Revista Mexicana de Física **34** *No. 2(1988) 265–268*

One dimensional fluid model, a comment

J. Vila

Instituto de Matemática Aplicada San Luis,
Universidad Nacional de San Luis–CONICET, Ejército de los Andes 950–(5700),
San Luis, Argentina

(recibido el 30 de julio de 1987; aceptado el 2 de febrero de 1988)

Abstract. In the present comment we show how the analysis developed by D. Poland and H. Scheraga of a one dimensional lattice fluid model leads in a straightforward form the Takahashi equation of state.

PACS: 05.20.Gg

Poland and Scheraga [1] have shown how the one dimensional lattice fluid model can be extrapolated to obtain a classical continuum fluid in one dimension through a very simple and illustrative analysis.

The model developed by these authors has some intrinsic interest. First of all, the authors approach the continuum by means of a lattice variable, thus allowing one to see the accuracy of lattice models. Also they were able to connect the different types of ensembles, *i.e.* the Partition Function (PF), the Gran Partition Function (GPF), and the Generalized Ensemble (GE), with the emphasis placed on the equivalence of the results obtained from the evaluation of the GPF or the GE.

However, the primary interest of these authors is to illustrate the use of the matrix technique discussed in their book and also to show the analogies between classical physics problems with biophysics problems, *i.e.* transition helix $\rightarrow$ coil, denaturation of DNA, etc. On the other hand, in the present comment we show that the analysis developed by these authors leads in a straighforward way the Takahashi [2] equation of state, when we let the variable lattice, $\delta \rightarrow 0$, and assume that the interaction potential between nearest neighbor particles is arbitrary.

It is important to mention that Poland and Scheraga [1] do not consider the lattice as a physical grating, such as a crystal lattice where an atom occupies each lattice sites. Such view makes a lattice fluid to appear as a slightly sloppy crystal. This theoretical approach is often criticized, since a fluid obviously is not restricted to an artificial lattice. However, in the model proposed by these authors, the lattice is an artificial construction to approximate the PF numerically. Thus, an atom is not restricted to a given lattice site, but rather, in the lattice model of these authors, an atom is assigned the constant interatomic potential $\phi(n)$ over the interatomic distance $r_0\delta(n - 1/2)$ to $r_0\delta(n + 1/2)$ (where $[r_0\delta]$ appears as a lattice constant for each value of δ, and r_0 can be seen as the van der Waals radius of the atoms, *i.e.* two atoms cannot come much closer than r_0); as $\delta \to 0$, $\phi(n)$ approaches the smooth function $\phi(r)$. On this as well as on other assumptions, these authors solve the problem through a very simple analysis that involves the use of the PF, the GPF, and the GE. In such analysis, attention has been focused on the GE. The reasons for this are the following. Generally, the PF will be represented by one summation, the GPF by two summations an the GE by three summations, and as it is known, it is easier to evaluate three summations than two, and it is easier to evaluate two than one (because, of course, summations replace constraints). From this mathematical point of view, the use of the GE represents a further step in the direction of relaxing constraints [3, 4]. Furthermore, from a physical point of view, the GE is an ensemble where we sum over all the extensive variables of the system (which are not independent, and in fact, they are related by the Gibbs–Duhem equation [3]). Hence, they obtain for the GE the expression

$$\gamma = \sum_{N=0}^{\infty} \left\{ y \sum_{n=1}^{\infty} q_n x^{-n} \right\}^N . \tag{1}$$

