right)$$

$$\left(1 + \frac{3}{(1+\delta)^2} \right) (3 + 3\delta - 1) = 8(1+t)$$

$$(4 - 6\delta)(2 + 3\delta) = 8(1+t)$$

$$\Rightarrow 8 - 18\delta^2 = 8 + 8t$$

$$\delta^2 = -\frac{4}{9}t$$

$$(V_r - 1) = \pm \frac{2}{3} \left(1 - \frac{T}{T_c} \right)^{1/2}$$

$$(V_{gs} - V_{liq}) \propto (T_c - T)^\beta$$

$$\beta = \frac{1}{2}$$

Experimentally $\beta \approx \frac{1}{3}$!

OTHER SINGULARITIES

$$\chi = - \frac{\partial V}{\partial p} \sim (T - T_c)^{-\gamma}$$

$\gamma = 1$ VdW

$\gamma_{exp} \sim 1.25$

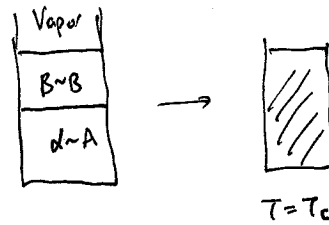
$$C \sim (T - T_c)^{-\alpha}$$

VdW ΔC_V for $T < 0$.
($T - T_c < 0$).

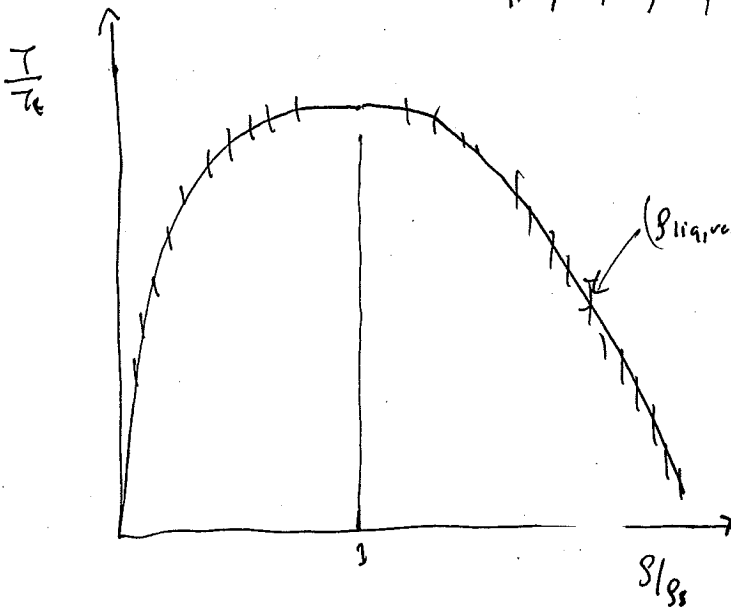
Exp $\alpha \sim 1/3 - 1/9$ all gases

OTHER SYSTEMS + SIMILAR BEHAVIOUR

- Binary Mixtures.



Ar, A, Kr, Xe, N₂, O₂, CO, CH₄



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of a physical connection between the condition of the sun's surface, and the meteorology and magnetism of our globe.

"In the first place, we have the observations of Sir E. Sabine, which seem to indicate a connection between sun-spots and magnetic disturbances, inasmuch as both phenomena are periodical, and have their maxima and minima at the same times.

"On the other hand, the researches of Messrs. Baxendell and Meldrum appear to indicate a relation between the wind-currents of the earth and its magnetism, and also between the earth's wind-currents and the state of the sun's surface.

"In the last place, the researches of Messrs. De la Rue, Stewart, and Loewy appear to indicate a connection between the behaviour of sun-spots and the positions of the more prominent planets of our system. Whatever be the probability of the conclusions derived from these various researches, they at least show the wisdom of studying together for the future these various branches of observational science."

A further report by the same committee tells us that "It is not enough to obtain a record of the areas and positions of the various sun-spots. The velocity of cyclonic motion, the chemical nature of the outbursts, the disposition and character of the faculae and prominences, and many other points, are, as shown by Mr. Lockyer, even more characteristic of the nature of solar action than the magnitude of the spotted area, and are equally worthy of a careful and constant study."

The evidence in favour of some strange and variable action of the sun may, perhaps, be compared to that in favour of the existence of America before that continent was discovered by Columbus; and it might have been thought that in an age like the present the difficulty of organising solar research would be very much less than that experienced by Columbus in organising an American expedition; but this is not the case. Indeed, it is not very creditable to the scientific authorities of this country that they have not entered more readily into a subject of this importance. From the quotations given above, our readers will see that this is not the first time the subject has been brought before the British Association.

A large and influential committee, embracing in its ranks many of the most distinguished members of the Association, endeavoured to bring the subject before the Administrative Council of that body, but did not succeed in getting the Council to move in the matter, or even to pronounce any opinion upon the subject. We hardly think this was proper treatment of an important problem, which had found such advocates as Col. Strange, Drs. De la Rue and Joule, Messrs. Baxendell, Lockyer, and Meldrum, as well as the general support of the most distinguished physicists of the country.

Clearly Col. Strange is right in supposing that a problem of this importance and extent can be properly undertaken only by Government. His remarks on this subject are so well put that we will report them here. Starting with the fundamental axiom that private enterprise should be allowed the most perfect freedom from interference or competition by the State, he lays down the following conditions for Government action in any scientific problem:—

(a) That the probable results of the research be beneficial, in the widest sense of that term, to the community at large, or to the various departments of the State.

(b) That the research is too costly or commercially

too unremunerative to be undertaken and vigorously prosecuted by individuals.

(c) That the research requires continuous, uninterrupted work, extending over very long periods, and conducted by systematically organised establishments.

It will at once be seen that all these conditions apply to solar research; and the Governments of other nations have already perceived the fact. Our readers are aware that the Governments of France and America have it in contemplation to establish solar observatories, and a recent number of this periodical informs them that the German Government has already founded one on a large scale, of which it is possible the illustrious Kirchhoff will be the Director.

In conclusion, as we are advocating a question of reform, it is desirable that something in the shape of practical suggestions should be made. Now, in the first place and with reference to the great problem of Solar Physics, we think that this should certainly be encouraged by the establishment of a distinct central observatory devoted to the purpose; for it would be manifestly unfair to our illustrious Astronomer Royal to throw upon him the additional burden of an institution so very different from that over which he now presides.

In the next place, with reference to photographic delineations of the solar disc, Col. Strange has made a suggestion, at once so practical and simple, that we cannot do better than quote his own words:—

"With respect to sun-spot researches, it fortunately happens that the photographic records need not be all taken at the same station. The record of one day taken in England can be combined with the record of the next day taken at the other side of the globe. Hence, in order to obtain this daily record it is only necessary to select a certain number of stations in localities such that there shall always be clear weather at one of them. India offers peculiar facilities for such a selection of stations, owing to the great variety of climate to be found in that country during the same period of the year. Perhaps four or five such stations would suffice for India, and if absolute continuity of record could not be obtained by them, the deficiencies could easily be made good by stations in our colonial possessions."

It is well known how slowly such things march in this country; nevertheless we look with much confidence to the forthcoming report of the Royal Commission appointed to investigate matters of this nature, and to urge upon Government such means as they consider shall tend to the advancement of science and to the good of the country.

BALFOUR STEWART

VAN DER WAALS ON THE CONTINUITY OF THE GASEOUS AND LIQUID STATES

Over de continuïteit van den gas- en vloeïstoftoestand. Academisch proefschrift. Door Johannes Diderik van der Waals. (Leiden: A. W. Sijthoff, 1873.)

