EXAM

3 HOURS ; DOCUMENTS AND POCKET CALCULATORS NOT ALLOWED

Tentative scale : 7 points for problem I, 6 points for problem II and 7 points for problem III

I Fluctuations of work in the Jepsen gas

N.B. This problem may be seen as the follow-up of the home assignment of April-May 2010 ; it is however completely independent and self-contained.

In recent years, remarkable results have been derived in the realm of non equilibrium statistical mechanics. One of the most well known example is provided by the Jarzynski relation, that reads

$$\left\langle e^{-\beta W} \right\rangle = e^{-\beta \Delta F}. \tag{1}$$

In this equality, W is the work received by the system when its macroscopic states evolves under the action of an external perturbation, such as an external field, while ΔF is the corresponding free energy variation. The system, supposed to be Hamiltonian and classical, is initially at thermal equilibrium at temperature T (we denote $\beta^{-1} = k_B T$ the inverse temperature). The brackets $\langle \ldots \rangle$ stand for an average over the different possible realizations of the experimental protocol (where the initial and final states are fixed).

The goal here is to explicitly check Jarzynski equality, together with a more general one coined Crooks relation, on an exactly solvable one dimensional model : the Jepsen gas. We shall consider an assembly of N identical point particles with mass m, that move on a line that defines the x-axis. These particles undergo binary elastic collisions that conserve linear momentum and kinetic energy. The particles are initially uniformly distributed in the interval $[-L, 0]$, with a Maxwellian velocity distribution :

$$\phi(v) = \sqrt{\frac{m\,\beta}{2\pi}}\, e^{-\beta m v^2/2}. \tag{2}$$

The gas is confined by a piston of large mass compared to m, and therefore assumed infinite. This piston is moved with velocity V. If t denotes the duration of the "experiment", the piston then moves from the initial position $X = 0$ to the final position $X = Vt$.

1. **Collision law**.
   (a) Whenever two particles collide, we note (v_1, v_2) their precollisional velocities, and (v_1', v_2') the postcollisional velocities. Show that $v_1' = v_2$ and $v_2' = v_1$.
   (b) Establish that a particle with velocity v colliding elastically with the piston bounces off with velocity $v' = 2V - v$. It turns useful to consider the collision in the piston frame.
   (c) What is the kinetic energy variation of a particle colliding with the piston ?
2. **Expressing the work**. Question 1a) shows that inter-particle collisions amount to a simple label exchange of the particles (assumed indistinguishable). We can therefore ignore these collisions, and consider that the particles do not interact. Only the collisions with the piston do matter. In addition, we will assume in the sequel that L is very large (and we shall take the thermodynamic limit in due course), which allows for the neglect of particle-piston recollisions –a given particle cannot collide with the piston more than once– and additionnaly indicates that the velocity distribution function does not depend on time.
   (a) Explain qualitatively this latter assumption (recollision neglected).

(b) Show that the work received by the gas in the time interval t reads

$$W = \sum_{j=1}^{N} \Delta W_j = \sum_{j=1}^{N} 2m\, V(V - v_j)\, \theta(x_j + v_j t - Vt), \tag{3}$$

where θ stands for the Heaviside distribution, and where the meaning of the different quantities will be explained. How does the sign of W depend on the sign of V ?

3. **Jarzynski relation.**

   (a) We first focus on the right hand side of equation (1). What is the expression of the force exerted by the gas (the density of which is supposed to remain uniform at all times) on the piston ? The result will be expressed as a function of N, β and the length $\mathcal{L}$ occupied by the gas at a given time t ($\mathcal{L} = L + Vt$). What is then the free energy variation ΔF ? Other methods may be used to compute ΔF, if necessary. Show that in the thermodynamic limit where $L \to \infty$, $N \to \infty$ with fixed density $n = N/L$, one has

   $$e^{-\beta \Delta F} = e^{\alpha\, n\, V\, t}, \tag{4}$$

   where α is a numerical coefficient to be precised.

   (b) We are now interested in the left hand side of relation (1). Show that upon neglecting recollisions and for L big enough,

   $$\left\langle e^{-\beta W} \right\rangle \simeq \left\{ 1 + \int_V^\infty \frac{(v-V)\, t}{L} \left[e^{2\beta m V(v-V)} - 1 \right] \phi(v)\, dv \right\}^N \tag{5}$$

   (c) Show that $\displaystyle\int_V^\infty (v - V) \left[e^{2\beta m V(v-V)} - 1 \right] \phi(v)\, dv = \gamma\, V$. What is the value of γ ? It is useful here to note that the product $e^{2\beta m V(v-V)} \phi(v)$ defines a “shifted” Gaussian probability distribution function $\phi(v - 2V)$.

