On the Microscopic Theory of Phase Transitions

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Abstract. In this paper a classical gas consisting of N particles in the volume V with pair interactions is considered. From the grand canonical partition function analytical functions for the pressure $p\ (z)$ and the specific volume $v\ (z)$ of the gas are determined using the methods of statistical physics. Eliminating the variable z the equation of state $p\ (T, V)$ is calculated for both the finite and the infinitely large system. It is shown that phase transitions into the liquid state are only observed in the latter case thereby confirming the Lee-Yang theory. Furthermore, a general microscopic description of the gas is presented using its phase space volume. A proof is given that the complete thermodynamics of the many particle system can be derived in the case of the asymptotic limit $N \ \rightarrow\ \infty$.

Keywords: microscopic description of a gas, statistical physics, finite and infinite systems, phase transitions.

1.Introduction Phase transitions are transitions from one state of a medium to another. One distinguishes between structural phase transitions between crystal structures of a solid material (example face centered cubic, body centered cubic or simple cubic), magnetic phase transitions (example ferromagnetic to paramagnetic phase), or electrical phase transitions (between the superconducting, metallic, and insulating phase). According to the Ehrenfest classification [1] first order phase transitions exhibit discontinuities in the first derivative of the free energy with respect to the external magnetic field, for example

$$M = -\frac{1}{V}\left(\frac{\partial G}{\partial B}\right)_T \tag{1}$$

Here M denotes the magnetization, B the external magnetic field, V the volume, and T the temperature. Corresponding second order phase transitions are continuous, see for example the magnetization $M(T)$ of a ferromagnetic material.

However, second derivatives of the free energy, for example

$$X_T = -\frac{\mu_0}{V}\left(\frac{\partial^2 G}{\partial B^2}\right)_T = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial H^2}\right)_T \tag{2}$$

show discontinuities. Note that the response function X_T denotes the susceptibility while the fields H and B are related via

$$B = \mu_0 H$$

The Ehrenfest classification was first questioned when Onsager [2] solved the two-dimensional Ising model exactly obtaining a second order phase transition with a diverging susceptibility at the Curie temperature

$$k_B\ T_C = \frac{2J}{\ln(1+\sqrt{2})} \tag{3}$$

Here the parameter J represents the nearest neighbor exchange integral describing the strength of the coupling between the magnetic moments; k_B is the Boltzmann constant.

Modern discussions of phase transitions concentrate on the phenomenological theory of L D Landau [3,4] covering the role of critical exponents, spatial fluctuations, and the correlation length, dynamical phase transitions

in the ferromagnetic XY-model [5], and liquid glass transitions in polymers [6]. A comprehensive overview of the phase transition phenomenon can be found in the book by W Nolting [7].
The article is structured as follows. In the next section a simple model of a gas consisting of N particles in the volume V with pair interactions is discussed both for a finite and the infinitely large system. It is shown that phase transitions are only observed in the latter case. This conclusion is further confirmed in Section 3 where a general statistical description of macroscopic systems is presented. It is shown that all thermodynamic phenomena result from the asymptotic limit of the microscopic description of the gas.

2.Methods

2.1 A Simple Model of a Phase Transition The gas is described as a classical system consisting of N particles in the volume V with pair interactions. A suitable Hamiltonian would then have the form

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + U$$

$$U = \frac{1}{2} \sum_{i,j}^{i \neq j} \varphi(r_i - r_j) \qquad (4)$$

Here the p_i, r_i are the particle coordinates with respect to momentum and position and U is the potential energy of the system. The pair potential $\varphi(r)$ is of the general form

$$\varphi\,(r) = \frac{A}{r^2} - \frac{B}{r}$$

where r is the interatomic distance while A, B represent constant values chosen to fit the model calculation. The pair potential makes sure that an energy minimum $u = \varphi\,(r = r_0\,)$ is obtained at an equilibrium distance $r = r_0$ so that $\frac{d\,\varphi}{dr}\ (r = r_0\,) = 0$

On the other hand, for large particle distances

$$\lim_{r \to \infty} \varphi\,(r) = 0$$

meaning that in this case particles do not interact any more with one another. These facts are summarized in the schematic plot of Fig 1 below.

