On the gas-liquid transition

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Abstract

The gas-condensate transition is reviewed and the gas-liquid transition is described, as based on the theory of liquids derived previously. The pressure-volume phase diagram (isotherms) is obtained.

In recent papers,[1] a model of condensation of a classical ideal gas into liquid droplets was described. The model starts with the chemical potential of the classical ideal gas

$$\mu = -(3/2)T\ln(T/T_0) \ , \tag{1}$$

where $T_0 \simeq \hbar^2 n^{2/3}/m$ is a characteristic temperature of the gas, $n = N/V$ is the particle concentration, N is the number of molecules, V is the gas volume and m is the molecular mass. Equation (1) is valid for temperature $T \gg T_0$. The equation of state is given by the thermodynamic potential $\Omega = -pV = -NT$, where p is the pressure, the energy is $E = 3NT/2$, the heat function is $W = 5NT/2$, the entropy is $S = (3N/2)\ln(T/T_0) + 5N/2$ and the heat capacity at constant volume is $C = 3N/2$.

It is found[1] that the condensate is dominated by composite particles made up of $s = 2$ original molecules. They form an ideal classical gas with the chemical potential given by

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

where ε_0 is an average cohesion energy per molecule, $n_c = N/sV_c$ is the concentration of the droplets, and V_c is the volume of the condensate. The equation of state is given by $\Omega_c = -pV_c = -NT/s$, and, at equilibrium, the pressure is the same, the concentration is the same, so that $N/V = N/sV_c$, $i.e.$ the volume of the condensate is $V_c = V/s$. This shows that indeed there is a condensation of the original gas at the transition temperature

$$T_t \simeq \frac{2s}{3(s-1)} \cdot \frac{\varepsilon_0}{\ln(\varepsilon_0/T_0)} \ , \tag{3}$$

for $s \simeq 2$, obtained by equating the two chemical potentials. At the transition temperature there are discontinuities in the thermodynamic potential Ω (relative jump $1 - 1/s$), as well as in the other thermodynamic functions. For instance, the energy of the condensate is given by $E_c = -N\varepsilon_0 + 3NT/2s$, and it exhibits a relative jump $\simeq -(1 - 1/s)$. The heat function of the condensate is $W_c = -N\varepsilon_0 + 5NT/2s$, so the latent heat of the transition is $Q = W_c - W = -N\varepsilon_0 + 5(1-s)NT_t/2s$. The entropy of the condensate is given by $S_c = (3N/2s)\ln(T/T_0) + 5N/2s$,
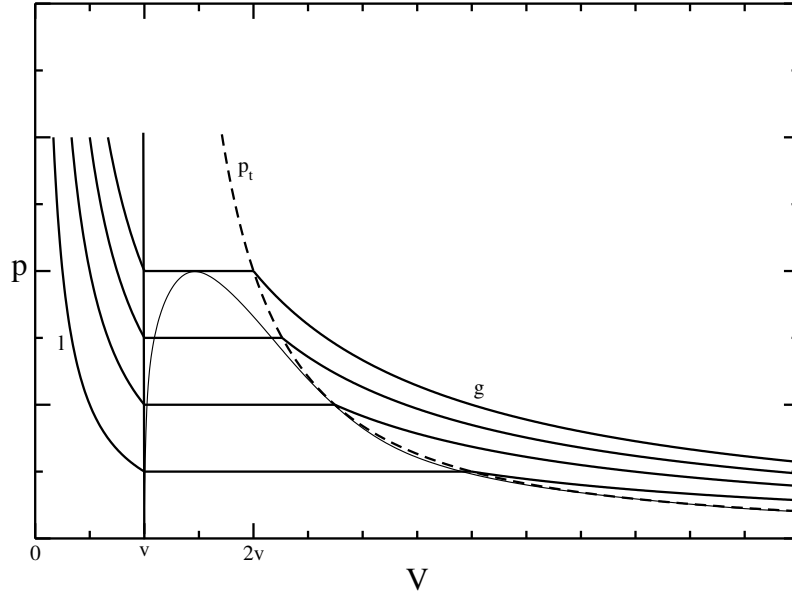
Figure 1: Schematic representation of the gas-liquid isotherms (curves g and, respectively, l), with the critical region indicated by the cutoff volume v to $2v$. The coexistence curve p_t is given by equation (5).

