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Lattice gas with a weak long-range positive potential

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Abstract. In this paper we present a statistical mechanical analysis for a one-dimensional lattice gas in which the pair interaction potential is exponential and repulsive of Kac type $\phi(x) = \alpha \exp(-\gamma|x|)$ with $\alpha > 0$, $|x| > 0$ (this analysis is complementary to the one studied by Newman for a one-dimensional fluid).

The main objectives of this work are the following. First, we derive an analytical expression (in the weak long-range limit, $\gamma \to 0$) for the traces and the maximum eigenvalues of the Kac operators. Second, we derive the equation of state for the repulsive lattice gas in the weak long-range limit. Furthermore, we mention the possibility of the application of this model to study classical problems in biophysics. Third, we find interesting properties for the non-Hermitian Kac operator which suggest that the spanning property for this operator is possible.

1. Introduction

As is known, statistical mechanical analysis for a one-dimensional lattice gas, in which the pair potential interaction is of Kac [1] type: $\phi(x) = -\alpha \exp(-\gamma|x|)$, leads to the existence of a phase transition [3, 4] if one sets $\alpha = \alpha_0\gamma$ and then lets $\gamma \to 0$ (i.e. for a weak and very long range force). These models are of great interest because the partition function can be treated rigorously and exact results are obtained. Furthermore, a parallel analysis can be made for $\alpha < 0$, because the kernel that appears in the integral equation remains Hermitian, i.e. Ising model field free [5].

However, there are exceptions as a lattice gas (equivalent to the Ising model with field [4]) where the kernel that appears in the integral equation is algebraically symmetric but not Hermitian. A similar case has been studied by Newman [2] (for a one-dimensional fluid), who pointed out that the eigenvalue expansion for this kernel may not be justified in this case (as in the case of the symmetric kernel that appears in the Kac model).

In § 1 we find an analytic expression for two kernels, i.e. for $K^{(>)}(x, y)$ and for $K^{(<)}(x, y)$ when we assume repulsive and attractive Kac potentials respectively. The superscript is used to appoint the type of potential, i.e. repulsive ($>$) or attractive ($<$). Then using a very simple heuristic argument that involves the result mentioned above, we find an analytic expression for the maximum eigenvalue, for the non-Hermitian kernel, in the weak long-range limit (i.e. $\gamma \to 0$). Then we derive the equation of state for the repulsive lattice gas in a straightforward form and prove that the transition phase is not possible in this system, as is known. Furthermore in this section, we mention the application of this model to concrete biophysical processes, i.e. to study the conformational transition in homopolypeptide, induced by pH change. It is important to point out that if we are only interested in computing the equation of state

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for the repulsive lattice gas in the long-range limit, it can be derived from the virial expansion if we assume that the physical system consists of a single fluid phase [2]. However, in this application to biophysical problems [6, 7] we have been able to show the importance of knowing an analytic expression for the maximum eigenvalue.

Finally, in § 3 we show that the differential equation which satisfied the non-Hermitian kernel $K^{(>)}(x, y)$ to order γ, can be considered as an analytic continuation of one differential equation for which the spanning property is known to hold. Furthermore, some of the mathematical difficulties to be overcome are outlined, i.e. the proof that the spanning properties for the non-Hermitian kernel persist when γ vanishes.

2. The maximum eigenvalue of $K^{(>)}(x, y)$ in the long-range limit, $\gamma \to 0$

The grand partition function for the one-dimensional model of lattice gas is [4]

$$\Xi(L, \lambda, T) = \sum_{\varepsilon_1=0}^{1} \cdots \sum_{\varepsilon_L=0}^{1} \lambda^{\Sigma_i \varepsilon_i} \exp\left(\beta \sum_{i<j} \gamma\phi(\gamma|i-j|)\varepsilon_i\varepsilon_j\right) \tag{1}$$

$$= \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \mathrm{d}x_1 \cdots \mathrm{d}x_L \, W(x_1)(1+\lambda \, \mathrm{e}^{\sqrt{\nu}x_L}) \times \prod_{j=1}^{L-1} P(x_j|x_{j+1}; 1)(1+\lambda \, \mathrm{e}^{\sqrt{\nu}x_j}) \tag{2}$$

