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The condensation of matter.
A model of phase transition of the first kind

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Abstract

A model of phase transition of the first kind is introduced, based on the assumption that a classical gas of particles condenses in composite particles made up of various numbers of gas molecules. The transition temperature and the latent heat are derived, and the phase diagram is characterized.

Phase transitions represent a well-studied field of research in condensed matter. Comparatively, and in spite of their ubiquitous occurrence, the phase transitions of the first kind, which exhibit finite discontinuities in thermodynamic funcions, received less attention than the phase transitions of the second kind, characterized by discontinuities in the derivatives of the thermodynamic potentials. It is known that the latter are associated with a symmetry breaking and quantal-statistical correlations. Typical examples are the superconductivity, the superfluidity, or the structural modifications of the solids. Technically, they are driven by a continuous change in an order parameter, which generates singularities characterized by power laws with critical exponents (indices). The particular mechanisms for the phase transitions of the first kind remain elusive, though both kinds of transitions are related to a certain condensation to a macroscopically-occupied state. The typical instance of such phase transitions is the gas-liquid transition. The van der Waals theory, which captures much of the general features of the problem is an interpolation between an ideal classical gas and a strongly interacting gas, and views the particle density as an order parameter, thus having much in common with the phase transitions of the second kind. On the other hand, dealing with an interacting ensemble of particles, the van der Waals theory fails to incorporate the particle condensation in the form of bound states. Previous attempts to describe the condensation of matter are known,[1]-[11], as quoted by ter Haar.[12] We present here a direct condensation in the phase space of the molecules of a classical gas, in the form of composite particles, which exhibits typical features of a phase transition of the first kind. It may be viewed as a generic model for such phase transitions.

Let an ideal classical gas of N molecules with mass m be enclosed in volume V at temperature T. As it is well-known, leaving aside the internal motion of the molecules, the particle distribution is given by

$$dN = \frac{gV}{(2\pi\hbar)^3} e^{\mu/T} e^{-p^2/2mT} d\mathbf{p} \ , \tag{1}$$

where g is the statistical weight, μ is the chemical potential and $\mathbf{p}$ denotes the particle momentum. The energy is $E = 3NT/2$ and the thermodynamic potential $\Omega = -pV = -NT$, where p is the pressure. The chemical potential is given by

$$\mu = -T\ln[g(mT/2\pi\hbar^2)^{3/2}/n] \ , \tag{2}$$

where $n = N/V$ is the density, and $g(mT/2\pi\hbar^2)^{3/2}/n \gg 1$ (condition for a classical gas). We introduce the characteristic temperature $T_0 = \hbar^2 n^{2/3}/m$, and write approximately $\mu \simeq -(3/2)T\ln(T/T_0)$ for $T \gg T_0$.

We assume that the gas condenses in various species labelled by $j = 1, 2, 3...$, consisting of composite particles made up of $n_j = 2, 3, ...$ original molecules. These composite particles have an energy $\varepsilon_j = -\varepsilon_{0j} + p^2/2M_j$, where $-\varepsilon_{0j} < 0$ is their cohesive energy and M_j is the mass of the j-th particle. These condensed species form an ideal classical gas. We impose the conservation of the number of gas molecules

$$N_c = \sum n_j \rho_j \ , \tag{3}$$

and the conservation of the energy E_c of the condensed phase,

$$E_c = \sum \varepsilon_j \rho_j \ , \tag{4}$$

where $\rho_j = dN_j/dn_j d\mathbf{p}_j$ is the probability distribution of N_j particles in species j over phase space $(n_j, \mathbf{p}_j)$. The summations in (3) and (4) are extended to all the states of the particles, characterized by number n_j and momentum $\mathbf{p}_j$. Then, we get straightforwardly the distribution of particles in the condensed phase

$$dN_j = \frac{g_j V_c}{(2\pi\hbar)^3} e^{\mu_c n_j/T} e^{-\varepsilon_j/T} dn_j d\mathbf{p}_j \ , \tag{5}$$

where g_j is the statistical weight of the j-th species, μ_c is the chemical potential of the condensate and V_c is the volume of the condensate. We leave aside other degrees of freedom, corresponding to the internal motion of the composite particles. We write n_j as a continuous variable for convenience, but we understand the summation over discrete values $n_j = 2, 3, ...$

