

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

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email: apoma@theory.nipne.ro**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 widely-investigated field of research in condensed matter, especially in connection with their critical behaviour. Comparatively, and despite their ubiquitous occurrence, the phase transitions of the first kind, which exhibit finite discontinuities in thermodynamic functions, 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 quantum-statistical correlations. Typical examples are superconductivity, superfluidity, or structural modifications of 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. A typical example of such phase transitions is provided by 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 (liquid). Near the critical point, the particle density may be viewed as an order parameter, as for a phase transition 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] They are mainly related to the droplet model,[13]-[16] and extensive studies regarding metastable states and the kinetics (nucleation, coalescence, Oswald ripening, etc) of the phase transition of the first kind,[17] as well as scaling and renormalization-group properties of their critical behaviour have been advanced.[18],[19] Such subjects are still a matter of current investigations.[20],[21] The equivalence of a latticial gas with the Ising ferromagnet in an external magnetic field is also known,[1] where the gas-liquid transition in the former is associated to the jump in the magnetization of the latter. 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 of mass m be enclosed in a volume V at temperature T . As it is well-known, leaving aside the internal degrees of freedom 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 $j = 1, 2, 3, \dots$, consisting of composite particles made up of $n_j = 2, 3, \dots$ original molecules.¹ These composite particles have an energy $\varepsilon_j = -\varepsilon_{0j} + p^2/2M_j$, where $-\varepsilon_{0j} < 0$ is their cohesion 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 $n_j = 2, 3, \dots$

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.* $M_j = mn_j$ and, similarly, ε_{0j} is an increasing function of n_j which goes like $\varepsilon_{0j} \sim n_j$ for large n_j . We assume $\varepsilon_{0j} = \varepsilon_0 n_j$, where ε_0 is a parameter of the average cohesion energy. Any other reasonable function $\varepsilon_{0j}(n_j)$ can be used, without affecting the subsequent conclusions. 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 condensed particles is given by

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

¹This assumption could be related to the comments made by L. van Hove, *Revs. Mod. Phys.* **29** 200 (1957), p. 202, on the coexistence of distinct phases during transition. See also related comments[1] on Mayer's theory.

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

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

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

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

and the thermodynamic potential Ω_c is given by $\Omega_c = -p_c V_c = -T \sum_j N_j$. The summations 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

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

Hence, we get straightforwardly the chemical potential of the condensate

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

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 $V_c = V/s$, which shows indeed that this is a condensation. 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

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

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

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

for $T, \varepsilon_0 \gg T_0$. Its solution gives the transition temperature²

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

The chemical potential acquires the value $\mu_t \simeq -s\varepsilon_0/(s-1)$ at the transition temperature. Below the transition temperature the condensate is favoured ($\mu_c < \mu$ for $T < T_t$), while above the critical temperature it is the gas which is favoured ($\mu_c > \mu$ for $T > T_t$), 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

$$p = (m/\hbar^2)^{3/2} T^{5/2} \exp[-s\varepsilon_0/(s-1)T] . \quad (16)$$

²For a general function $\varepsilon_{0j}(n_j)$ for the cohesion energy the parameter ε_0 in equation (15) is replaced by $\varepsilon_0(s)/s$.

In-between the two isotherms $pV = N_c T$ and $pV_c = N_s T$ there exists a plateau at the transition 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 $N_c T$ from $N_c T_t$ to $N_s T_t = N_c T_t/s$.

Below the transition 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 $\Omega_c = -pV_c = -NT_t/s$ differs from $\Omega = -NT_t$ 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 $E_c = -N\varepsilon_0 + 3N_s T_t/2 = -N\varepsilon_0 + 3NT_t/2s$, and exhibits a discontinuity given by $\Delta E = 3NT_t(1-s)/2s$. The heat function of the original gas is given by $W = E + pV = 5NT/2$, while the heat function of the condensate reads $W_c = -N\varepsilon_0 + 5N_s T/2 = -N\varepsilon_0 + 5NT/2s$, so the latent heat is $Q = W_c - W = -N\varepsilon_0 + 5(1-s)NT_t/2s$. 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 $\Delta S = S_c - S = -N\varepsilon_0/T_t + 5(1-s)N/2s = (1/s - 1)S$ at equilibrium. One can check that the latent heat is given by $Q = T_t \Delta S$, 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 approximated by an integral, according to