   (d) What does expression (5) become in the thermodynamic limit where $N \to \infty$ with $n = N/L$ fixed ? Conclude.

4. **Crooks relation** (*this question is more difficult*). It is possible to check a more general relation than that of Jarzynski, by relating the probability density function of the work W for the ”forward” protocol (that we shall denote $P_V(W)$), to the probability density $P_{-V}(W)$ of the reverse protocol, where the sign of the velocity has been changed. The so-called Crooks relation indeed states that

   $$P_V(W)\, e^{-\beta W} = e^{-\beta \Delta F}\, P_{-V}(-W) \ ; \tag{6}$$

   it is our purpose here to check that it is indeed fulfilled.

   (a) Making use of the representation $\delta(x) = \int \exp(ikx) dk/(2\pi)$ of Dirac distribution, establish that in the thermodynamic limit :

   $$P_V(W) = \int \frac{dk}{2\pi} \exp[ikW + ntC(k,V)] \quad \text{where} \quad C(k,V) = \int_V^\infty (v-V) \left[e^{2ikmV(v-V)} - 1 \right] \phi(v)\, dv. \tag{7}$$

   (b) Show that the following symmetry property holds :

   $$C(k,V) = V + C\,(-k - \beta i, -V)\,. \tag{8}$$

   (c) Deduce Crooks relation from the above equality.

   (d) Explain why the behaviour of the function $C(k,V)$ at small k allows for the calculation of the mean values $\langle W \rangle$, $\langle W^2 \rangle - \langle W \rangle^2$ etc. If you are courageous, you may compute the first moment $\langle W \rangle$. It may be useful to introduce the dimensionless variables $\widetilde{W} = \beta W$, $\widetilde{v} = v(m\beta/2)^{1/2}$, $\tau = nt[2/(m\beta)]^{1/2}$ and to make use of the annex appended below.

    (e) In which limit does one expect to have a Gaussian work probability distribution function ?

5. **An apparent paradox. . .** We imagine that the piston is moved very quickly, with $V > 0$, much quicker than the typical velocity of the molecules in the gas (what is the corresponding order of magnitude ?). One may then expect that the particle-piston collisions become very unlikely, so that W could ultimately become small if not vanishing. In these circumstances, how can Jarzynski equality hold (it should, irrespective of $V \ldots$) ?
6. **Another paradox ? Joule expansion. . .** *(This question is more difficult, but admits short answers).* We consider a system slightly different from the above one ; it is made up of two compartments. One (say the left compartment) initially contains the gas (segment $[-L, 0]$), and the other (the right compartment, segment $[0, Vt]$), is initially empty. We assume here $V > 0$. The wall between the two compartments is then removed instantaneously, without any work performed. We note that ΔF does not vanish though, and has the same value as with the protocol described in the above questions. Since $W = 0$, Jarzynski equality seems to be violated. What is the problem ?

Annex : The definition of the complementary error function is recalled

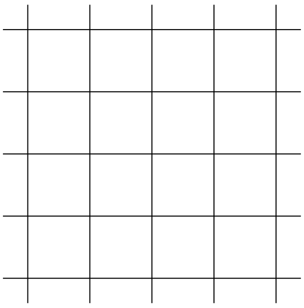
$$\mathrm{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-t^2}\, dt, \qquad \text{so that} \quad \mathrm{erfc}(0) = 1. \tag{9}$$

For large arguments ($x \to \infty$), we have $\mathrm{erfc}(x) \sim \dfrac{e^{-x^2}}{x\sqrt{\pi}}$.

Reference :
Jarzynski equality for the Jepsen gas, I. Bena, C. Van den Broeck, R. Kawai, Europhys. Lett. **71**, 879 (2005).

II The critical temperature of the bidimensional Ising model

We shall study the Ising model on the bidimensional square lattice schematized on the figure below.