THAT the same substance at the same temperature and pressure can exist in two very different states, as a liquid and as a gas, is a fact of the highest scientific importance, for it is only by the careful study of the difference between these two states, the conditions of the substance passing from one to the other, and the phenomena which occur at the surface which separates a liquid from its vapour, that we can expect to obtain a dynamical

theory of liquids. A dynamical theory of "perfect" gases is already in existence; that is to say, we can explain many of the physical properties of bodies when in an extremely rarefied state by supposing their molecules to be in rapid motion, and that they act on one another only when they come very near one another. A molecule of a gas, according to this theory, exists in two very different states during alternate intervals of time. During its encounter with another molecule, an intense force is acting between the two molecules, and producing changes in the motion of both. During the time of describing its free path, the molecule is at such a distance from other molecules that no sensible force acts between them, and the centre of mass of the molecule is therefore moving with constant velocity and in a straight line.

If we define as a perfect gas a system of molecules so sparsely scattered that the aggregate of the time which a molecule spends in its encounters with other molecules is exceedingly small compared with the aggregate of the time which it spends in describing its free paths, it is not difficult to work out the dynamical theory of such a system. For in this case the vast majority of the molecules at any given instant are describing their free paths, and only a small fraction of them are in the act of encountering each other. We know that during an encounter action and reaction are equal and opposite, and we assume, with Clausius, that on an average of a large number of encounters the proportion in which the kinetic energy of a molecule is divided between motion of translation of its centre of mass and motions of its parts relative to this point approaches some definite value. This amount of knowledge is by no means sufficient as a foundation for a complete dynamical theory of what takes place during each encounter, but it enables us to establish certain relations between the changes of velocity of two molecules before and after their encounter.

While a molecule is describing its free path, its centre of mass is moving with constant velocity in a straight line. The motions of parts of the molecule relative to the centre of mass depend, when it is describing its free path, only on the forces acting between these parts, and not on the forces acting between them and other molecules which come into play during an encounter. Hence the theory of the motion of a system of molecules is very much simplified if we suppose the space within which the molecules are free to move to be so large that the number of molecules which at any instant are in the act of encountering other molecules is exceedingly small compared with the number of molecules which are describing their free paths. The dynamical theory of such a system is in complete agreement with the observed properties of gases when in an extremely rare condition.

But if the space occupied by a given quantity of gas is diminished more and more, the lengths of the free paths of its molecules will also be diminished, and the number of molecules which are in the act of encounter will bear a larger proportion to the number of those which are describing free paths, till at length the properties of the substance will be determined far more by the nature of the mutual action between the encountering molecules than by the nature of the motion of a molecule when describing its free path. And we actually find that the properties of the substance become very different after it has reached

a certain degree of condensation. In the rarefied state its properties may be defined with considerable accuracy in terms of the laws of Boyle, Charles, Gay-Lussac, Dulong and Petit, &c., commonly called the "gaseous laws." In the condensed state the properties of the substance are entirely different, and no mode of stating these properties has yet been discovered having a simplicity and a generality at all approaching to that of the "gaseous laws." According to the dynamical theory this is to be expected, because in the condensed state the properties of the substance depend on the mutual action of molecules when engaged in close encounter, and this is determined by the particular constitution of the encountering molecules. We cannot therefore extend the dynamical theory from the rarer to the denser state of substances without at the same time obtaining some definite conception of the nature of the action between molecules when they are so closely packed that each molecule is at every instant so near to several others that forces of great intensity are acting between them.

The experimental data for the study of the mutual action of molecules are principally of two kinds. In the first place we have the experiments of Regnault and others on the relation between the density, temperature, and pressure of various gases. The field of research has been recently greatly enlarged by Dr. Andrews in his exploration of the properties of carbonic acid at very high pressures. Experiments of this kind, combined with experiments on specific heat, on the latent heat of expansion, or on the thermometric effect on gases passing through porous plugs, furnish us with the complete theory of the substance, so far as pure thermodynamics can carry us.

For the further study of molecular action we require experiments on the rate of diffusion. There are three kinds of diffusion—that of matter, that of visible motion, and that of heat. The inter-diffusion of gases of different kinds, and the viscosity and thermal conductivity of a gaseous medium, pure or mixed, enable us to estimate the amount of deviation which each molecule experiences on account of its encounter with other molecules.

M. Van der Waals, in entering on this very difficult inquiry, has shown his appreciation of its importance in the present state of science; many of his investigations are conducted in an extremely original and clear manner; and he is continually throwing out new and suggestive ideas; so that there can be no doubt that his name will soon be among the foremost in molecular science.

He does not, however, seem to be equally familiar, as yet, with all parts of the subject, so that in some places, where he has borrowed results from Clausius and others, he has applied them in a manner which appears to me erroneous.

He begins with the very remarkable theorem of Clausius, that in stationary motion the mean kinetic energy of the system is equal to the mean virial. As in this country the importance of this theorem seems hardly to be appreciated, it may be as well to explain it a little more fully.

When the motion of a material system is such that the sum of the moments of inertia of the system about three axes at right angles to each other through its centre of mass does not vary by more than small quantities from a constant value, the system is said to be in a state of sta-

tionary motion. The motion of the solar system satisfies this condition, and so does the motion of the molecules of a gas contained in a vessel.

The kinetic energy of a particle is half the product of its mass into the square of its velocity, and the kinetic energy of a system is the sum of the kinetic energy of its parts.

When an attraction or repulsion exists between two points, half the product of this stress into the distance between the two points is called the Virial of the stress, and is reckoned positive when the stress is an attraction, and negative when it is a repulsion. The virial of a system is the sum of the virial of the stresses which exist in it.

If the system is subjected to the external stress of the pressure of the sides of a vessel in which it is contained, the amount of virial due to this external stress is three halves of the product of the pressure into the volume of the vessel.

The virial due to internal stresses must be added to this.

The theorem of Clausius may now be written—

$$\frac{1}{2} \Sigma (m \bar{v}^2) = \frac{3}{2} p V + \frac{1}{2} \Sigma \Sigma (R r)$$

The left-hand member denotes the kinetic energy.

On the right hand, in the first term, p is the external pressure on unit of area, and V is the volume of the vessel.

The second term represents the virial arising from the action between every pair of particles, whether belonging to different molecules or to the same molecule. R is the attraction between the particles, and r is the distance between them. The double symbol of summation is used because every pair of points must be taken into account, those between which there is no stress contributing, of course, nothing to the virial.

As an example of the generality of this theorem, we may mention that in any framed structure consisting of struts and ties, the sum of the products of the pressure in each strut into its length, exceeds the sum of the products of the tension of each tie into its length, by the product of the weight of the whole structure into the height of its centre of gravity above the foundations. (See a paper on "Reciprocal Figures, &c." Trans. R. S. Edin., vol. xxvi. p. 14. 1870.)

In gases the virial is very small compared with the kinetic energy. Hence, if the kinetic energy is constant, the product of the pressure and the volume remains constant. This is the case for a gas at constant temperature. Hence we might be justified in conjecturing that the temperature of any one gas is determined by the kinetic energy of unit of mass.

The theory of the exchange of the energy of agitation from one body to another is one of the most difficult parts of molecular science. If it were fully understood, the physical theory of temperature would be perfect. At present we know the conditions of thermal equilibrium only in the case of gases in which encounters take place between only a pair of molecules at once. In this case the condition of thermal equilibrium is that the mean kinetic energy due to the agitation of the centre of mass of a molecule is the same, whatever be the mass of the molecule, the mean velocity being consequently less for the more massive molecules.

With respect to substances of more complicated constitution, we know, as yet, nothing of the physical condition on which their temperature depends, though the researches of Boltzmann on this subject are likely to result in some valuable discoveries.