and 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 $S_c < S$, *i.e.* the condensate is indeed a more ordered phase. One can check also the Clapeyron-Clausius law $Q = T_t\Delta S$. The heat capacity of the condensate is $C_c = 3N/2s$, and it also exhibits a jump ($\Delta C = (1/s - 1)C$). All these are typical characteristics of a first-order phase transition, which describes the condensation of matter.

Making use of $n = N/V = p/T$ for $T_0 \simeq \hbar^2 n^{2/3}/m$ in equation (3) we get the (p, T)-equilibrium curve

$$p = (m/\hbar^2)^{3/2} T^{5/2} \exp[-s\varepsilon_0/(s-1)T] \tag{4}$$

of the gas-condensate ensemble. The gas-condensate coexistence curve $p_t(V)$ is given by $p_t V = NT_t$, where T_t is given by (3) (gas isotherms at the transition temperature). It reads

$$p_t(V) = \frac{s}{s-1} \cdot \frac{N\varepsilon_0}{V \ln(V/v)} \quad, \tag{5}$$

where $v = N(\hbar^2/m\varepsilon_0)^{3/2}$ is a cutoff volume (corresponding to the localization of each molecule with energy ε_0).

It was shown[1] that the condensation is an unstable phenomenon, which evolves rapidly towards the liquid state (made up, practically, of only one, big "composite" particle), so the condensate volume is limited by $V_c = v$. All this information is shown in Fig. 1, where the horizontal platteaux begin at

$$V = v \exp[s\varepsilon_0/(s-1)T] \quad, \tag{6}$$

obtained from the intersection of the gas isotherms $p = NT/V$ with the coexistence curve $p = NT/V = p_t(V)$. The horizontal platteaux are limited by $V = sv$, where V is given by (6), for $s \simeq 2$. This limitation sets up a critical volume in the range v to sv, corresponding to a critical temperature $T_c \simeq s\varepsilon_0/(s-1)\ln s$, as given by (6), and a critical pressure $p_c = p_T(sv) = N\varepsilon_0/(s-1)v\ln s$. These critical quantities satisfy the (p, T)-equilibrium equation (4) (up to minor numerical factors originating in the approximations used in solving the transcedental equations),

and indicate the point *terminus* for this curve, *i.e.* the critical point. Making use of the van der Waals critical quantities $T_c = 8a/27b$ and $p_c = a/27b^2$, we get the van der Waals parameters $b = sv/8N$ and $a = 27s^2 v \varepsilon_0/64(s-1)N \ln s$. The van der Waals critical volume $V_c = 3Nb = 3sv/8$ ($= 3v/4$ for $s = 2$) agrees with the critical volume v to $2v$ given here. However, the equations used here are valid for $V \gg v$.

In Fig. 1 the gas isotherms (curves g), the *rhs* coexistence curve $p_t(V)$, the horizontal platteaux and the critical point corresponding to the critical volume v to $2v$ are calculated (or estimated) by using the condensation model.[1] The liquid isotherms (curves l) and the *lhs* coexistence curve in Fig. 1 are idealized curves. In order to estimate them, we need a liquid model.

Such a model was described recently.[2] It assumes a constraining volume b for the motion of the liquid particles (distinct from the van der Waals excluded volume), a cohesion energy per particle $-\varepsilon_0$ as for the condensate and an energy parameter ε_1, which is the inter-spacing between the energy levels of the liquid particles, assumed to be those of a linear harmonic oscillator. These assumptions correspond to our representation of liquids as ensembles of strongly interacting and correlated particles. In contrast with the condensate above, the dependence of the parameter ε_0 (and ε_1) on concentration cannot be neglected now.