when we assume the Kac type potential: $\phi(x) = -\alpha \exp(-\gamma|x|)$. The derivation of equation (3) (the Kac equation) is given by [4] and it is not reproduced here. We simply give the main result

$$\int_{\infty}^{\infty} K^{(<)}(x, y)\psi(x) \, \mathrm{d}x = E^{(<)}\psi(y) \tag{3}$$

where the symmetric kernel is given by

$$K^{(<)}(x, y) = \left((1+\lambda \, \mathrm{e}^{\sqrt{\nu}x})(1+\lambda \, \mathrm{e}^{\sqrt{\nu}y}) \frac{W(x)}{W(y)}\right)^{1/2} P(x|y; 1) \tag{4}$$

and the factors in the kernel $K^{(<)}(x, y)$ are

$$P(x|y; 1) = [2\pi(1-\mathrm{e}^{-2\gamma})]^{-1/2} \exp\left(-\frac{(y-x \, \mathrm{e}^{-\gamma})^2}{2(1-\mathrm{e}^{-2\gamma})}\right)$$

$$W(x) = \frac{1}{\sqrt{2\pi}} \exp\left(\frac{-x^2}{2}\right) \qquad \text{and} \qquad \nu = \beta\alpha\gamma = \hat{\nu}\gamma.$$

On the other hand, if we choose the repulsive potential ($\alpha < 0$) the non-Hermitian kernel $K^{(>)}(x, y)$ replaces $K^{(<)}(x, y)$ in the integral equation given by (3), where now $K^{(>)}(x, y)$ verifies

$$K^{(>)}(x, y) = \left([1+\lambda \exp(\mathrm{i}\sqrt{\nu}x)][1+\lambda \exp(\mathrm{i}\sqrt{\nu}y)] \frac{W(x)}{W(y)}\right)^{1/2} P(x|y; 1). \tag{5}$$

It is well known that in the thermodynamic limit the maximum eigenvalue of the Kac integral equation, given by (3), and the grand partition function, given by equation (1), are related by the following expression

$$\lim_{L\to\infty} \frac{1}{L} \ln \Xi = \ln E_0.$$

Then, all the thermodynamic parameters are given in terms of E_0 or appropriate derivates thereof. Instead of finding the maximum eigenvalue E_0 directly from (3) we consider more convenient an analysis which involves the traces for $K^{(>)}(x, y)$ and $K^{(<)}(x, y)$. To do this we will show first that it is possible to obtain the trace $\sigma_N^{(<)}$, for the kernel $K^{(<)}(x, y)$ from the trace $\sigma_N^{(>)}$, for the kernel $K^{(>)}(x, y)$, in the long-range limit, if we make the substitution $\hat{\nu} \to -\hat{\nu}$ for any value of N. Second, using the above result we will show that the maximum eigenvalue for the non-Hermitian kernel can be obtained using a simple heuristic argument.

For the evaluation of the trace, it is necessary to solve

$$\sigma_N = \int_{-\infty}^{\infty} K_{(N)}(x, x)\, dx \tag{6}$$

where $K_{(N)}$ is the Nth iterate of the kernel $K(x, y)$. When the pair potential is repulsive, the kernel $K^{(>)}(x, y)$ is given by (5). For this case the trace is given by (6) and it can be written as

$$\sigma_N^{(>)} = \int_{-\infty}^{\infty} \cdots \int \prod_{i=1}^{N} P(x_i|x_{i+1}) + \sum_{k=1}^{N-1} \lambda^k \int_{-\infty}^{\infty} \cdots \int \sum_{j_1 \neq j_2 \; j_k \neq j_{k+1}} \exp Z(x_{j_1} + \ldots + x_{j_k})$$

$$\times \prod_{i=1}^{N} P(x_i|x_{i+1})\, dx_i + \int_{-\infty}^{\infty} \cdots \int \prod_{i=1}^{N} e^{zx_i} P(x_i|x_{i+1})\, dx_i \tag{7}$$

where $Z = i(\hat{\nu}\gamma)^{1/2}$ and j_k is either element of ensemble $(1, \ldots, k)$. In (7) we can see the first and last terms are a particular case of the intermediate term. Then the problem to solve is

$$\int_{-\infty}^{\infty} \cdots \int \left(\sum_{\substack{j_1 \neq j_2 \\ \vdots \\ j_k \neq j_{k+1}}} \exp Z(x_{j_1} + \ldots + x_{j_k}) \right) \prod_{j=1}^{N} P(x_j|x_{j+1}). \tag{8}$$