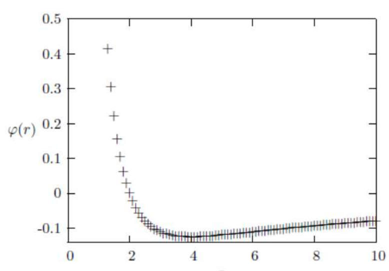

Fig 1: Pair potential $\varphi\,(r)$ as a function of particle distance r.

All this furthermore implies the existence of an equilibrium particle density

$$v_0^{-1} = \frac{N_0}{V} \qquad (5)$$

N_0 is the maximum number of particles that fit into the volume V with v_0^{-1} being the corresponding maximum particle density (saturation value). Beyond this particle density the gas atoms come too close and repel each other; the system becomes unstable. This simple model is in the following subsections evaluated for both the finite and the infinitely large system.

3. Results

3.1 The finite system For a finite system the grand canonical partition function is a finite polynomial of the order N_0 and can be written as

$$\Xi_z\,(T,V) = 1 + \sum_{N=1}^{N_0} z^N \; Z_N\,(T,V)$$
$$= 1 + z\,Z_1\,(T,V) + z^2\; Z_2\,(T,V) + \cdots$$

Here $z = e^{\beta\mu}$ denotes the fugacity and defines the chemical potential μ while $Z_N\,(T,V)$ is the corresponding canonical partition function.

Using the methods of Statistical Mechanics we may from Eq (6) determine both the pressure

$$p(z) \;=\; \frac{1}{V\,\beta}\;\; \ln \Xi_z\;(T,V) \qquad (7)$$

and the specific volume $v\,(z)$

$$v^{-1}\,(z) \;=\; \beta\, z\,\frac{\partial}{\partial z}\; p(z) \qquad (8)$$

as a function of z. By eliminating z one may then obtain an equation of state $p = p\;(T,v)$ of the gas.

For small z-values the sum in Eq (6) can be reduced to the first two terms and we may approximate

$$\Xi_z\,(T,V) \;\cong\; 1 \,+\, z\;\; Z_1\;\,(T,V)$$
$$p(z) \sim z \qquad (9)$$

On the other hand, for large z-values the higher terms in the polynomial dominate and we find

$$\Xi_z\;\,(T,V) \;\cong\; z^N\; Z_N\,(T,V)$$
$$p(z) = \;\frac{N}{V\,\beta}\;\;\ln z \qquad (10)$$

Combining the results of (9) and (10) we obtain for the full range of z-values the functional behavior of Fig 2 below.

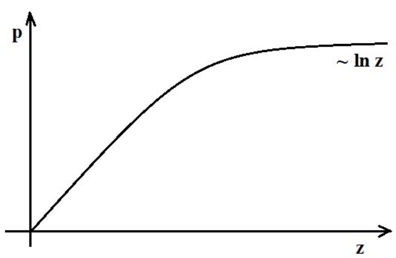

Fig 2: $p(z)$ as a function of z in the case of a finite system.

Note the linear behavior of $p\;(z)$ for small z-values and the proportionality to $\ln z$ for larger z.
For the specific volume $v(z)$ similar conclusions can be drawn. Whereas for small z-values one finds

$$v^{-1}\,(z)\;\sim z$$

the result for large z-values, i.e.

$$v^{-1}\,(z) = \;v_0^{-1} \;=\; \frac{N_0}{V}$$

approaches the above mentioned saturation density therefore yielding the graph of Fig 3 below.

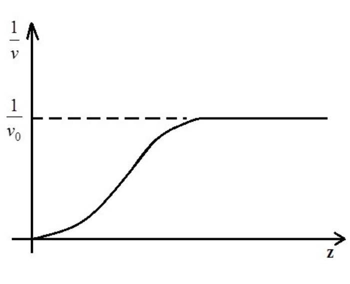

Fig 3: $v^{-1}(z)$ as a function of z in the case of a finite system.