The form in which the authors used the Generalized Ensemble is

$$\gamma^{-1} = 0. \tag{2}$$

Then, applying (2) to (1), we obtain

$$y \sum_{n=1}^{\infty} q_n x^{-n} = 1, \tag{3}$$

where y is the fugacity, q_n the Boltzmann factor assigned to a pair of atoms separated by n lattice sites, and defined as

$$q_n = e^{-\beta\phi(nr_0\delta)}, \tag{4}$$

The parameter x is defined as $x = e^{\beta p \delta}$; then equation (3) is an equation for the unknown p, the largest root of which gives p_1, where p_1 is the real pressure. Naturally, if we know the maximum eigenvalue x_1 of equation (3), we can compute the equation of state through the relation

$$\rho = \delta^{-1} y(\partial x_1/\partial_y)/x_1. \tag{5}$$

But, for δ small, it is impossible to solve equation (3) for x in analytic form, because this equation represents a polynomial of order $n_0 = 2/\delta$. As a matter of fact, in this discussion we take the potential as: $\phi(r) = 0$ for $r \geq 2r_0$ or, since $r = nr_0\delta$, $q_n = 1$ for $n \geq 2/\delta$, then we can see n_0 as the number of lattice sites beyond which the potential is truncated to zero. However, taking into account that $(\partial\mu/\partial p) = l = \rho^{-1}$ (where μ is the chemical potential and l the average length per atom) we can compute (5) for the linear density as

$$\rho = \delta^{-1}(\partial \ln y/\partial \ln x)^{-1}. \tag{6}$$

In this case, using equation (3) for y, we obtain for any value of δ

$$\rho = \frac{\sum_{n=1}^{\infty} q_n x^{-n}}{\sum_{n=1}^{\infty} (n\delta) q_n x^{-n}}. \tag{7}$$

In particular, if we are interested in obtaining the equation of state for a continuum fluid, it is not difficult to see that the above expression can be written as

$$\lim_{\delta \to 0} \rho = \frac{\int_0^{\infty} dr\, e^{-\beta(pr+\phi(r))}}{\int_0^{\infty} dr\, r e^{-\beta(pr+\phi(r))}}, \tag{8}$$

which represents the Takahashi [2] equation of state, this is to say, the more general solution for a one dimensional fluid when we assume that there exists an arbitrary interaction between nearest neighbor particles only.

We can solve many other cases of physical interest in straightforward form through the earlier procedure. For example, we can deduce the Tonks [5] equation of state or the *hard-rod* equation of state through equation (3). It is important to note that a method alternative to that here presented to derive the above mentioned Tonks or *hard-rod* equation of state can be found in the existing literature [6]. However the extension of this alternative method to solve more general cases (such as the Takahashi equation of state) is not clear, and more complex models can be solved with our method. In particular, we have generalized the method to solve the binary mixture in one dimension (work along this line is in progress and will be reported elsewhere).

We think that the earlier analysis, together with the discussion over the one dimensional fluid lattice model developed by Poland and Scheraga (which involves the connection between different ensembles) would be useful for the physicists, because it provides an alternative point of view for deriving many classical results in Statistical Mechanics.

Finally, it is worthwhile to point out that the result obtained in equation (8) can be derived through a more sofisticated analysis which involves a sparse matrix of order n_0 [7].

Acknowledgments

The author wishes to thank the referee for pointing out reference [5].

Reference

1. D. Poland and H. Scheraga, *Theory of Helix Coil Transition in Biopolymers*, Academic Press, New York, USA (1970).
2. Takahashi, *Proc. Phys. Math. Soc. Japan* **24** (1942) 60.
3. T.L. Hill, *Statistical Mechanics*, McGraw Hill, New York, USA (1956) 59–64.
4. T.L. Hill, *An Introduction to Statistical Thermodynamics*, Addison-Wesley, New York, USA (1960).
5. L. Tonks, *Phys. Rev.* **50** (1936) 955.
6. F. del Río, E. Martina and M. Leiva, *Am. Jour. of Phys.* **42** (1974) 1083.
7. J. Vila, *J. Phys.* **A20** (1987) 3353.

Resumen. En el presente comentario mostramos cómo el análisis desarrollado por D. Poland y H. Scheraga, acerca de un modelo de red de fluido unidimensional permite obtener en forma directa la ecuación de estado de Takahashi.