The integration over momenta p_j in (5) is straightforward. It gives

$$dN_j = g_j V_c (M_j T/2\pi\hbar^2)^{3/2} e^{\mu_c n_j/T} e^{\varepsilon_{0j}/T} dn_j \ . \tag{6}$$

It is reasonable to assume that the condensate is a multiple of its constituents, *i.e.* $\varepsilon_{0j} = \varepsilon_0 n_j$ and $M_j = m n_j$, where ε_0 is a parameter of the cohesive energy, so that equation (6) becomes

$$dN_j = g_j V_c (mT/2\pi\hbar^2)^{3/2} n_j^{3/2} e^{(\mu_c+\varepsilon_0)n_j/T} dn_j \ . \tag{7}$$

The number total of species is then given by

$$\sum_j N_j = V_c (mT/2\pi\hbar^2)^{3/2} \sum_{n_j} g_j n_j^{3/2} e^{(\mu_c+\varepsilon_0)n_j/T} \ , \tag{8}$$

and the number of the original particles in the condensate given by (3) reads

$$N_c = V_c (mT/2\pi\hbar^2)^{3/2} \sum_{n_j} g_j n_j^{5/2} e^{(\mu_c+\varepsilon_0)n_j/T} \ . \tag{9}$$

Similarly, the energy of the condensate given by (4) reads now

$$E_c = -N_c \varepsilon_0 + (3/2)T \sum_j N_j \ , \tag{10}$$

and the thermodynamic potential Ω_c is given by $\Omega_c = -p_c V_c = -T \sum_j N_j$. The sumations in (8) and (9) are convergent, since the chemical potential μ_c assumes large, negative values, as for a classical gas.

Let us first consider only one type of composite particles, labelled by $j = s-1$, with a constituency $n_j = s$. Then, the summations in (8) and (9) reduce to the s-th term only, and we get

$$N_s = V_c(mT/2\pi\hbar^2)^{3/2}g_s s^{3/2}e^{(\mu_c+\varepsilon_0)s/T} = N_c/s \ . \tag{11}$$

Hence, we get straightforwardly the chemical potential of the condensate

$$\mu_c = -\varepsilon_0 - (T/s)\ln[g_s s^{3/2}(mT/2\pi\hbar^2)^{3/2}/n_c] \ , \tag{12}$$

where $n_c = N_s/V_c$. The pressure of the condensate is given by $p_c = TN_s/V_c$, while the pressure of the original gas is given by $p = TN_c/V$. At equilibrium, the two values of the pressure must be equal, $p_c = p$, and, since $N_s = N_c/s$, it follows that $V_c = V/s$. It follows that at equilibrium the two concentrations, $n = N_c/V$ of the original gas and $n_c = N_s/V_c$ of the condensate, are equal, $n = n_c$, while the number N_s of particles in the condensate and the volume V_c of the condensate are decreased by factor s, according to $N_s = N_c/s$ and $V_c = V/s$, respectively. The chemical potential of the condensate given by (12) becomes

$$\mu_c = -\varepsilon_0 - (T/s)\ln[g_s s^{3/2}(mT/2\pi\hbar^2)^{3/2}/n] \ , \tag{13}$$

and it may be compared now with the chemical potential of the original gas of molecules given by (2). The equilibrium between the two phases, the original gas and the resulting condensate, is attained for $\mu_c = \mu$. Making use of (2) and (13), this equation can be written as

$$\frac{3(s-1)}{2s}\ln(T/T_0) = \varepsilon_0/T \ , \tag{14}$$

for $T, \varepsilon_0 \gg T_0$. Its solution gives the critical temperature

$$T_c \simeq \frac{2s}{3(s-1)} \cdot \frac{\varepsilon_0}{\ln(\varepsilon_0/T_0)} \ . \tag{15}$$