By introducing the new variables

$$\begin{aligned} \xi_1 &= (x_2 - x_1 e^{-\gamma})\varepsilon \qquad \text{where } \varepsilon = (1 - e^{-2\gamma})^{-1/2} \\ &\vdots \qquad\qquad \vdots \\ \xi_j &= (x_{j+1} - x_j e^{-\gamma})\varepsilon \end{aligned} \tag{9}$$

with the Jacobian

$$\mathbb{J} = \frac{\partial(\xi_1 \ldots \xi_j)}{\partial(x_1 \ldots x_j)} = \begin{vmatrix} \partial\xi_1/\partial x_1 & \partial\xi_1/\partial x_2 & 0 & 0 & 0 \\ 0 & \partial\xi_2/\partial x_2 & \partial\xi_2/\partial x_3 & 0 & 0 \\ 0 & 0 & 0 & \partial\xi_{j-1}/\partial x_{j-1} & \partial\xi_{j-1}/\partial x_j \\ \partial\xi_j/\partial x_1 & 0 & 0 & 0 & \partial\xi_j/\partial x_j \end{vmatrix} \tag{10}$$

and solving this expression for $3, 4, \ldots, k$ we can obtain by induction

$$\mathbb{J}_j = (1 - e^{-\gamma j})/(1 - e^{-2\gamma})^{j/2}. \tag{11}$$

Then we solve the system given by (9) for ξ as

$$\begin{aligned} x_1 &= \{\xi_j + \xi_{j-1}e^{-\gamma} + \ldots + \xi_1 \exp[-(j-1)\gamma]\}[1-\exp(-j\gamma)]^{-1}\varepsilon^{-1} \\ x_j &= \{\xi_{j-1} + \xi_{j-2}e^{-\gamma} + \ldots + \xi_j \exp[-(j-1)\gamma]\}[1-\exp(-j\gamma)]^{-1}\varepsilon^{-1}. \end{aligned} \tag{12}$$

Now, if we expand the exponential for γ small and retain the $O(\gamma)$ term, the next expression is obtained

$$\begin{aligned} x_1 &= \{\xi_j + \xi_{j-1}(1-\gamma) + \ldots + \xi_1[1-(j-1)\gamma]\}\sqrt{2}/j\gamma^{1/2} \\ x_j &= \{\xi_{j-1} + \xi_{j-2}(1-\gamma) + \ldots + \xi_j[1-(j-1)\gamma]\}\sqrt{2}/j\gamma^{1/2}. \end{aligned} \tag{13}$$

Then in the limit $\gamma \to 0$ we obtain the following expressions for x

$$Z(x_1 + x_2 + \ldots + x_k) = \hat{Z}_k(\xi_1 + \xi_2 + \ldots + \xi_k)\sqrt{2}/j \tag{14}$$

where

$$\hat{Z} = \mathrm{i}\sqrt{\hat{\nu}}.$$

The above equation is valid for any k, which verified $0 \leqslant k \leqslant N$. Then we obtain for the trace, in the long-range limit, the expression

$$\lim \gamma \to 0(\gamma\sigma_N^{(>)}) = (2\pi)^{-N/2}N^{-1}\sum_{k=0}^{N}\lambda^k C_k\left(\int_{\infty}^{\infty}\exp[\mathrm{i}\sqrt{\hat{\nu}}(k/N)\xi]\exp(-\xi^2/2)\,\mathrm{d}\xi\right)^N \tag{15}$$

where C_k represents the number of ways to take k elements of N. In the derivation of (15) we take into account that the Jacobian is given by

$$\mathbb{J}_j = (2\pi)^{-j/2}/j\gamma \qquad \text{for } \gamma \text{ small.} \tag{16}$$