M. Van der Waals seems, therefore, to be somewhat too hasty in assuming that the temperature of a substance is in every case measured by the energy of agitation of its individual molecules, though this is undoubtedly the case with substances in the gaseous state.

Assuming, however, for the present that the temperature is measured by the mean kinetic energy of a molecule, we obtain the means of determining the virial by observing the deviation of the product of the pressure and volume from the constant value given by Boyle's law.

It appears by Dr. Andrews' experiments that when the volume of carbonic acid is diminished, the temperature remaining constant, the product of the volume and pressure at first diminishes, the rate of diminution becoming more and more rapid as the density increases. Now, the virial depends on the number of pairs of molecules which are at a given instant acting on one another, and this number in unit of volume is proportional to the square of the density. Hence the part of the pressure depending on the virial increases as the square of the density, and since, in the case of carbonic acid, it diminishes the pressure, it must be of the positive sign, that is, it must arise from *attraction* between the molecules.

But if the volume is still further diminished, at a certain point liquefaction begins, and from this point till the gas is all liquefied no increase of pressure takes place. As soon, however, as the whole substance is in the liquid condition, any further diminution of volume produces a great rise of pressure, so that the product of pressure and volume increases rapidly. This indicates negative virial, and shows that the molecules are now acting on each other by *repulsion*.

This is what takes place in carbonic acid below the temperature of 30.92°C . Above that temperature there is first a positive and then a negative virial, but no sudden liquefaction.

Similar phenomena occur in all the liquefiable gases. In other gases we are able to trace the existence of attractive force at ordinary pressures, though the compression has not yet been carried so far as to show any repulsive force. In hydrogen the repulsive force seems to prevail even at ordinary pressures. This gas has never been liquefied, and it is probable that it never will be liquefied, as the attractive force is so weak.

We have thus evidence that the molecules of gases attract each other at a certain small distance, but when they are brought still nearer they repel each other. This is quite in accordance with Boscovich's theory of atoms as massive centres of force, the force being a function of the distance, and changing from attractive to repulsive, and back again several times, as the distance diminishes. If we suppose that when the force begins to be repulsive it increases very rapidly as the distance diminishes, so as to become enormous if the distance is less by a very small quantity than that at which the force first begins to be repulsive, the phenomena will be precisely the same as those of smooth elastic spheres.

M. Van der Waals makes his molecules elastic spheres, which, when not in contact, attract each other. His treatment of the "molecular pressure" arising from their attraction seems ingenious, and on the whole satisfactory, though he has not attempted a complete calculation of the attractive virial in terms of the law of force.

His treatment of the repulsive virial, however, shows a departure from the principles on which his investigation is founded. He considers the effect of the size of the molecules in diminishing the length of their "free paths," and he shows that this effect, in the case of very rare gases, is the same as if the volume of the space in which the molecules are free to move had been diminished by four times the sum of the volumes of the molecules themselves. He then substitutes for V , the volume of the vessel in Clausius' formula, this volume diminished by four times the molecular volume, and thus obtains the equation—

$$\left(\phi + \frac{a}{V^2}\right)(V - b) = R(1 + at),$$

where ϕ is the externally applied pressure, $\frac{a}{V^2}$ is the molecular pressure arising from attraction between the molecules, which varies as the square of the density, or inversely as the square of the volume. The first factor is thus what he considers the total effective pressure. V is the volume of the vessel, and b is four times the volume of the molecules. The second factor is therefore the "effective volume" within which the molecules are free to move.

The right hand member expresses the kinetic energy, represented by the absolute temperature, multiplied by a quantity, R , constant for each gas.

The results obtained by M. Van der Waals by a comparison of this equation with the determinations of Regnault and Andrews are very striking, and would almost persuade us that the equation represents the true state of the case. But though this agreement would be strong evidence in favour of the accuracy of an empirical formula devised to represent the experimental results, the equation of M. Van der Waals, professing as it does to be derived from the dynamical theory, must be subjected to a much more severe criticism.

It appears to me that the equation does not agree with the theorem of Clausius on which it is founded.

In that theorem ϕ is the pressure of the sides of the vessel, and V is the volume of the vessel. Neither of these quantities is subject to correction.

The assumption that the kinetic energy is determined by the temperature is true for perfect gases, and we have no evidence that any other law holds for gases, even near their liquefying point.

The only source of deviation from Boyle's law is therefore to be looked for in the term $\frac{1}{2} \Sigma \Sigma (Rr)$, which expresses the virial. The effect of the repulsion of the molecules, causing them to act like elastic spheres, is therefore to be found by calculating the virial of this repulsion.

Neglecting the effect of attraction, I find that the effect of the impulsive repulsion reduces the equation of Clausius to the form—

$$\phi V = \frac{1}{3} \Sigma (m \bar{v}^2) \left\{ 1 - 2 \log \left(1 - 8 \frac{\rho}{\sigma} + 17 \frac{\rho^2}{\sigma^2} - \&c. \right) \right\}$$

where σ is the density of the molecules and ρ the mean density of the medium,

The form of this equation is quite different from that of M. Van der Waals, though it indicates the effect of the impulsive force in increasing the pressure. It takes no account of the attractive force, a full discussion of which would carry us into considerable difficulties.

At a constant temperature the effect of the attractive virial is to diminish the pressure by a quantity varying as the square of the density, as long as the encounters of the molecules are, on the whole, between two at a time, and not between three or more. The effect of the attraction in deflecting the paths of the molecules is to make the number of molecules which at any given instant are at distances between r and $r + dr$ of each other greater than the number in an equal volume at a greater distance in the proportion of the velocities corresponding to these distances. As the temperature rises, the volume being constant, the ratio of these velocities approaches to unity, so that the distribution of molecules according to distance becomes more uniform, and the virial is thus diminished.

If there is a virial arising from repulsive forces acting through a finite distance, a rise of temperature will increase the amount of this kind of virial.

Hence a rise of temperature at constant volume will produce a greater increase of pressure than that given by the law of Charles.

The isothermal lines at higher temperatures will exhibit less of the diminution of pressure due to attraction, and as the density increases will show more of the increase of pressure due to repulsion.

I must not, however, while taking exception to part of the work of M. Van der Waals, forget to add that to him alone are due the suggestions which led me to examine the theory of virial more carefully in order to explore the continuity of the liquid and the gaseous states.

I cannot now enter into the comparison of his theoretical results with the experiments of Andrews, but I would call attention to the able manner in which he expounds the theory of capillarity, and to the remarkable phenomenon of the surface tension of gases which he tells (p. 38) has been observed by Bosscha in tobacco smoke. As tobacco smoke is simply warm air with a slight excess of carbonic acid, carrying solid particles along with it, the change of properties at the surface of the cloud must be very slight compared with that at the surface where two really different gases first come together. If, therefore, the phenomenon observed by Bosscha is a true instance of surface-tension, we may expect to discover much more striking phenomena at the meeting-place of different gases, if we can make our observations before the surface of discontinuity has been obliterated by the inter-diffusion of the gases.

J. CLERK-MAXWELL

LETTERS TO THE EDITOR

[The Editor does not hold himself responsible for opinions expressed by his correspondents. Neither can he undertake to return, or to correspond with the writers of, rejected manuscripts. No notice is taken of anonymous communications.]