Note that in the case of an ideal gas the slope of the curve $v^{-1}(z)$ is expected to be

$$\frac{\partial}{\partial z} \ v^{-1}(z) = \frac{1}{V\,z} \ \langle N \rangle \ = const$$

The differences to Fig 3 above are then due to the particle interactions and the finite volume V of the system. Furthermore, both functions $p(z)$ and $v^{-1}(z)$ are monotonously increasing functions of z meaning the inverse function $z = z\,(v^{-1})$ exists. z may then be eliminated yielding the equation of state

$$\beta \ p(v) = \frac{1}{v} \quad \ln \frac{1}{v - v_0} \tag{11}$$

Note the two limiting results

$$\lim_{v \to v_0} p(v) \ \ \to \ \ \infty$$

If the specific volume v approaches its smallest possible value v_0 the pressure becomes infinitely large.

$$\lim_{v \to \infty} p(v) = 0$$

On the other hand, if the gas atoms are far away from one another (diluted gas) the pressure vanishes. The equation of state $p = p\,(T, v)$ of the finite system is plotted in Fig 4.

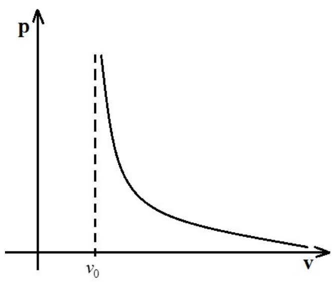

Fig 4: Equation of state $p = p\,(T, v)$ for the finite system.

Fig 4 resembles the isotherms of a van der Waals gas for temperatures $T \ > \ T_c$ where no phase transition into the liquid state is observed. The finite system shows no phase transition. To reproduce a phase transition one has to consider the system in the thermodynamic limit $V \ \to \ \infty$. This is to be investigated further in the next section.

3.2 The thermodynamic limit To model an infinitely large system, i.e. the thermodynamic limit firstly, the grand canonical partition function of the previous section becomes an infinite series and secondly, the final equations have to be evaluated in the limit $V \ \to \ \infty$. In order to do this the volume V of the gas is partitioned into microscopic cells of volume V_0 so that

$$V = n \ V_0 \qquad\qquad n = 1,2,3, \ldots \ldots \ldots \ldots . \infty$$

and the grand canonical partition function can be written as

$$\Xi_z \ (V) = \ (1+z)^V \ \ \frac{1 - z^{V+1}}{1-z}$$

$$\lim_{V \to \infty} \frac{1}{V} \ \ \ln \Xi_z \ (V) \ = \ \ln(1+z) \ + \ \ln z \tag{12}$$

$\Xi_z\,(V)$ is a polynomial in z of the order $2V$. Its roots lie on a unit circle in the complex z-plane. For a finite system they form a discrete set with constant angular distance

$$\Delta\varphi = \frac{2 \ \pi}{V+1}$$

between the points while in the thermodynamic limit $\Delta\varphi \ \ \to 0$ and the roots continuously occupy the unit circle including the physically relevant point $z = 1$. Using the same method described in the previous section for the finite system the pressure $p(z)$ is then calculated as

$p(z) = \ \ k_B\,T \ \ \ln z\,(1+z) \qquad$ if $|z| \ > 1$
$p\,(z) = \ \ k_B\,T \ \ \ln(1+z) \qquad$ if $|z| \ < 1$.

The function $p\,(z)$ is monotonously increasing and continuous even at $z = 1$ as

$$\lim_{z \to 1} p(z) \ \ = \ \ k_B \ T \ \ \ln 2$$

coming from both larger and smaller z-values. For the specific volume $v\,(z)$ we find

$v\,(z) = \ \frac{1+z}{1+2z}$ if $|z| \ > 1$

$v\ (z) = \frac{1+z}{z}$ if $|z| \ < 1$.
$v\ (z)$ is a monotonously decreasing function of z with

$$\lim_{z \to \infty} v\ (z) = v_0 = \frac{1}{2}$$

again representing the smallest possible volume per particle. The specific volume $v\ (z)$ is discontinuous at $z = 1$ as

$\lim_{z \to 1} v\ (z) = \frac{2}{3} = v_b$ if $|z| \ > 1$
$\lim_{z \to 1} v\ (z) = 2 = v_a$ if $|z| \ < 1$.

The discontinuity at $z = 1$ indicates a phase transition into the liquid phase. This is to be investigated further using the equation of state that is obtained by eliminating z.

$p(v) = k_B\ T \ \ln\left(\frac{v(1-v)}{(2v-1)^2}\right)$ if $|z| \ > 1$

$p(v) = k_B\ T \ \ln\left(\frac{v}{v-1}\right)$ if $|z| \ < 1$. (13)

The results for $|z| \ > 1$ represent the liquid phase while for $|z| \ < 1$ the vapour phase is observed. The corresponding numerical results are plotted in Figure 5 below.