$$\sum_j N_j = V_c g_c (mT/2\pi\hbar^2)^{3/2} \int_s dn \cdot n^{3/2} e^{(\mu_c + \varepsilon_0)n/T} , \quad (17)$$

where g_c is a mean statistical weight and the lower limit of integration is $s = 2$. Integrating by parts, the integral in (17) can be written as

$$\int_s dn \cdot n^{3/2} e^{-\lambda n} = \frac{s^{3/2}}{\lambda} e^{-\lambda s} + \frac{3s^{1/2}}{2\lambda^2} e^{-\lambda s} + \frac{3s^{-1/2}}{4\lambda^3} e^{-\lambda s} + \dots, \quad (18)$$

where $\lambda = -(\mu_c + \varepsilon_0)/T$. Since $\lambda \gg 1$ we may approximate this integral by the first term in the *rhs* of (18), so that equation (17) becomes

$$\lambda e^{\lambda s} \simeq g_c s^{3/2} (mT/2\pi\hbar^2)^{3/2} / n , \quad (19)$$

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

$$\begin{aligned} \lambda &= (1/s) \ln[g_c s^{3/2} (mT/2\pi\hbar^2)^{3/2} / n] - \\ &- (1/s) \ln(1/s) \ln \{ [g_c s^{3/2} (mT/2\pi\hbar^2)^{3/2} / n] \} + \dots, \end{aligned} \quad (20)$$

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

$$\mu_c \simeq -\varepsilon_0 - (T/s) \ln[g_c s^{3/2} (mT/2\pi\hbar^2)^{3/2} / n] , \quad (21)$$

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

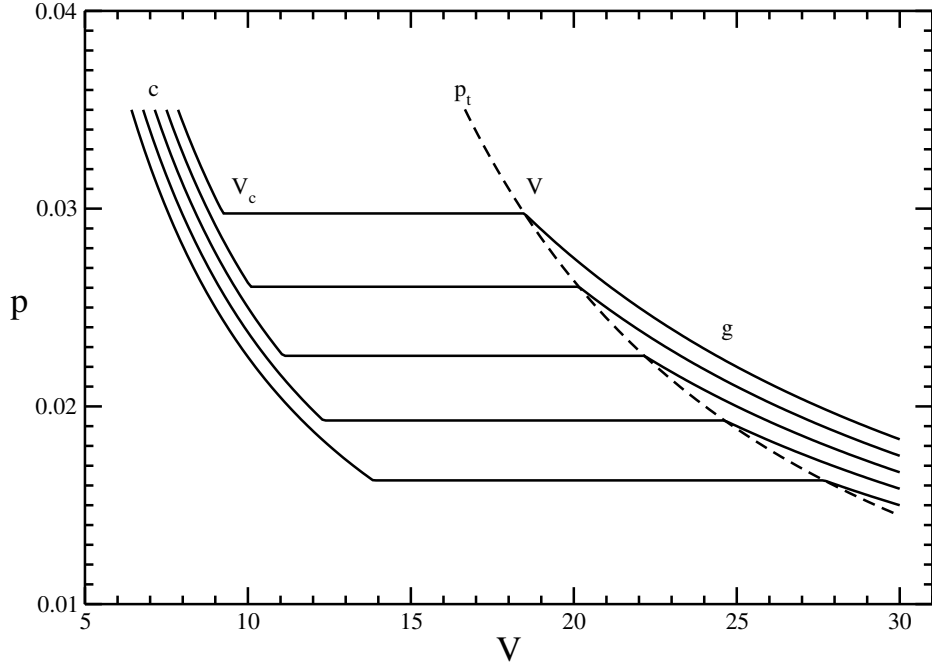


Figure 1: Gas-condensate isotherms $p = NT/V$ (gas, curves g), $p = NT/sV$ (condensate, curves c) and the transition (coexistence) curve p_t given by $p_t = NT_t/V = sN\varepsilon_0/(s-1)V \ln(V/v)$ according to equation (22) for $sN\varepsilon_0/(s-1) = 1$, $(s-1)T/s\varepsilon_0 = 0.450, 0.475, \dots, 0.550$ (step 0.025), $v = 3$ and $s = 2$. The hs coexistence curve is pushed in fact toward a limiting volume v (not shown in figure), as discussed in text and shown in Fig. 2.

they are given by $\langle(\delta n_j)^2\rangle^{1/2} \simeq (s-1)T_t/\varepsilon_0$. According to the approximation employed here for solving equation (17), the number of particles in species with $s+1$, $s+2$, ... particles are exponentially small in comparison with the number of particles corresponding to $s=2$.