An Anagram

THE practice of enclosing discoveries in sealed packets and sending them to Academies, seems so inferior to the old one of

LATTICE GAS

$$Q_1 = V \lambda^{-3}$$

$$Q_N = \frac{1}{N!} (Q_1)^N$$

$$H = k + u$$

$$Q = \frac{1}{N!} \int \prod_{i=1}^N \frac{d^3 p_i d^3 q_i}{h^3} e^{-H/k_B T}$$

$$Q = \frac{\lambda^{-3N}}{N!} \int \prod_{j=1}^N d^3 r_j \exp[-U/k_B T]$$

Simplified

- Only sites of cubic lattice
- One particle at most
- $\epsilon =$ energy of n.n.

$$Q_N = \lambda^{-3N} \sum_{\{\tau_i\}} \delta_{N, \sum \tau_i} \exp \left[\sum \frac{\epsilon}{k_B T} \tau_i \tau_j \right]$$

$$\sum \tau_i = N.$$

$$Z_{GC} = \sum_{N=0}^{\infty} e^{mNB} Q_N = \sum_{\tau} \exp \left[-\frac{H}{k_B T} \right]$$

$$H = - \sum_{\langle ij \rangle} \tau_i \tau_j - \sum \tilde{\mu} \tau_j$$

$$\tilde{\mu} = \mu - 3k_B T \ln 2$$

$$\langle x \rangle = \langle \tau \rangle = \frac{1}{N} \sum \tau_i$$

ISING MODEL

$$\sigma_i = 2\tau_i - 1$$

$$H = -J \sum \sigma_i \sigma_j - \sum h \sigma_i$$

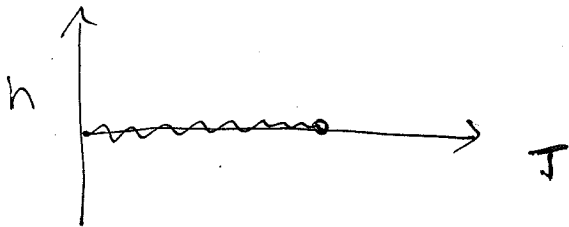
$$J = e/4 \quad h = (\mu + e\beta)/2$$

Coexistence curve $\mu = \mu^*(\tau)$

$$x^+ = \lim_{\mu \rightarrow \mu^+} x(\mu, T) \quad x^- = \lim_{\mu \rightarrow \mu^{*-}} x(\mu, T)$$

$$(x^+ - x^-) \propto (T - T_c)^\beta$$

J = coord #.



Monte Carlo Simulations: Ising Model

The Monte Carlo method is a numerical scheme to average over the Canonical ensemble. We have, for example the Ising model

$$H = J \sum_{\langle i,j \rangle} \sigma_i \cdot \sigma_j - B \sum_j \sigma_j \quad \sigma_i = \pm 1$$

and we would like to implement an ensemble in which the probability of a configuration is

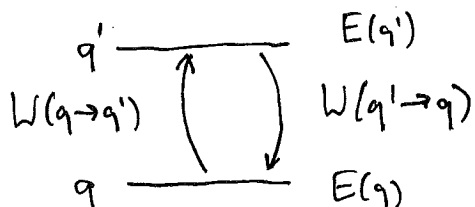
$$P[\{\sigma\}] \propto e^{-\beta H[\{\sigma\}]}$$

The Monte Carlo approach, invented by Metropolis, Rosenbluth, Rosenbluth, Teller & Teller (1953) carries out "importance sampling" of the ensemble by using an update method that preserves detailed balance.

Suppose $W(q \rightarrow q')$ is the rate to make transitions from state q

to state q' , then the distribution will evolve according to

$$P(q, t+1) = P(q, t) + \sum_{q'} P(q', t) W(q' \rightarrow q) - \sum_{q'} P(q, t) W(q \rightarrow q')$$



Stationarity will occur when $P(q, t) = P_{eq}(q, t)$, such that

$$\sum_{q'} P_{eq}(q') W(q' \rightarrow q) = P_{eq}(q) \sum_{q'} W(q \rightarrow q')$$

Detailed balance requires that the rate of transition $q \rightarrow q'$ is equal to the rate $q' \rightarrow q$ i.e

$$P_{eq}(q') W(q' \rightarrow q) = P_{eq}(q) W(q \rightarrow q')$$

$$\Rightarrow \boxed{W(q \rightarrow q') = \exp(-\beta \Delta E) W(q' \rightarrow q)} \quad \Delta E = E(q') - E(q)$$

$$\boxed{\begin{aligned} W(q \rightarrow q') &= 1 \quad \text{if} \quad \Delta E \leq 0 \\ W(q \rightarrow q') &= \exp(-\beta \Delta E) \quad \Delta E > 0 \end{aligned}} \quad \text{Metropolis algorithm}$$

If $[SE < 0 \parallel \text{Random}[] < \text{Exp}[-SE/T], S_i = -S_i, \{\}]$

With this procedure we can simply sample configurations

$$\langle H \rangle \approx \frac{1}{N_{\text{steps}}} \sum_{j=1}^{N_{\text{steps}}} E(t_j)$$

$$\langle M \rangle = \frac{1}{N_{\text{sites}} N_{\text{steps}}} \sum_{j=1}^{N_{\text{steps}}} \sum_i \delta(i, t_j)$$

We can calculate more involved quantities.

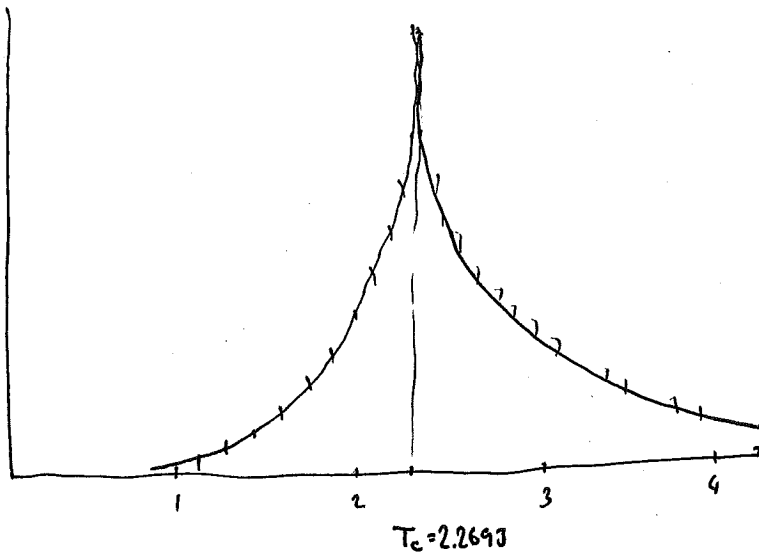
$$C_V = \frac{\langle H^2 \rangle - \langle H \rangle^2}{k_B T^2}$$

$$\langle H^2 \rangle = \frac{\sum E(t_j)^2}{N_{\text{steps}}}$$

$$\langle H \rangle = \frac{\sum E(t_j)}{N_{\text{steps}}}$$

$$\langle M \rangle = \sum_{\{s\}} \frac{M e^{-\beta(H - BM)}}{Z}$$

$$\begin{aligned} \chi &= \frac{\partial \langle M \rangle}{\partial B} = \frac{1}{k_B T} \left(\frac{\sum M^2 e^{-\beta H}}{Z} - \left(\frac{\sum M e^{-\beta H}}{Z} \right)^2 \right) \\ &= \frac{\langle M^2 \rangle - \langle M \rangle^2}{k_B T} \end{aligned}$$

$\frac{C_V}{N_{\text{sites}}}$ 

Good agreement between exact & M.C on 128×128 lattices
with $10^5 - 10^6$ Monte Carlo updates per spin!

Generally - first thermalize - then measure.

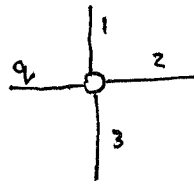
1. Generate random initial config.

