13. *Statistical Mechanics and Thermodynamics* (Spring 2004)

A van der Waals gas has the following equation of state:

$$P(T, V) = \frac{NkT}{(V - bN)} - a\left(\frac{N}{V}\right)^2$$

This gas is held in a container of negligible mass which is isolated from its surroundings. The gas is initially confined to 1/3 of the total volume of the container by a partition (a vacuum exists in the other 2/3 of the volume). The gas is initially in thermal equilibrium with temperature T_i. A hole is then opened in the partition, allowing the gas to irreversibly expand to fill the entire volume (V). What is the new temperature of the gas after thermal equilibrium has been re-established? (Hint: Note that the specific heat at constant volume for a van der Waals gas is the same as that for an ideal gas.)

Before   **After**

See Reif Page 177. The concept here is that the gas will do work against its own van der Waals attraction forces when it expands, which lowers the temperature of the gas.

Start with $C_v = \left(\frac{dQ}{dT}\right)_v = T\left(\frac{\partial S}{\partial T}\right)_v$ and $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$.

The first is only true for quasistatic situations and this expansion is not quasistatic, but we will use dQ as the change in internal energy of the gas rather than heat exchanged with the environment, and the change in energy of the gas can be quasistatic. By the chain rule,

$$dS = \left(\frac{\partial S}{\partial T}\right)_v dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$= \frac{C_v}{T} dT + \left(\frac{\partial P}{\partial T}\right)_v dV$$

$$\Rightarrow T dS = C_v dT + T\left(\frac{\partial P}{\partial T}\right)_v dV$$

$$dE = TdS - pdV \Rightarrow dE = C_v dT + T\left(\frac{\partial P}{\partial T}\right)_v dV - p dV$$

$$= C_v dT + \frac{NKT}{(V-bN)} dV - \left(\frac{NKT}{(V-bN)} - a\left(\frac{N}{V}\right)^2\right) dV$$

$$= C_v dT + a\left(\frac{N}{V}\right)^2 dV$$

No work done on environment and no heat exchanged $\Rightarrow dE = 0$

$$\Rightarrow C_v dT = -a\left(\frac{N}{V}\right)^2 dV$$

Assume $C_v = \frac{3}{2}NK$ like ideal gas even though it isn't true,

$$\Rightarrow \Delta T = \int dT = -\frac{2}{3}\frac{a}{K}N\int_{V/3}^{V}\frac{1}{V^2}dV = \frac{2}{3}\frac{a}{K}N\left(\frac{1}{V} - \frac{1}{V/3}\right) = -\frac{4}{3}\frac{a}{K}\frac{N}{V}$$

$$\Rightarrow T_f = T_i - \frac{4}{3}\frac{a}{K}\frac{N}{V}$$