The chemical potential acquires the value $\mu_{crit} \simeq -s\varepsilon_0/(s-1)$ at the critical temperature. Below the critical temperature the condensate is favoured ($\mu_c < \mu$ for $T < T_c$), while above the critical temperature it is the gas which is favoured ($\mu_c > \mu$ for $T > T_c$), as expected. Introducing $T_0 = \hbar^2(p/T)^{2/3}/m$ in (14) we get the (p,T)-equilibrium curve of the gas-condensate ensemble. It reads $p = (m/\hbar^2)^{3/2}T^{5/2}\exp[-s\varepsilon_0/(s-1)T]$. In-between the two isotherms $pV = N_cT$ and $pV_c = N_sT$ there exists a plateau at the critical temperature, as it can be seen from the decreasing of the volume from V to $V_c = V/s$ and the decreasing of the constant N_cT from N_cT_c to $N_sT_c = N_cT_c/s$. The critical temperature given by (15) decreases slowly with increasing s.

Below the critical temperature the condensation is fully attained, and $N_c = N$. The thermodynamic potentials suffer a discontinuity at the transition temperature, as a result of the condensation. For instance, the thermodynamic potential of the condensate $\Omega_c = -pV_c = -NT_c/s$ differs from $\Omega = -NT_c$ by a relative jump $-(1-s)/s$, and the volume of the condensate decreases to $V_c = V/s$. Similarly, the energy of the condensate given by (10) reads now $E_c = -N\varepsilon_0 + 3N_sT_c/2 = -N\varepsilon_0 + 3NT_c/2s$, and exhibits a discontinuity as given by $\Delta E = 3NT_c(1-s)/2s$. The heat function of the original gas is given by $W = E + pV = 5NT/2$, while the heat function of the condensate reads $W_c = -N\varepsilon_0 + 5N_sT/2 = -N\varepsilon_0 + 5NT/2s$, so the latent heat is $Q = W_c - W = -N\varepsilon_0 + 5(1-s)NT_c/2s$. Similarly, the entropy of the original gas can be written as $S = (3N/2)\ln(T/T_0) + 5N/2$, while the entropy of the condensate is given by $S_c = (3N/2s)\ln(T/T_0) + 5N/2s$, and, by making use of equation (14), one gets $\Delta S = S_c - S = -N\varepsilon_0/T_c + 5(1-s)N/2s$ at equilibrium. One can check that the latent heat

is given by $Q = T_c \Delta S$, according to the Clapeyron-Clausius law. There is also a jump in heat capacities, which are given by $C = 3N/2$ and, respectively, $C_c = 3N/2s$, at constant volume.

We pass now to the estimation of the entire ensemble of composite particles in the condensate. The summation in equation (8) can be aproximated by an integral, according to

$$\sum_j N_j = V_c g_c (mT/2\pi\hbar^2)^{3/2} \int_s dn \cdot n^{3/2} e^{(\mu_c + \varepsilon_0)n/T} \ , \tag{16}$$

where g_c is a mean statistical weight and the lower limit of integration is $s = 2$. Integrating by parts, the integral in (16) can be written as

$$\int_s dn \cdot n^{3/2} e^{-\lambda n} = \frac{s^{3/2}}{\lambda} e^{-\lambda s} + \frac{3s^{1/2}}{2\lambda^2} e^{-\lambda s} + \frac{3s^{-1/2}}{4\lambda^3} e^{-\lambda s} + ..., \tag{17}$$

where $\lambda = -(\mu_c + \varepsilon_0)/T$. Since $\lambda \gg 1$ we may approximate this integral by the first term in the *rhs* of (17), so that equation (16) becomes

$$\lambda e^{\lambda s} \simeq g_c s^{3/2} (mT/2\pi\hbar^2)^{3/2}/n \ , \tag{18}$$

where $n = \sum_j N_j/V_c$, as for equilibrium. The solution of this equation for large values of λ can be written as

$$\lambda = (1/s)\ln[g_c s^{3/2}(mT/2\pi\hbar^2)^{3/2}/n] - (1/s)\ln\{(1/s)\ln[g_c s^{3/2}(mT/2\pi\hbar^2)^{3/2}/n]\} + ..., \tag{19}$$

and we may retain only the first term in this expansion. Thus, we get the chemical potential of the condensate