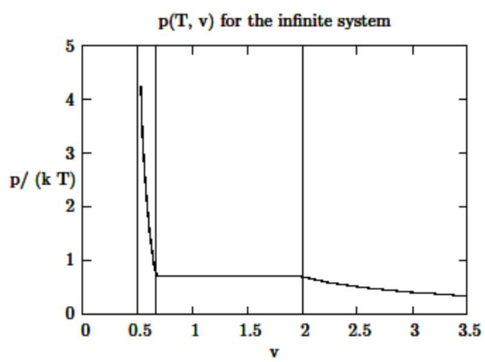

Fig 5: Equation of state $p = p\ (T, v)$ for the infinite system.

Interesting again are the two limits, i.e.

$$\lim_{v \to v_0} p(v) \ \to \ \infty$$

If the specific volume approaches its minimum value v_0 the pressure becomes infinitely large.

$$\lim_{v \to \infty} p(v) = 0$$

If the distance between particles becomes infinitely large (diluted gas), the pressure vanishes. These two limiting results are identical to those already obtained in the previous section for the finite system. However, in between these two limits the results now become different as the equation of state has the form of a phase diagram. For $v_0 \ \le v \ \le \ v_b$ the system is in a homogeneous liquid state while for specific volumes $v \ \ge \ v_a$ the vapour phase is observed. In both phases $p\ (v)$ decreases as a function of v. At a constant pressure such that

$$p_{sat}\ (T) = \ k_B\, T \ \ln 2$$

the volume is increased from $v = \ v_b$ to $v = \ v_a$ along the horizontal line parallel to the v-axis describing a liquid vapour phase transition. The pressure where the phase transition occurs is temperature dependent and is identical to the saturated vapour pressure.

Phase transitions are obviously only observed for the infinitely large system $N \ \to \ \infty$ thereby confirming the theory of T D Lee and C N Yang [8,9]. They are the results of mathematical singularities that only occur in the thermodynamic limit. However, phase transitions in finite systems have been reported in small open systems, for example metal clusters or ferromagnetic garnet systems [10, 11] thereby displaying behavior different from that of the bulk material. Phase transitions in finite systems can be explained on the grounds of their topological anomalies and the fact that the statistical ensembles are in the case of finite systems not equivalent anymore.

The results presented in this section are also consistent with the general theme of statistical physics that the results of equilibrium thermodynamics are the asymptotic limit of the microscopic description of the gas consisting of N particles. This will be further discussed in Section 3.

3.3 A Statistical Description of Macroscopic Systems

An isolated container of volume V contains a gas of N particles. The container is then partitioned into two chambers of volume V_1 and $V_2 = V - V_1$ respectively.

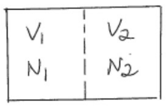

Fig 6: Partitioning of the container of volume V into two chambers of volumes V_1 and V_2 respectively.

The probability to find N_1 particles in V_1 and N_2 particles in V_2 is given by the expression

$$\omega_N\,(N_1) = \binom{N}{N_1}\; p_1^{N_1}\; p_2^{N-N_1} \tag{14}$$

with $p_1 = \frac{V_1}{V}$ and $p_2 = \frac{V_2}{V} = 1 - p_1$.

An alternative expression for the probability (14) is given by the Gaussian distribution

$$G\,(N_1) = A\; e^{-\,(N_1 - \widehat{N_1})^2 / \sigma^2} \tag{15}$$

Here $\widehat{N_1}$ is the most probable particle number which is equal to the point where $G\,(N_1)$ attains a maximum value. Note that $G\,(N_1)$ is symmetric around the maximum value $\widehat{N_1}$.

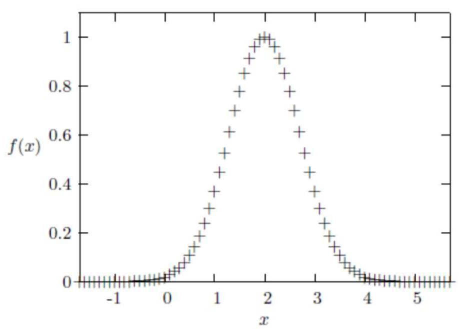

Fig 7: Gaussian function $G\,(x)$ as a function of x.