The thermodynamics of such a liquid model (which is that of a two-dimensional ideal gas of bosons, or fermions)[2] is governed by the parameter $C = b\varepsilon_1/a^3 T$, where a is the mean inter-particle distance ($V/N = a^3$). For high temperatures, $C \ll 1$ (as for classical liquids), the energy of the liquid is $E = -N\varepsilon_0 + NT$, the entropy is $S = 2N - N \ln(b\varepsilon_1/a^3 T)$, the free energy is $F = -N\varepsilon_0 - NT + NT \ln(b\varepsilon_1/a^3 T)$, the thermodynamic potential is $\Omega = -NT$ and the heat function is $W = -N\varepsilon_0 - (N^2/V)\varepsilon_0' + 2NT$, where ε_0' is the derivative of ε_0 with respect to the concentration $n = N/V$ (the concentration dependence of ε_1 is neglected). The chemical potential of the liquid is given by

$$\mu = -\varepsilon_0 + T \ln(b\varepsilon_1/a^3 T) \ , \tag{7}$$

and the pressure (equation of state) is

$$p = -(N^2/V^2)\varepsilon_0' + NT/V \ . \tag{8}$$

All this, together with the isothermal and adiabatic compressibilities and the coefficient of thermal expansion,[2] provide a reasonable picture of liquids for a limited range of density and temperature. In particular, equation (8) gives the liquid isotherms (curves l in Fig. 1), providing the concentration dependence of the cohesion energy per particle ε_0 is known (it is valid for $\partial p/\partial V < 0$).

At equilibrium the two chemical potentials given by (1) and (7) must be equal, and the two pressures, the gas pressure NT/V and the liquid pressure given by (8), must also be equal. This provides two equations,

$$-\varepsilon_0 + T \ln(b\varepsilon_1 n_l/T) = T \ln[(\hbar^2/mT)^{3/2}n] \ ,$$

$$-n_l^2 \varepsilon_0' + n_l T = nT \ , \tag{9}$$

for the transition temperature and the liquid concentration n_l. The first equation (9) can also be written as

$$T \ln(n_l/n) = \varepsilon_0 + T \ln(\lambda_l^2 \lambda_T/b) \ , \tag{10}$$

where $\lambda_1 = (\hbar^2/m\varepsilon_1)^{1/2}$ is a quantal localization length corresponding to energy ε_1 and $\lambda_T = (\hbar^2/mT)^{1/2}$ is a similar length for temperature T. We get

$$n_l = n(\lambda_1^2 \lambda_T/b)e^{\varepsilon_0/T} \ . \tag{11}$$
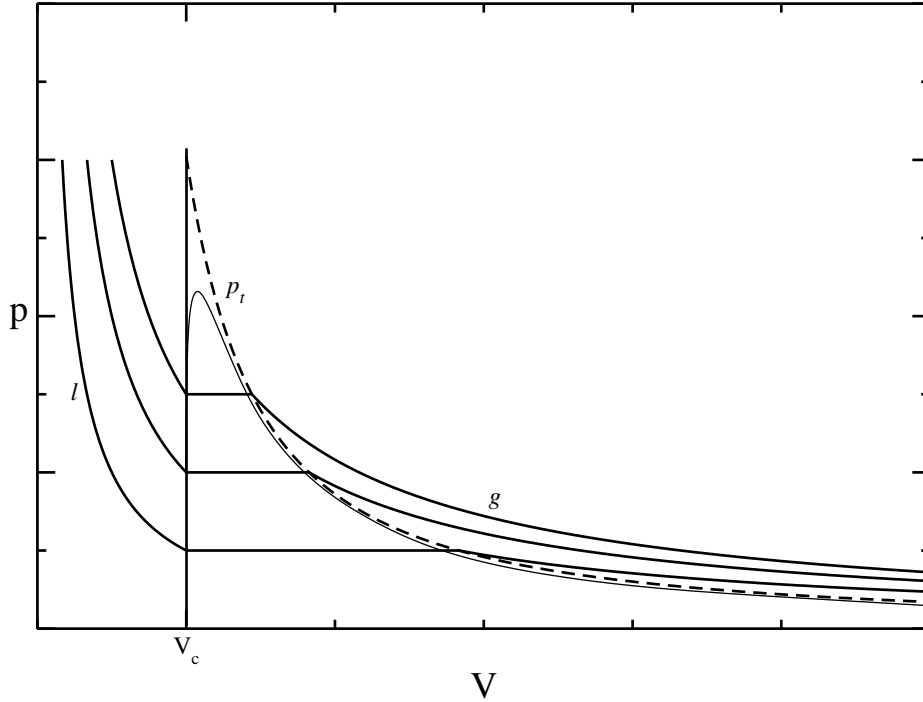
Figure 2: Schematic representation of the gas-liquid isotherms with critical volume V_c.