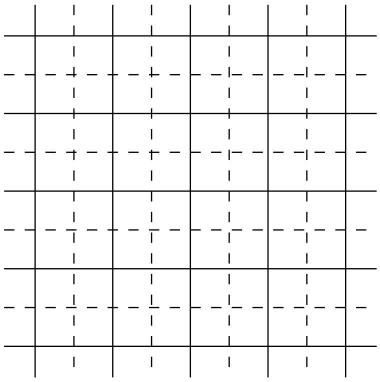
The degrees of freedom are $N = L^2$ Ising spins $\sigma_i = \pm 1$ placed on the vertices of a part of the lattice of length L. The energy of a configuration is defined as

$$H(\sigma_1, \ldots, \sigma_N) = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j \ , \tag{10}$$

where the sum is over the links of the lattice, and one uses periodic boundary conditions in the two directions. The goal of the exercise is to compute the critical temperature T_c of the model.

1. What is the sign of J in order for the interactions to be ferromagnetic ?
2. How many terms are there in the sum of the equation (10) ?
3. Show that one can write $e^{\beta J \sigma_i \sigma_j} = c(1 + t\sigma_i\sigma_j)$, where you will give the value of the constants c and t.

4. Deduce from that the following expression of the partition function for N spins, at the inverse temperature β :
$$Z_N(\beta) = c^{2N} \sum_{\sigma_1,\dots,\sigma_N} \prod_{\langle ij \rangle} (1 + t\sigma_i\sigma_j) \ . \tag{11}$$
How many terms are there in the expansion of the product in this equation ?
5. To each of these terms is associated a diagram, i.e. a subset of the links of the lattice, corresponding to the factors where one retains $t\sigma_i\sigma_j$ in the expansion. Characterize the diagrams which contribute to the equation (11). A few drawings may be useful.
6. **High-temperature expansion**. This expansion is ordered according to the power of t, defining the coefficients $a_{N,n}$ as
$$Z_N(\beta) = (2c^2)^N \sum_{n=0}^{\infty} a_{N,n} t^n \ . \tag{12}$$
Justify the name "high-temperature expansion" given to this series. In the following we shall denote $A_N(x) = \sum_n a_{N,n} x^n$.
7. Compute the values of $a_{N,n}$ for $n = 0, 1, \dots, 6$.
8. Give a definition, without any computation, of the coefficient $a_{N,n}$ for any n.
9. **Low-temperature expansion**. What is the order of magnitude for the temperature that discriminates the high against the small temperatures ?
10. Which are the configurations which minimize the Hamiltonian (10) ? Give their number and their energy E_0.
11. What is the energy $E_1 > E_0$ of the first excited levels ? Describe the corresponding configurations, and give their number.
12. Same question for the following level, of energy $E_2 > E_1$.
13. Deduce from that the following low-temperature expansion,
$$Z_N(\beta) = 2e^{2N\beta J} \left(b_{N,0} + b_{N,4} \left(e^{-2\beta J}\right)^4 + b_{N,6} \left(e^{-2\beta J}\right)^6 + o\left(\left(e^{-2\beta J}\right)^6\right) \right) \ , \tag{13}$$
where you shall give the values of the coefficients $b_{N,n}$. Compare them to the coefficients $a_{N,n}$ of the high-temperature expansion.
14. *More difficult question.* Show that the low-temperature expansion can be written $Z_N(\beta) = 2e^{2N\beta J} A_N(e^{-2\beta J})$, where $A_N(x)$ is the function defined in question 6. You can consider the diagrams of the dual lattice, shown with dashed lines on the figure below.



15. **Transition temperature**.
We denote $f(\beta) = -\frac{1}{\beta} \lim_{N\to\infty} \frac{1}{N} \log Z_N(\beta)$ the free-energy per spin in the thermodynamic limit. Deduce from the high and low temperature expansions two expressions of $f(\beta)$; you will define $g(x) = \lim_{N\to\infty} \frac{1}{N} \log A_N(x)$.

16. We admit that the model exhibits a single critical temperature, and hence that $f(\beta)$ is singular at a single point β_c. Show that
$$\beta_c J = \frac{1}{2}\log(1+\sqrt{2}) \ . \tag{14}$$
17. (extra-question) Compare the critical temperature T_c^{cm} obtained with the mean-field approximation, with the exact result above (T_c)? How does the ratio T_c^{cm}/T_c depend on the connectivity of the lattice (number of nearest neigbors), for a given spatial dimension? Finally, how does this ratio depend on the spatial dimension (for a given topology of the network)?

III Rotator phases of alkane molecules

Between their liquid and crystalline phases, linear alkanes may exhibit a variety of so-called "rotator" phases (Fig. 1), The molecules are then arranged in layers, on the sites of a three dimensional lattice (long range spatial order); the molecules can rotate around the mean axis of the carbon chain.