ISING MODEL : Mean Field Theory

$$\Psi = \langle \sigma_j \rangle = \frac{1}{N} \sum_j \langle \sigma_j \rangle = \frac{N_\uparrow - N_\downarrow}{N}$$

$$\left. \begin{aligned} N_\uparrow &= \frac{N}{2} (1 + \Psi) \\ N_\downarrow &= \frac{N}{2} (1 - \Psi) \end{aligned} \right\} M = (N_\uparrow - N_\downarrow) = N \mu \Psi$$

$$\mathcal{H} = -J \sum \sigma_i \sigma_j - \mu B \sum \sigma_i$$



$q = \#$ nearest neighbors

$$-J \sum \sigma_i \sigma_j \rightarrow -J q \Psi \sum_j \sigma_j$$

How?

$$\sigma_i = \langle \sigma_i \rangle + \delta_i \Leftrightarrow \delta_i = \sigma_i - \langle \sigma_i \rangle$$

$$\begin{aligned} \sigma_i \sigma_j &= (\langle \sigma_i \rangle + \delta_i) (\langle \sigma_j \rangle + \delta_j) \\ &= \langle \sigma_i \rangle \langle \sigma_j \rangle + \langle \sigma_i \rangle \delta_j + \langle \sigma_j \rangle \delta_i + \overbrace{\delta_i \delta_j}^{\text{ignore second order term}} \\ &= \langle \sigma_i \rangle \langle \sigma_j \rangle + \langle \sigma_i \rangle (\sigma_j - \langle \sigma_j \rangle) + \langle \sigma_j \rangle (\sigma_i - \langle \sigma_i \rangle) + O(\delta^2) \\ &= -\langle \sigma_i \rangle \langle \sigma_j \rangle + \langle \sigma_i \rangle \sigma_j + \langle \sigma_j \rangle \sigma_i \\ &= -\Psi^2 + \Psi(\sigma_i + \sigma_j) + O(\delta^2) \end{aligned}$$

$$\Rightarrow -J \sum \sigma_i \sigma_j = N \left[-\Psi^2 \right] - J q \Psi \sum_{i=1}^N \sigma_i$$

$$\begin{aligned} \mathcal{H}_{\text{MFT}} &= -\left(J q \Psi + \mu B \right) \sum_{i=1}^N \sigma_i + \frac{N J q \Psi^2}{2} \\ &= -\mu (B + B_{\text{Weiss}}) \sum \sigma_i + N \frac{(\mu B_{\text{Weiss}})^2}{2 J q} \\ B_{\text{Weiss}} &= J q \Psi / \mu \end{aligned}$$

H_{MF}

$$Z = \sum_{\{\sigma_i\}} e^{-\beta H_{MF}(\sigma_i)} = e^{-\beta A}$$

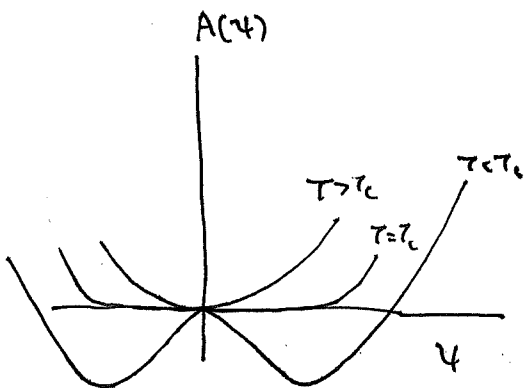
$$= \left[\sum_{\sigma_i} \left(e^{-\beta \left(\frac{Jq}{2} \psi^2 - \mu(B + B_{\text{eff}}) \sigma_i \right)} \right) \right]^N$$

$$= \left(e^{-\beta Jq \psi^2 / 2} 2 \cosh \left(\beta \frac{\mu(B + B_{\text{eff}})}{k_B T} \right) \right)^N = e^{-\beta A}$$

$$\Rightarrow A = -k_B T \ln Z = N \left[\frac{Jq}{2} \psi^2 - k_B T \ln \left(2 \cosh \left(\frac{\mu B + qJ\psi}{k_B T} \right) \right) \right]$$

$$= A[\psi]$$

$$\ln \left(1 + \frac{x^2}{2} + \frac{x^4}{4!} \right) = \frac{x^2}{2} - \frac{x^4}{12} + \dots$$



$$\frac{A[\psi]}{N} = \frac{Jq}{2} \psi^2 - k_B T \left[\frac{(\beta q J \psi)^2}{2} - \frac{(\beta q J \psi)^4}{12} \right] + \dots$$

$$= \frac{Jq}{2} \left(1 - \frac{T_c}{T} \right) \psi^2 + \frac{k_B T}{12} (\beta q J)^4 \psi^4$$

$$k_B T_c = qJ$$

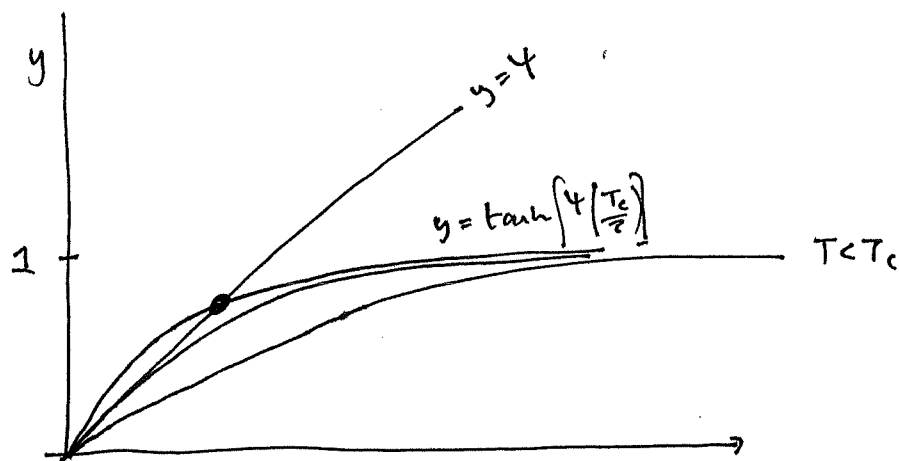
$$\boxed{\frac{A[\psi]}{N} \approx -Jq \left(1 - \frac{T}{T_c} \right) \psi^2 + \frac{qJ}{12} \psi^4 + o(\psi^6)}$$

"LANDAU THEORY"

$$\frac{\partial A}{\partial \psi} = J_q \psi - J_q \tanh\left(\frac{\mu B + q J \psi}{k_B T}\right) = 0$$

$$\Rightarrow \psi = \tanh\left(\frac{\mu B + q J \psi}{k_B T}\right)$$

$$B \rightarrow 0 \quad \psi = \tanh\left(\frac{q J \psi}{k_B T}\right)$$



If $T < T_c = \frac{qJ}{k_B}$, then removal of field

leaves behind a long-range, static order parameter

$$\psi = \langle \sigma_i \rangle.$$

For $T < T_c$ $\text{tanh } x \approx x - x^3/3$ $\psi = \text{tanh}\left(\frac{T_c}{T} \psi\right)$

$$\psi = \frac{T_c}{T} \psi - \frac{1}{3} \left(\frac{T_c}{T} \psi\right)^3$$

$$\Rightarrow 1 = \frac{T_c}{T} \left(1 - \frac{1}{3} \left(\frac{T_c}{T}\right)^2 \psi^2\right)$$

$$\Rightarrow \left(\frac{T_c}{T} \psi\right)^2 = 3 \left(1 - \frac{T}{T_c}\right)$$

$$\psi = \pm \sqrt{3 \left[\left(\frac{T}{T_c}\right)^2 - \left(\frac{T}{T_c}\right)^3 \right]}$$

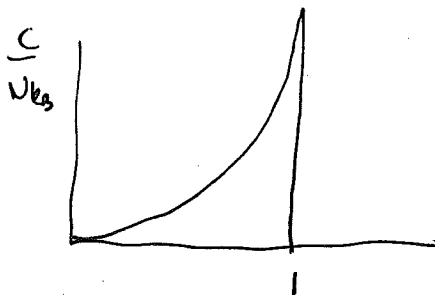
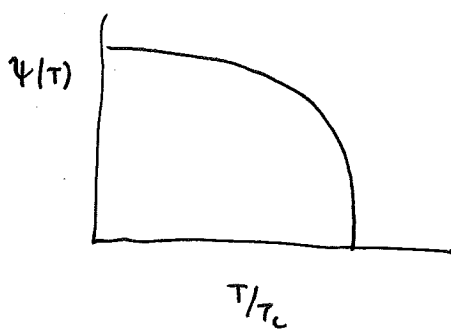
$$\approx \pm \sqrt{3 \left[1 - \frac{T}{T_c} \right]}$$

Broken Symmetry.