Within the range of temperatures characteristic of liquids, one can see that the liquid concentration n_l is much higher than the gas concentration n (we can take, tentatively, $\varepsilon_0 \sim 100meV$ and $\varepsilon_1 \sim 1meV$, for instance). The second equation in (9) becomes then

$$\varepsilon_0 \simeq T \ln[T/n\varepsilon_0'(\lambda_1^2\lambda_T/b)] \ , \tag{12}$$

which leads to the transition temperature

$$T_t \simeq \frac{\varepsilon_0}{\ln[(\varepsilon_0/n\varepsilon_0'(\lambda_1^2\lambda_0/b)]} \ , \tag{13}$$

where $\lambda_0 = (\hbar^2/m\varepsilon_0)^{1/2}$ $(v = \lambda_0^3)$. For realistic liquids $\varepsilon_0 \gg n\varepsilon_0'(\lambda_1^2\lambda_0/b)$.

This gas-liquid transition temperature is very similar to the gas-condensate transition temperature given by (3). The difference arises (apart from the approximations made in solving the corresponding transcendental equations) in the absence of a well-determined mechanism of interaction between the gas molecules, and its solution for the cohesive liquid state. At the transition temperature the thermodynamic quantities given above for gas and liquid are discontinuous, indicating a first-order phase transition, as expected. Introducing (13) in (11) (liquid isotherms for the transition temperature) we get the *lhs* coexistence curve in Fig. 2, as given by the equation

$$V = V_c \simeq N(\varepsilon_0'/\varepsilon_0) \ . \tag{14}$$

The cutoff volume v in Fig. 1 must therefore be replaced by the critical volume V_c given by equation (14), as shown in Fig. 2. The inequality $V_c \gg v$, *i.e.* $\varepsilon_0'/\varepsilon_0 \gg \lambda_0^3 = (\hbar^2/m\varepsilon_0)^{3/2}$, holds.

The intersection of the vertical line $V = V_c$ with the *rhs* coexistence curve given by (5) and (6) provides the critical pressure and temperature

$$p_c = T_c/\varepsilon_0' = \frac{s}{s-1} \cdot \frac{\varepsilon_0/\varepsilon_0'}{\ln(\varepsilon_0'/\varepsilon_0\lambda_0^3)} \ ,$$

for $s \simeq 2$. They are similar with the critical quantities obtained above for the gas-condensate transition. The van der Waals parameters can be extracted from these critical quantities. In particular, we get for the van der Waals parameter b in the critical volume $V_c = 3Nb$ the value $b = \varepsilon_0'/3\varepsilon_0$. It is worth emphasizing, however, that near the critical point neither the formulae of the classical ideal gas, nor the formulae employed here for the liquid, are valid.

References

[1] M. Apostol, J. Theor. Phys. **123** (2006); *ibid*, **147** (2007).

[2] M. Apostol, J. Theor. Phys. **125** (2006); *ibid*, **148** (2007).