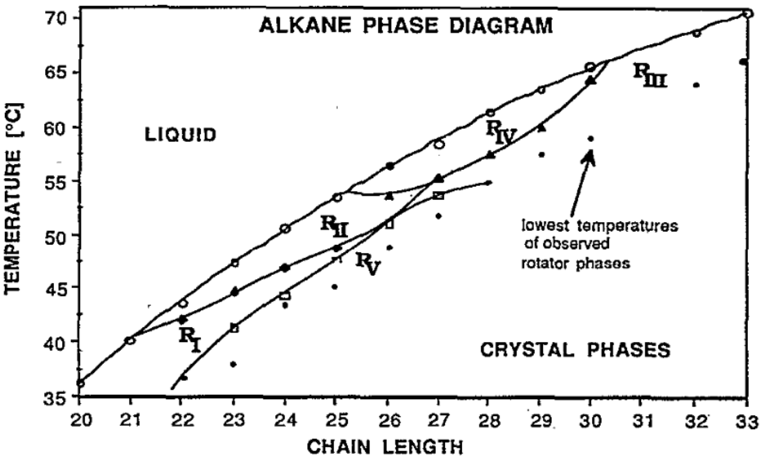


FIG. 1 – Phase diagram of linear alkanes, as a function of the number of carbon atoms.

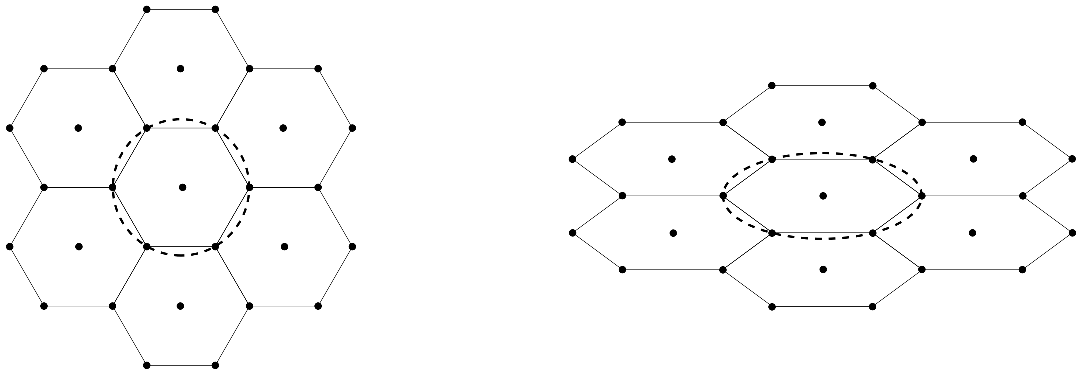
The goal is here to construct a Landau-like model to account for some of the phase transitions observed experimentally. For the sake of simplicity, we restrict the analysis to a unique layer of molecules.

A $R_{\mathrm{I}} - R_{\mathrm{II}}$ transition

In the R_{I} and R_{II} phases, all molecules are oriented perpendicular to the layer. The difference lies in the lattice on which the molecules are arranged within the layer. In the R_{I} phase, the molecules lie on the vertices of a triangular lattice that is compressed along one axis, while in the R_{II} phase, they are on a perfect triangular lattice (see Fig. 2). A group of 6 molecules is characterized by the ellipse that goes through their 6 positions. We denote B the length of the ellipse principal axis that relates two molecules, and A stands for the length of the perpendicular axis (see fig. 3). The following quantity is then defined :
$$D = \frac{B^2 - A^2}{B^2 + A^2} \ . \tag{15}$$

1. Explain why D may play the role of an order parameter for the $R_{\mathrm{I}} - R_{\mathrm{II}}$ transition. In which interval does D vary?

For a given configuration charaterized by the parameter D, we assume the free enthalpy at temperature T to be of the mean-field form :
$$G_D(T,D) = G_0(T) + \frac{1}{2}a(T)D^2 - \frac{1}{3}bD^3 + \frac{1}{4}cD^4. \tag{16}$$



PHASE R_{II} PHASE R_I

FIG. 2 – Pictorial view of phases R_{II} and R_{I}. The points represent the intersection of the plane of the layer with the axis of the carbon chain of each alkane molecule. The circle (or ellipse) shown with a dashed line is used to define the quantity D (see below).