Isotherms of the gas-condensate ensemble are shown in Fig. 1. They consist of two families of curves, denoted by g for gas and, respectively, c for condensate. The g -curves are given by $p(V) = NT/V$, while the c -curves are given by $p(V) = \left(\sum_j N_j\right) T/V \simeq NT/sV$ for various $T = const$. These two families of isotherms are linked to each other by horizontal plateaux, connecting the points corresponding to the abscissa V to points corresponding to the abscissa $V_c \simeq V/s$. The connecting points V are given by the intersection of the gas isotherms $p(V) = NT/V$ with the transition (coexistence) curve $p_t(V) = NT_t/V$, where T_t is given (15). The equation of this curve reads

$$p_t(V) = \frac{s}{s-1} \cdot \frac{N\varepsilon_0}{V \ln(V/v)} , \tag{22}$$

where $v = N(\hbar^2/m\varepsilon_0)^{3/2}$ is a cutoff volume corresponding to the localization (condensation) of a gas molecule with cohesion energy ε_0 , for all the gas molecules. The volume V in Fig. 1, where the transition is initiated, is given by

$$V = v \exp[s\varepsilon_0/(s-1)T] . \tag{23}$$

The isotherms shown in Fig. 1 for the present model of condensation differ from the van der Waals isotherms by the discontinuities corresponding to the horizontal plateaux, instead of the continuous transition region of the latter. At the same time, the transition region is open (in contrast with the van der Waals isotherms), as defined by the curves $p_t(V)$ and $p'_t(V) = p_t(sV)$ (the latter not shown explicitly in Fig. 1). However, the validity of these isotherms is limited to

$V \gg v$. As we shall see below, they are in fact limited by a critical point, and the *lhs* coexistence curve $p'_t(V) = p_t(sV)$ in Fig. 1 is in fact pushed toward the limiting volume v , as shown in Fig. 2.

It is worth noting that the essential element of the condensation mechanism presented here for a 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 transition 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 transition at temperature T_t , then the equilibrium is given by the equality of the two chemical potentials $\mu_1(T_t) = \mu_2(T_t)$ (for the same pressure, *i.e.* density). In the neighbourhood of the transition temperature T_t we may expand the chemical potentials as $\mu_1 = \mu_1(T_t) + (T - T_t)(\partial\mu_1/\partial T)_t$ and $\mu_2 = \mu_2(T_t) + (T - T_t)(\partial\mu_2/\partial T)_t$, and one can see that $\mu_1 < \mu_2$ for $T > T_t$, and, similarly, $\mu_1 > \mu_2$ for $T < T_t$, *i.e.* we have a phase transition, providing $(\partial\mu_1/\partial T)_t < (\partial\mu_2/\partial T)_t < 0$. 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 volume, $S \sim \ln \Delta q \Delta p$, 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 diminish. We can see indeed that $S_1 > S_2 > 0$, *i.e.* the condensed phase is indeed more "macroscopically-occupied", and, in addition, we see that the relative jump in entropy is $1/s - 1 = (1 - s)/s$, as obtained in the model described above.

The mechanism of condensation described herein is unstable with respect to formation of composite particles. Indeed, at the transition temperature given by (15) the condensate is dominated by composite particles with constituency $s = 2$. They may be viewed as a gas with characteristic temperature $T'_0 = T_0/2$ (since the mass of its molecules is $m' = 2m$, while its concentration is almost the same as that of the original gas). The condensation mechanism can be applied to this gas, with the parameter $\varepsilon'_0 = 2\varepsilon_0$. Its transition temperature T'_t is therefore given by equation (15) with $\varepsilon_0 \rightarrow \varepsilon'_0 = 2\varepsilon_0$ and $T_0 \rightarrow T'_0 = T_0/2$. It is easy to see that $T'_t > T_t$, *i.e.* the new condensate, made out, mainly, of particles with constituency $n_j = 4$ now, is already formed at the transition temperature T_t .³ This holds also for all values of n_j , so that one may say that at the temperature T_t there appears an avalanche of bigger and bigger composite particles, which evolves quickly toward the liquid state. Therefore, the liquid volume is limited by a cutoff volume v , and the transition region in Fig. 1 can be viewed as being limited, in fact, on its left-hand side, approximately, by the vertical line $V = v$, as shown in Fig. 2. The actual form of the *lhs* coexistence curve cannot, however, be determined without a particular mechanism of interaction between the gas molecules, and its solution for the liquid state.