$$\mu_c \simeq -\varepsilon_0 - (T/s)\ln[g_c s^{3/2}(mT/2\pi\hbar^2)^{3/2}/n] \ , \tag{20}$$

which is identical with the one given by (13) for $s = 2$. We can say that the condensate is dominated by pair composites made out of two particles of the original gas. Therefore, the discussion made above for one type of composite applies here for the entire ensemble of the condensate, for $s = 2$. In particular the transition temperature is given by (15) for $s = 2$. The fluctuations in the size of the composite particles are readily obtained as $\langle(\delta n_j)^2\rangle \simeq T^2/(\mu_c + \varepsilon_0)^2$. At the transition temperature they are given by $\langle(\delta n_j)^2\rangle^{1/2} \simeq (s-1)^{1/2}T_c/\varepsilon_0$. According to the approximation employed here for solving equation (16), the number of particles in species with $s+1$, $s+2$, ... particles are exponentially small in comparison with the number of particles corresponding to $s = 2$.

It is worth noting that the essential element of the mechanism presented here, which captures the nature of the first-order phase transition, consists in the conservation of the number of condensed particles as expressed by equation (3). It makes possible to express the chemical potentials of the two phases, say μ_1 and μ_2, in terms of the same quantities, namely the density of the original particles (beside temperature), making thus possible their comparison for identifying the equilibrium and the critical temperature. In addition, it is also worth noting that, technically, the mechanism described here is not limited to the classical statistics (though this is the most typical situation). In general, if there is a critical point at the transition temperature T_c, then the equilibrium is given by the equality of the two chemical potentials $\mu_1(T_c) = \mu_2(T_c)$ (for the same pressure, *i.e.* density). In the neighbourhood of the critical temperature T_c we may expand the chemical potentials as $\mu_1 = \mu_1(T_c) + (T - T_c)(\partial\mu_1/\partial T)_c$ and $\mu_2 = \mu_2(T_c) + (T - T_c)(\partial\mu_2/\partial T)_c$, and one can see that $\mu_1 < \mu_2$ for $T > T_c$, and, at the same time, $\mu_1 > \mu_2$ for $T < T_c$, *i.e.* we have a phase transition, providing $(\partial\mu_1/\partial T)_c < (\partial\mu_2/\partial T)_c < 0$. On the other hand, $\partial\mu/\partial T = -S$,

where S denotes the entropy per particle, so that the above inequalities read $S_1 > S_2 > 0$, *i.e.* the transition to the condensed phase (phase 2) implies a decrease of entropy, *i.e.* the condensed phase is more "macroscopically-occupied" than the original one, as expected. If we express the entropy as the logarithm of the phase-space element, $S \sim \ln \Delta q \Delta p$, then for s independent particles we have the entropy per particle $S_1 \sim (1/s) \ln(\Delta q \Delta p)^s = \ln \Delta q \Delta p$, while for a composite made up of s particles we have the entropy per particle $S_2 \sim (1/s) \ln \Delta q \Delta p$, because their phase space diminished. We can see that indeed $S_1 > S_2 > 0$, *i.e.* the condensed phase is indeed more "macroscopically-occupied", and, in addition, we see that the relative jump in the entropy is $1/s - 1 = (1-s)/s$, as obtained in the model described above.

It may be viewed that the liquid state is attained for all the N_j vanishing, except for one $N_j = 1$. The liquid is then made of only one, big composite "particle", consisting of $s = N \to \infty$ particles of the original gas. The distributions given by (7) lose then their statistical meaning (the entropy vanishes), and the chemical potential of the liquid is exactly $\mu_c = -\varepsilon_0$. The critical temperature of the gas-liquid transition is given by equation (15) for $s \to \infty$. It reads $T_c \simeq 3\varepsilon_0/2\ln(\varepsilon_0/T_0)$. The liquid has the volume $V_c = V/N$ and density $N/V_c = N^2/V$ (distinct from density $n_c = 1/V_c = N/V = n$ which enters the equation of state $p_c V_c = T$). The thermodynamics of this liquid state has then to be re-constructed on new statistical assumptions. This conclusion is very similar with the well-known previous analysis made in Refs. 13-14.

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