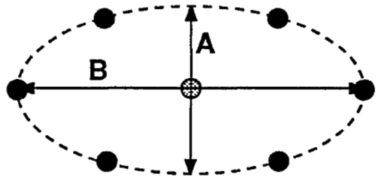


FIG. 3 – Definition of the parameter D.

2. What is the meaning of $G_0(T)$?
3. At high temperature, the system is in the R_{II} phase. Explain why there is no linear term in D in equation (16). What is the sign of $a(T)$ at high temperature ?
4. Why does equation (16) include a term in D^3 ?
5. Why was the term in D^4 considered in equation (16) ? What should be the sign of c ?
6. At arbitrary temperature, what is the equation fulfilled by the equilibrium value of D ?

In all the following, it is assumed that $a(T) = a_0(T - T_1)$.

7. Upon schematically drawing $G_D(T, D)$ versus D for different temperatures, show that there exists a transition between R_{II} and R_{I} at temperature $T_{\mathrm{I-II}}$. What is the order of the transition ?
8. We note $D_{\mathrm{I}}(T)$ the value of D at equilibrium in the R_{I} phase at temperature T. Write the two equations fulfilled by $D_{\mathrm{I}}(T_{\mathrm{I-II}})$.
9. Solve the two above equations and express $D_{\mathrm{I}}(T_{\mathrm{I-II}})$ and $T_{\mathrm{I-II}} - T_1$ as a function of a_0, b and c.
10. What does T_1 represent ?
11. Give the expression of the latent heat L of the transition.
12. We define the heat capacity jump at the transition as $\Delta C_{\mathrm{P}} = C_p(\text{phase } R_{\mathrm{I}}) - C_p(\text{phase } R_{\mathrm{II}})$. Show that
$$\Delta C_{\mathrm{P}} = \mathcal{C}\,\frac{{a_0}^2}{c} T_{\mathrm{I-II}}. \tag{17}$$
What is the value of the constant $\mathcal{C}$? It is recalled that $C_p = T \left.\dfrac{\partial S}{\partial T}\right|_P$.
13. Express $T_{\mathrm{I-II}} - T_1$ as a function of L and ΔC_{P}. For n-tricosane ($C_{23}H_{48}$), one measures $L = 0.6\,\mathrm{kJ\,mol^{-1}}$ and $\Delta C_{\mathrm{P}} = 1.5\,\mathrm{kJ\,mol^{-1}K^{-1}}$; compute $T_{\mathrm{I-II}} - T_1$.

B Transition $R_{\mathrm{I}} - R_{\mathrm{V}}$

We are now interested in the transition between phase R_{I} and phase R_{V}. The R_{V} phase differs from R_{I} in that the molecules may be tilted from the normal to the layer. We note θ the mean tilt angle in phase R_{V}.

1. Explain why θ may play the role of an order parameter for the $R_{\mathrm{I}} - R_{\mathrm{V}}$ transition. In which interval does θ vary ?

We note $G(T, D, \theta)$ the free enthalpy at temperature T of a configuration with parameters D and θ. We first consider the situation with no coupling between D and θ. We then write

$$G(T, D, \theta) = G_0(T) + \frac{1}{2}a(T)D^2 - \frac{1}{3}bD^3 + \frac{1}{4}cD^4 + \frac{1}{2}\alpha(T)\theta^2 + \frac{1}{4}\beta\theta^4 + \frac{1}{6}\delta\theta^6, \tag{18}$$

with $a(T) = a_0(T - T_1)$, $\alpha(T) = \alpha_0(T - T_2)$, and a_0, α_0, b, c, β and δ positive. We also have $T_2 < T_1$.

2. Write the equation fulfilled by θ at equilibrium. Discuss the number and stability of solutions as a function of temperature.
3. Find the temperature where the transition between R_{I} and R_{V} occurs. Give the expression of θ at equilibrium in the vicinity of that temperature. What is the order of the transition ?

We now address the coupled $D - \theta$ case, and seek for the influence of that coupling on equilibrium parameters D and θ of phase R_{V}. To that end, we assume that these parameters are close to those of the R_{I} phase. We note D_0 the value of D at equilibrium in phase R_{I}. **We will assume D_0 independent of T**, and we write :

$$G(T, D, \theta) = G_{\mathrm{I}}(D_0) + \frac{1}{2}u(D - D_0)^2 + \frac{1}{2}\alpha(T)\theta^2 + \frac{1}{4}\beta\theta^4 + \frac{1}{6}\delta\theta^6 + \gamma D\theta^2 + \frac{1}{2}\eta D^2\theta^2, \tag{19}$$

making use of previous notations and where $G_{\mathrm{I}}(D_0)$ is the free enthalpy of phase I at equilibrium, $u > 0$, $\gamma < 0$ and $\eta > 0$. No attempt will be made at computing u.