Alternatively for $\frac{A[\psi]}{N} = J_q \left[- \left(1 - \frac{T}{T_c}\right) \psi^2 + \frac{\psi^4}{12} \right]$

$$\frac{\partial A}{\partial \psi^2} = 0 \Rightarrow \left(1 - \frac{T}{T_c}\right) = \frac{\psi^2}{3}$$

$$\Rightarrow \psi = \pm \sqrt{3 \left(1 - \frac{T}{T_c}\right)}$$



The energy is given by

$$E = -\frac{1}{2} q J N \psi^2$$

$$C(T) = \frac{\partial E}{\partial T} = -q J N \psi_0 \frac{\partial \psi_0}{\partial T}$$

$$\psi = \tanh\left(\frac{\tau_c \psi}{T}\right) \Rightarrow \frac{d\psi}{dT} = -\frac{\tau_c}{T^2} \psi (1-\psi^2) + \frac{\tau_c}{T} (1-\psi^2) \frac{d\psi}{dT}$$

$$\Rightarrow \frac{d\psi}{dT} = \frac{-(1-\psi^2) \left(\frac{\tau_c}{T^2}\right) \psi}{1 - \frac{\tau_c}{T} (1-\psi^2)}$$

$$\Rightarrow C(T) = \frac{N k_B \psi^2}{\left(\frac{T}{\tau_c}\right)^2 / (1-\psi^2) - T/\tau_c}$$

$$C_v(T^-) = \lim_{T \rightarrow \tau_c} C(T) = \frac{3}{2} N k_B$$

$$\text{Low } T \quad C(T) \sim N k_B \left(\frac{\tau_c}{T}\right)^2 e^{-2\tau_c/T}$$

$$\chi = \frac{\partial M}{\partial B} = N_{\mu} \left(\frac{\partial \psi}{\partial B} \right)_T$$

$$g \frac{J\psi + \mu B}{k_B T} = \ln h^{-2} \psi$$

$$= \frac{N_{\mu}^2}{k_B} \frac{1 - \psi^2}{T - T_c (1 - \psi^2)}$$

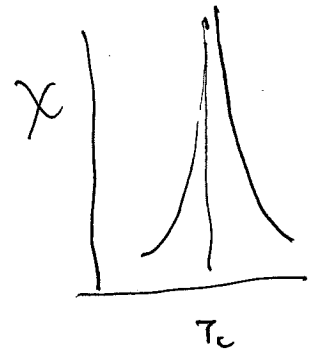
$\psi \ll 1$

$$\chi(T) = \frac{N_{\mu}^2}{k_B} \frac{1}{T - T_c}$$

$T < T_c$ $\psi = \sqrt{3(1 - T/T_c)}$

$$\chi = \frac{N_{\mu}^2}{2k} \frac{1}{(T_c - T)}$$

$T < T_c$



ORDER PARAMETER CONCEPT

Lev Landau 1937

- Snowflake
- Iron magnets
- Superfluidity + Superconductivity
- Electro-weak symmetry breaks after big bang.

} Unified by a single concept.

$$|\psi| = \begin{cases} 0 & T > T_c \\ |\psi_0| > 0 & T < T_c \end{cases}$$

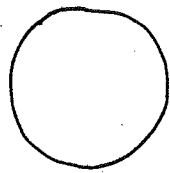
Scalar, real or complex, vector, spinor

$\psi = (\psi_1, \psi_2 \dots \psi_n)$ n-component real vector.

O.P	Realization	Microscopic
$m = \psi_1$	Ising F.M	$\langle \hat{\sigma}_z \rangle$
$\psi = \psi_1 + i\psi_2$	Superfluid, Superconductor	$\langle \hat{\psi}_B \rangle, \langle \psi_T \psi_L \rangle$
$\vec{M} = (\psi_1, \psi_2, \psi_3)$	Heisenberg magnet	$\langle \vec{\sigma} \rangle$
$\phi = \begin{pmatrix} \psi_1 + i\psi_2 \\ \psi_3 + i\psi_4 \end{pmatrix}$	Higg's field	$\begin{pmatrix} \langle \hat{\phi}_+ \rangle \\ \langle \hat{\phi}_- \rangle \end{pmatrix}$

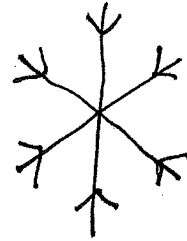
"Broken symmetry"

Water



$\psi=0$
spherical
symmetry

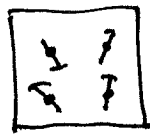
ICE



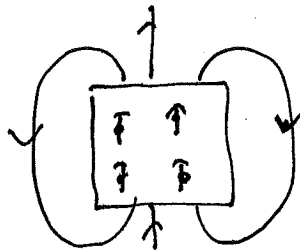
$\psi \neq 0$
six fold symmetry

BROKEN DOWN
TO \rightarrow

Superconductor/
FM

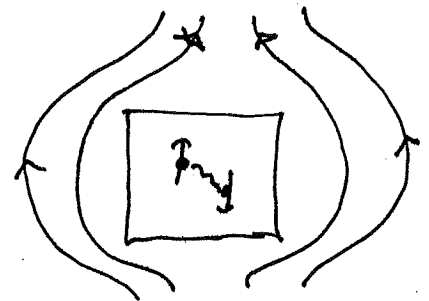


$\psi=0$



$\psi_{FM} \neq 0$

CREATES FIELD.



$\psi_{SC} \neq 0$

EXPELS FIELD

"Meissner Effect"

Approach provides a "coarse grain" description of physics, good

on length scales

$|x| > \xi_0 = \text{coherence length.}$

LANDAU THEORY

- Field cooling

$$H \rightarrow H - h \int d^3x \psi(x)$$

e.g. $\psi = M; \quad h = B \quad \text{F.M}$

$\psi = P; \quad h = E \quad \text{Ferro-electric}$

$$G[h] = F[\psi] - V\psi h$$

$$= -k_B T \ln Z[h] = -k_B T \ln \left[\text{Tr} \left(e^{-\beta(h - h \int \psi d^3x)} \right) \right]$$

$$\psi(h, V) = \frac{1}{Z[h]} \text{Tr} \left[\psi(x) e^{-\beta(h - h \int \psi d^3x)} \right] = \frac{-1}{V} \frac{\delta G(h)}{\delta h}$$

$$\delta G = -\delta h V \psi$$

$$\psi = \lim_{h \rightarrow 0} \lim_{V \rightarrow \infty} \psi(h, V)$$

Landau functional:

$$F[\psi] = G[h] + V\psi h = G[h] - h \frac{\partial G}{\partial h}$$

$$\delta F = -\delta h V \psi + V \delta(h\psi) = V h \delta \psi \Rightarrow hV = \frac{\delta F}{\delta \psi} = 0.$$

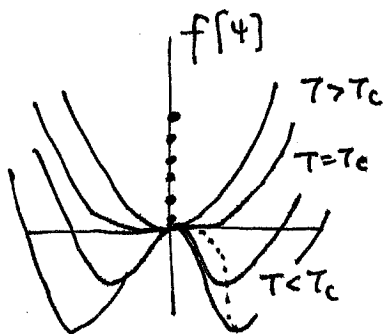
$$f_L[\psi] = \frac{1}{V} F[\psi] = \frac{r}{2} \psi^2 + \frac{u}{4} \psi^4 - h\psi$$

• Leading dependence of F on ψ .

