Series 1

The Van der Waals equation of state describes the relation between the volume and the pressure of a substance at constant temperature.

$$p = \frac{k_B T}{v-b} - \frac{a}{v^2}. \tag{1}$$

a) According to the temperature, it's possible to distinguish between different regimes, as shown in Fig. 1. Compute the critical temperature T_C at which two different extrema appear along the isotherms in the (p,v) diagram.

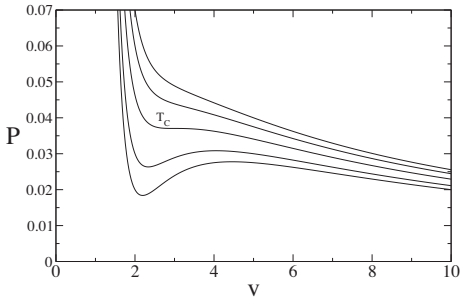

Figure 1: Isothermal curves for different temperatures

b) If $T < T_C$ explain why the values of v such that $\frac{\partial p}{\partial v} > 0$ are "instable".

c) The isotherms obtained experimentally have the behaviour showed in Fig.2 (solid line) while the solution of the Van der Waals equation corresponds to instable states (dashed line). The path ABCDE correspond to a phase transition: tipically if $v < v_A$ the substance is in the liquid phase, while for $v > v_E$ it's in the gaseous one. For $v_A < v < v_E$ there's a mixing of the two phases (droplets of liquid in the gas). Supposing that the Van der Waals equation can be experimentally realized, although not

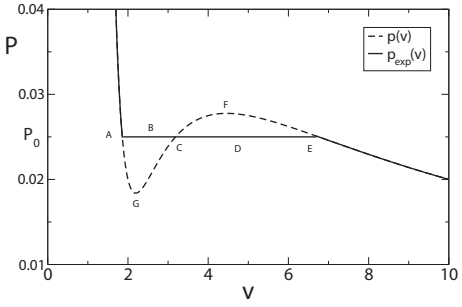

Figure 2: Comparison between the experimental results and the Van der Waals model

in equilibrium conditions, show, using only thermodynamics arguments (analyse the reversible cycle ABCDEFCGA), how can be derived the *vapour pressure* , P_0 (generally this condition brings a set of equations that have to be solved numerically). Remember that A and E are the same thermodynamic states in the two equations of state.

d) The pressure is given by $p = -(\partial F/\partial v)_T$. Analyze the *free energy* for the Van der Waals equation and for the experimental function. How can be translated the condition proved in the point c)?