The constant A is determined from the normalization condition

$$\int_{-\infty}^{+\infty} G\,(N_1)\; dN_1 = 1 \tag{16}$$

yielding $A = \frac{1}{\sigma\,\sqrt{\pi}}$. Note that σ measures the width of the Gaussian distribution with

$$\sigma = \Delta N_1 = \sqrt{2\,N\,p_1\,(1 - p_1)}$$

The integral of Eq (16) is interesting from the mathematical point of view as there is no indefinite integral for $\int e^{-x^2}\, dx$. However, the definite integral

$$\int_{-\infty}^{+\infty} e^{-x^2}\, dx \tag{17}$$

can be evaluated analytically using for example planar polar coordinates or the Gaussian definition of the Gamma function. The integral (17) can also be numerically evaluated.

Furthermore, the relative deviation of measured values from the average value is given by the expression $\Delta N_1 / N$ and is for asymptotically large systems

$$\frac{\Delta N_1}{N} = \sqrt{\frac{2 p_1 (1 - p_1)}{N}} \sim 10^{-11}$$

practically zero. The probability that a measurement yields a value outside the range $-10 \leq t \leq +10$ is with

$$1 - \frac{1}{\sqrt{\pi}} \int_{-10}^{+10} e^{-t^2} dt \cong 3 \cdot 10^{-5}$$

negligibly small. These results are confirmed when considering that the width ΔN_1 of the Gaussian distribution decreases with decreasing parameter σ while the maximum

$$G \left(N_1 = \widetilde{N_1} \right) = \frac{1}{\sigma \sqrt{\pi}} \xrightarrow[\sigma \to 0]{} \infty$$

becomes infinitely large. We may thus conclude

$$\lim_{\sigma \to 0} G_\sigma (N_1) = \delta (N_1 - \widetilde{N_1})$$

It then follows for the average particle number

$$\langle N_1 \rangle = \int_{-\infty}^{+\infty} N_1 \, G_\sigma (N_1) \, dN_1 = \int_{-\infty}^{+\infty} N_1 \, \delta (N_1 - \widetilde{N_1}) \, dN_1 = \widetilde{N_1}$$

The average value is equal to the most probable particle number, i.e. the particle number where the Gaussian distribution has a maximum value. For asymptotically large systems the results of measurements can be predicted with almost absolute accuracy. However, this is not necessarily the case for smaller systems where considerable deviations from the average value can be observed.

According to the Liouville theorem [12] the probability of above is related to the phase space volume Using the phase space volume of a gas consisting of N particles in the volume V, i.e.

$$\Gamma_N (E, V) = const \, V^N \, E^{3N/2}$$

we may conclude from

$$T^{-1} = k_B \frac{1}{\Gamma_N} \left(\frac{\partial \Gamma_N}{\partial E} \right)_{V,N}$$

the internal energy $E = \frac{3}{2} N k_B T$ of the gas. On the other hand, evaluating

$$p = k_B T \frac{1}{\Gamma_N} \left(\frac{\partial \Gamma_N}{\partial V} \right)_{E,N}$$

yields the ideal gas equation

$$p V = N k_B T$$

An important result of phenomenological thermodynamics is its second law which follows straightforwardly from the statistical definition of the entropy

$$S (E, V, N) = k_B \ln \Gamma_N (E, V)$$

Note that during the transition into an equilibrium state both Γ_N and S cannot decrease thereby confirming the 2nd law of thermodynamics. From the phase space volume the complete thermodynamics of the many particle system can obviously be derived. Equilibrium thermodynamics is the asymptotic limit of statistical physics.

4. Conclusions

In this article we considered a classical gas in the volume V with pair interactions. It was shown that the gas only exhibits phase transitions into the liquid state in the case of asymptotically large systems thereby confirming the results of Yang and Lee with regards to this phenomenon. For finite systems no phase transitions are observed. A general statistical description of macroscopic systems shows that -again in the limit $N \rightarrow \infty$ -deviations of measured values from the average become negligibly small, meaning results of measurements can be predicted with almost absolute accuracy. Statistics thus works best for infinitely large systems. On the other hand, for finite systems considerable deviations of measured values are expected. Furthermore, from the phase space volume of the gas its complete thermodynamics can be derived. Equilibrium thermodynamics is thus the result of a limiting process of the microscopic description of the many particle system.

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