• Ising o.p $H[\psi] = H[-\psi]$ "global Z_2 symmetry"
 $\psi \rightarrow \pm \psi$

Landau theory assumes

$$r = a(T - T_c)$$

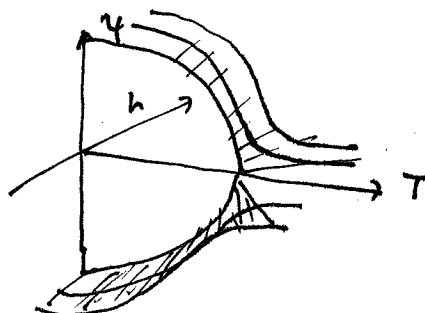
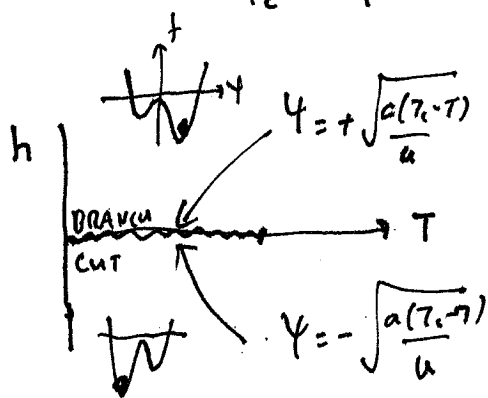
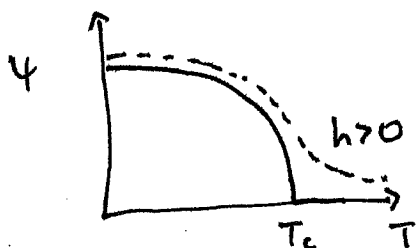


$$\frac{\partial f}{\partial \psi} = 0 = r\psi + u\psi^3 \Rightarrow \psi = \begin{cases} 0 & T > T_c \\ \pm \sqrt{\frac{a(T_c - T)}{u}} & T < T_c \end{cases}$$

In a field

$$\frac{\partial f}{\partial \psi} = r\psi + u\psi^3 - h = 0$$

$$h \rightarrow 0 \quad \psi = \text{sgn}(h) \sqrt{\frac{a(T_c - T)}{u}} \quad T < T_c$$



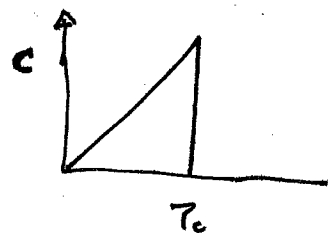
Singularities at the critical point

$$f_L = \begin{cases} 0 & T > T_c \\ -\frac{a^2}{4u} (T_c - T)^2 & T < T_c \end{cases}$$

$$C_V = -T \frac{\partial S}{\partial T} = -T \frac{\partial^2 F}{\partial T^2} = C_0(T) + \begin{cases} 0 & T > T_c \\ \frac{a^2 T}{2u} & (T < T_c) \end{cases}$$

$$\Delta C_V = \frac{a^2 T_c}{2u}$$

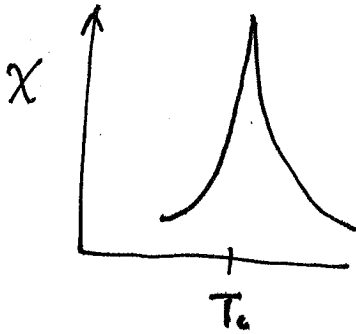
$$C_V \propto |T_c - T|$$



$$r\psi + u\psi^3 - h = 0$$

$$\Rightarrow \frac{\partial \psi}{\partial h} (r + 3u\psi^2) = 1$$

$$\chi = \frac{\partial \psi}{\partial h} = \frac{1}{r + 3u\psi^2} = \frac{1}{a|T - T_c|} \times \begin{cases} 1 & T > T_c \\ \frac{1}{2} & T < T_c \end{cases}$$



At $T = T_c$ the response is non-linear

$r = 0$

$$\psi = \left(\frac{h}{u} \right)^{1/3}$$

$$C_v \propto |T - T_c|^{-\alpha} \quad \text{S.H.}$$

$$\psi \propto \begin{cases} (T_c - T)^\beta \\ h^{1/\delta} \end{cases} \quad \text{O.P.}$$

$$\chi \propto (|T - T_c|)^{-\gamma} \quad \text{Susceptibility}$$

$$\alpha = 0, \beta = \frac{1}{2}, \delta = 3$$

& $\gamma = 1$ in MF7.

SCALING HYPOTHESIS : ONLY TWO INDEPENDENT EXPONENTS

$$f[\psi] = \frac{r t}{2} \psi^2 + \frac{u}{4} \psi^4 - h \psi \quad t = \left(\frac{T}{T_c} - 1 \right)$$

$$\frac{\partial f}{\partial \psi} = 0 \Rightarrow h(t, \psi) = r t \psi + u \psi^3$$

$$\psi_0 = \sqrt{\frac{r}{u} t}$$

$$h = \left(\frac{r^{3/2} |t|^{3/2}}{u^{1/2}} \right) \left(\text{sgn}(t) \left(\frac{\psi}{\psi_0} \right) + \left(\frac{\psi}{\psi_0} \right)^3 \right)$$

$$\begin{aligned} \Rightarrow \psi &= \psi_0 \times \text{function} \left(\frac{u^{1/2}}{r^{3/2}} \frac{h}{t^{3/2}} \right) \\ &= \frac{r^{1/2}}{u^{1/2}} |t|^{1/2} \times \underbrace{\text{function}}_{\Phi} \left(\frac{u^{1/2}}{r^{3/2}} \frac{h}{|t|^{3/2}} \right) \end{aligned}$$

In Landau theory $\Phi(x)$ is universal for all systems.

Similarly free energy

$$\begin{aligned} f[\psi] &= -h\psi + \frac{r t}{2} \psi^2 + \frac{u}{4} \psi^4 \\ &= \left(\frac{r^2 t^2}{u} \right) \left[\frac{-h \psi_0}{\left(\frac{r^2 t^2}{u} \right)} \left(\frac{\psi}{\psi_0} \right) + \left(\frac{\psi}{\psi_0} \right)^2 \text{sgn}(t) + \left(\frac{\psi}{\psi_0} \right)^4 \right] \\ &= \frac{r^2 t^2}{u} \times F \left[\frac{u^{1/2}}{r^{3/2}} \frac{h}{|t|^{3/2}} \right] \end{aligned}$$

Could have deduced this by using

$$\psi = - \frac{\partial f[t, h]}{\partial h} = \frac{r^{1/2} |t|^{1/2}}{u^{1/2}} \Phi \left[\frac{u^{1/2} h}{r^{3/2} |t|^{3/2}} \right]$$

$$\Rightarrow f[t, h] = \frac{r^{1/2} |t|^{1/2}}{u^{1/2}} \times \frac{r^{3/2} t^{3/2}}{u^{1/2}} \times F \left[\frac{u^{1/2} h}{r^{3/2} |t|^{3/2}} \right]$$

$$f[t, h] = \frac{r^2 t^2}{u} F \left[\frac{u^{1/2} h}{r^{3/2} |t|^{3/2}} \right]$$

where $F[x] = \int^x \Phi(x') dx'$

Generalized scaling

$$f[t, h] = t^{2-\alpha} F[h/t^\Delta]$$

Follows that

$$\psi(t, h) = - \frac{\partial f}{\partial h} = - t^{2-\alpha-\Delta} F' \left[\frac{h}{t^\Delta} \right]$$

$$\chi = - \frac{\partial^2 f}{\partial h^2} = - t^{2-\alpha-2\Delta} F'' \left[\frac{h}{t^\Delta} \right]$$