The extension of the transition region in Fig. 1 upward higher pressures is also limited by the condition $V_c = V/s = v$, *i.e.* $s\varepsilon_0/(s-1)T = \ln s$ according to equation (23), for $s = 2$. This may be taken as the critical point $T_c = 2\varepsilon_0/\ln 2$ for the gas-liquid transition, corresponding to a critical volume V_c of the order v to $2v$ and the critical pressure $p_c = N\varepsilon_0/v \ln 2$. These critical values for p_c and T_c agree with the (p, T) -curve given by equation (16) (up to some minor numerical factors arising from the approximations made in deriving the transition temperature T_t in equation (15) from equations (13) and (14)). At the same time, these critical values indicate the termination

³This is valid also for a general function $\varepsilon_{0j}(n_j)$ of cohesion energy.

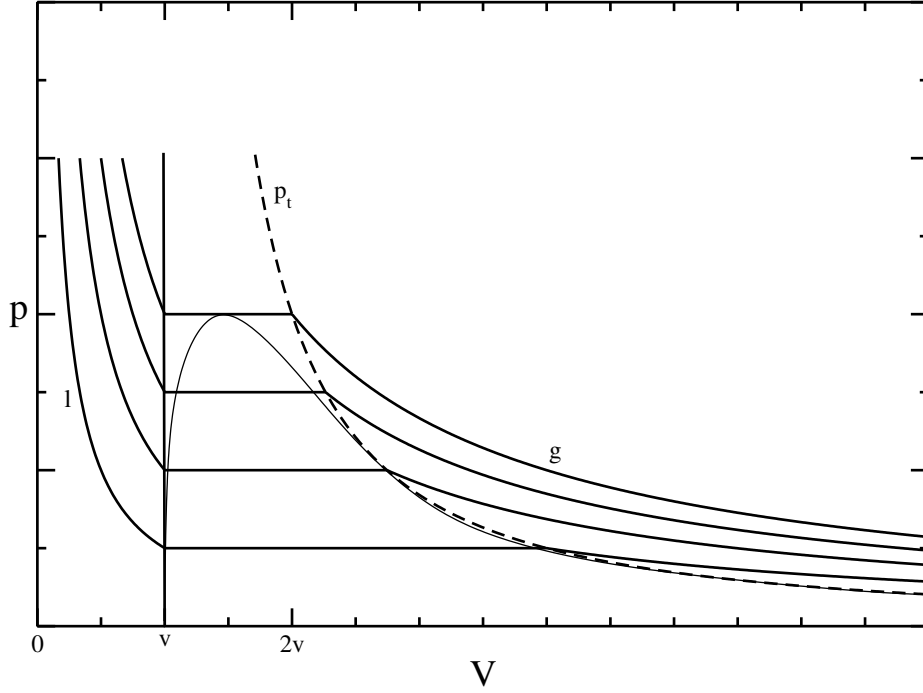


Figure 2: Schematic representation of the gas-liquid isotherms (curves g and, respectively, l), with the critical region indicated by the cutoff volume v to $2v$. The coexistence curve p_t is given by equation (22).

of the (p, T) -curve given by (16). Making use of the well-known van der Waals critical values $T_c = 8a/27b$ and $p_c = a/27b^2$ one can extract the van der Waals parameters $a = 27\varepsilon_0 v/16N \ln 2$ and $b = v/4N$ (they correspond to parameter ε_0 and to $s = 2$). The van der Waals critical volume $V_c = 3Nb = 3v/4$ agrees with the critical volume found here $V_c \sim v$. A schematic representation of the gas-liquid isotherms is given in Fig. 2. The equations employed here for characterizing the critical point $V_c \sim v$ are not valid for this region (they hold for $V \gg v$). The model presented here should in fact be employed with two parameters, one ε_0 and another a cutoff volume v (which is not given, in realistic situations, by the quantum localization corresponding to energy ε_0). As it was said above, the connection between two such parameters would require a well-determined mechanism of interaction between the gas molecules, and the corresponding solution for the cohesion of the liquid state.

Finally, we may note that, technically, according to the transition theory given here for an equilibrium process, it may also 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 $s = N \rightarrow \infty$ 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 then given by equation (15) for $s \rightarrow \infty$. The liquid would then have 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 such a liquid state is meaningless. This indicates that the transition proceeds in fact through the avalanche phenomenon described above.

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