4. Considering the θ dependence of G only, show that the phase R_{I} becomes unstable at a temperature T_{i} that you will provide.
5. Considering the D dependence of G only, show that the equilibrium solution D may be written in the form of the following expansion

$$D = D_0 - \epsilon\,\theta^2 + K\,\epsilon\,\theta^4 + \mathcal{O}(\theta^6). \tag{20}$$

   What are the expressions of K and ϵ ?
6. (*Requires some computations*) Making use of equations (19) and (20), write G in the form :

$$G = G_{\mathrm{I}}(D_0) + \frac{1}{2}\alpha_1(T - T_{\mathrm{i}})\theta^2 + \frac{1}{4}\beta_1\theta^4 + \frac{1}{6}\delta_1\theta^6 + \mathcal{O}(\theta^8), \tag{21}$$

   and give the expressions of α_1, β_1 and δ_1.
7. What is then the equation fulfilled by θ at equilibrium ? Give the expression of θ in the R_{V} phase.
8. We assume that $\beta_1 > 0$ and $\delta_1 > 0$. What is the value of θ in the R_{V} phase at temperature T_{i} where R_{I} becomes unstable ? Which conclusion can be drawned concerning the order of the $R_{\mathrm{I}} - R_{\mathrm{V}}$ transition ?
9. We assume that $\beta_1 < 0$ and $\delta_1 > 0$. What is the value of θ in the R_{V} phase at temperature T_{i} where R_{I} becomes unstable ? Which conclusion can be drawn concerning the order of the $R_{\mathrm{I}} - R_{\mathrm{V}}$ transition ?
10. X rays measurements allow to extract the parameters of the R_{V} phase (see figures below). Explain which coefficients of the model (or combinations thereof) the plots give access to.

References :

Landau theory of the rotator phases of alkanes, P.K. Mukherjee, M. Deutsch, Phys. Rev. B **60**, 3154 (1999).
Rotator phases of the normal alkanes : An x-ray scattering study, E.B. Sirota, H.E. King, D.M. Singer and H.H. Shao, J. Chem. Phys. **98**, 7 (1993).

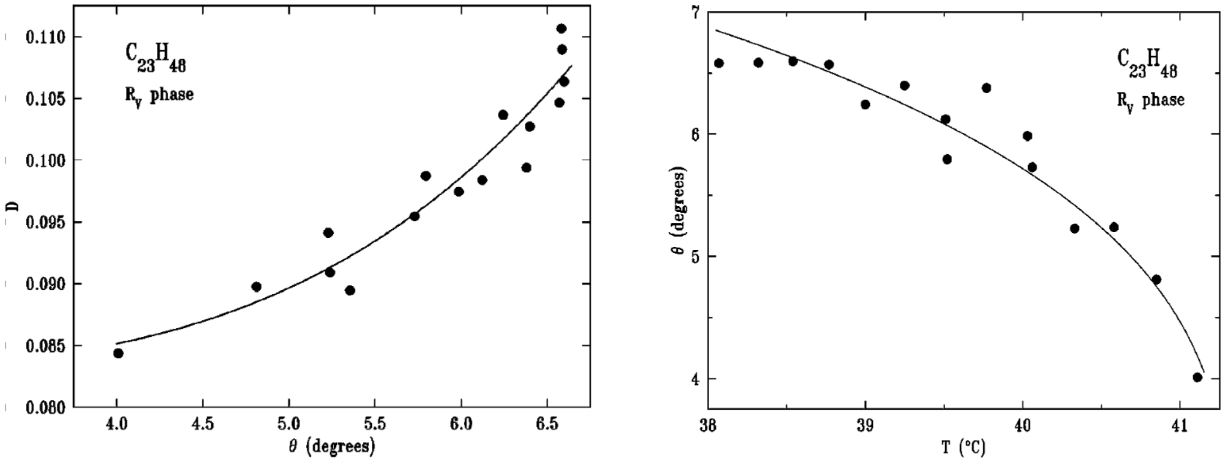


FIG. 4 – Parameters of the R_V phase for n-tricosane, as measured with X rays.