If we let $h \rightarrow 0$

$$\psi(t) = B |t|^\beta$$

$$\beta = 2 - \alpha - \Delta \quad *$$

$$B = -F'[0]$$

$$X(t, h=0) = |t|^{-\gamma} \times \begin{cases} C_+ & t > 0 \\ C_- & t < 0 \end{cases}$$

$$C_{\pm} = -F''_{\pm}[0]$$

$$\gamma = \alpha + 2\Delta - 2 \quad **$$

Combining * & **

$$\Delta = 2 - \alpha - \beta = \beta + \gamma$$

\Rightarrow

$$\alpha + 2\beta + \gamma = 2$$

To recover δ we write

$$\begin{aligned} \psi &= -t^\beta \underbrace{F'\left[\frac{h}{t^\Delta}\right]}_{F'(x) = x^{\beta/\Delta} g(x)} = -t^\beta \left(\frac{h}{t^\Delta}\right)^{\beta/\Delta} g\left[\frac{h}{t^\Delta}\right] \\ &= -h^{\beta/\Delta} g\left[\frac{h}{t^\Delta}\right] \end{aligned}$$

$$\Psi(h) = h^{\beta/\Delta} (-g(\infty)) \propto h^{\frac{1}{\delta}}$$

$$\Rightarrow \delta = \Delta/\beta = \frac{\beta + \gamma}{\beta}$$

$$\Rightarrow (\beta + \gamma) = \beta\delta \Rightarrow \gamma = (\beta\delta - \beta) = \beta(\delta - 1)$$

$$\alpha + 2\beta + \beta(\delta - 1) = 2$$

$$\boxed{\alpha + \beta(1 + \delta) = 2}$$

$$\Rightarrow \beta = \frac{2 - \alpha}{(1 + \delta)}$$

$$\gamma = (2 - \alpha) \frac{(\delta - 1)}{(\delta + 1)}$$

Finally

$$\boxed{C = -\frac{\partial^2 F}{\partial t^2} = t^{-\alpha}}$$

BROKEN CONTINUOUS SYMMETRIES : THE "MEXICAN HAT" POTENTIAL AND SUPERFLOW

$$\vec{\psi} = (\psi_1, \psi_2, \psi_3 \dots \psi_n)$$

$$\vec{\psi} \cdot \vec{\psi} = \psi_1^2 + \psi_2^2 + \dots + \psi_n^2$$

$$f_L[\vec{\psi}] = \frac{r}{2} [\vec{\psi} \cdot \vec{\psi}] + \frac{u}{4} [(\vec{\psi} \cdot \vec{\psi})]^2$$

$$r = \alpha(T - T_c)$$

$O(N)$ Landau Model.

$N=2$ superfluid, xy model

$N=3$ Heisenberg magnet.

$$\vec{\psi} \rightarrow R \vec{\psi}$$

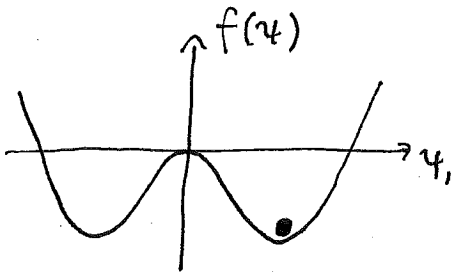
$O(N)$ Rotation

$$f_L(R\vec{\psi}) = f_L(\vec{\psi})$$

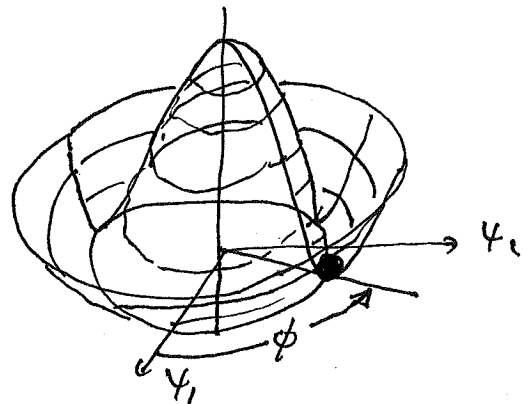
$O(N)$ symmetry.

$T < T_c$

$$\vec{\psi} = \sqrt{\frac{|r|}{4u}} \hat{n}$$



a) $\psi = \psi_1$



b) $\psi = \psi_1 + i\psi_2$

$$\psi = |\psi| e^{i\phi}$$

$$f[\psi] = r\psi^*\psi + \frac{u}{2} (\psi^*\psi)^2$$

$$\psi = \psi_1 + i\psi_2 = |\psi|e^{i\phi}$$

U(1) invariant
theory.

$$f[\psi] = f[e^{i\alpha}\psi]$$

U(1) gauge invariance

$$\psi = \sqrt{\frac{|\psi|}{u}} e^{i\phi}$$

LANDAU GINZBURG THEORY + SUPERFLOW

More general Ginzburg-Landau theory

$$f_{GL}[\psi] = s |\nabla\psi|^2 + r|\psi|^2 + \frac{u}{2} |\psi|^4$$

G-L Theory

• Microscopically in a superfluid $\psi = \langle \hat{\psi}(x) \rangle$

$$s |\nabla\psi|^2 = \frac{\hbar^2}{2m} \langle \nabla\hat{\psi}^\dagger \nabla\hat{\psi} \rangle$$

identified as the
kinetic energy.

• Can write as

$$r \left(\xi^2 |\nabla\psi|^2 + |\psi|^2 \right) + \frac{u}{2} |\psi|^4$$

Where

$$\xi = \sqrt{\frac{s}{r}} = \sqrt{\frac{s}{a(T-T_c)}} = \xi_0 \left(1 - \frac{T}{T_c}\right)^{-1/2}$$

defines the coherence length of the order parameter fluctuations.

- If we write $\psi = |\psi| e^{i\phi}$, then

$$\nabla\psi = (\nabla|\psi| + i\nabla\phi|\psi|) e^{i\phi}$$

$$|\nabla\psi|^2 = (\nabla|\psi|)^2 + (\nabla\phi)^2 |\psi|^2$$

$$f_{GL} = \underbrace{\left(\frac{\hbar^2}{2m} |\psi|^2 (\nabla\phi)^2 \right)}_{\text{KE - PHASE RIGIDITY}} + \underbrace{\left[\frac{\hbar^2}{2m} (\nabla|\psi|)^2 + r|\psi|^2 + \frac{u}{2} |\psi|^4 \right]}_{\text{AMPLITUDE FLUCT.}}$$

Microscopically

$$\vec{J} = -\frac{i\hbar}{2m} (\psi^\dagger \nabla \psi - (\nabla \psi^\dagger) \psi)$$

$$J_s = \langle \psi | J | \psi \rangle = -\frac{i\hbar}{2m} (\psi^* \nabla \psi - \nabla \psi^* \psi)$$

$$\psi = \sqrt{n_s} e^{i\phi(x)}$$

$$J_s = n_s \frac{\hbar}{m} (\nabla \phi) = n_s \vec{v}_s$$

$$\vec{v}_s = \frac{\hbar}{m} \nabla \phi$$