Solving the integral for ξ, we find

$$\lim \gamma \to 0(\gamma\sigma_N^{(>)}) = N^{-1}\sum_{k}^{N}\lambda^k C_k \exp(-\hat{\nu}k^2/N) \tag{17}$$

and this expression is valid for any value of N. Remember that the computation of trace is related to the maximum eigenvalue of the integral equation given by (3), through the relation:

$$\lim_{N\to\infty}(\delta_N)^{-1/N} = E_0^{-1} \tag{18}$$

where $\delta_N = \lim_{\gamma\to 0}(\gamma\sigma_N)$.

These relations, justified by Newman [2], facilitate the computation of the trace by interchanging the thermodynamic limit and the weak long-range limit.

If we repeat the above development, but for $K^{(<)}(x, y)$, it is not difficult to show that an equivalent expression for the trace is found:

$$\lim \gamma \to 0(\gamma\sigma_N^{(<)}) = N^{-1}\sum_{k}^{N}\lambda^k C_k \exp(\hat{\nu}k^2/N). \tag{19}$$

If we compare (17) for the trace of $K^{(>)}(x, y)$ and (19) for the trace of $K^{(<)}(x, y)$, we see that it is possible to obtain $\delta_N^{(<)}$ from $\delta_N^{(>)}$ making the substitution $\hat{\nu} \to \hat{\nu}$ for any value of N in the long-range limit.

With the above result, we can now reason heuristically as follows: we can obtain $\sigma_N^{(>)}$ from $\sigma_N^{(<)}$ in a straightforward form making the substitution $\hat{\nu} \to -\hat{\nu}$. As this change does not depend on the value of N, we hope that the result will be valid for $N \to \infty$. However, in the thermodynamic limit, if we use the relation

$$\lim N \to \infty (\delta_N)^{1/N} = E_0 \tag{20}$$

where $\delta_N = \lim \gamma \to 0 (\gamma \sigma_N)$. We can obtain the maximum eigenvalue $E_0^{(>)}$ for $K^{(>)}(x, y)$ from the maximum eigenvalue $E_0^{(<)}$ for $K^{(<)}(x, y)$, making the substitution $\hat{\nu} \to -\hat{\nu}$.

It is known [3] that, in this limit, the maximum eigenvalue is given by

$$\lim_{\gamma \to 0} \ln E_0^{(<)} = \ln(1 + \lambda\ \mathrm{e}^{\eta}) - \frac{\eta^2}{4\hat{\nu}} \qquad \eta = (\mu + \hat{\nu}) \tag{21}$$

as μ is a solution of

$$\mu = \hat{\nu} \frac{(\lambda\ \mathrm{e}^{\eta} - 1)}{(\lambda\ \mathrm{e}^{\eta} + 1)}. \tag{22}$$

Then $E_0^{(>)}$, the maximum eigenvalue for $K^{(>)}(x, y)$, is given by

$$\lim_{\gamma \to 0} \ln E_0^{(>)} = \ln(1 + \lambda\ \mathrm{e}^{\eta}) + \frac{\eta^2}{4\hat{\nu}} \qquad \eta = (\mu - \hat{\nu}) \tag{23}$$

as μ is a solution of

$$\mu = \hat{\nu} \frac{(1 - \lambda\ \mathrm{e}^{\eta})}{(1 + \lambda\ \mathrm{e}^{\eta})}. \tag{24}$$

Using the maximum eigenvalue, as is given by (23), we can obtain one analytic expression of the equation of state when the pair potential interaction is repulsive, computing the next relation (where the prime denotes differentiation with respect to λ, the activity):

$$\rho = \lambda E_0'^{(>)} = (1 + \lambda^{-1}\ \mathrm{e}^{-\eta})$$

and, by (24) eliminating λ and μ, we can find for p

$$\beta p = \beta \alpha \rho^2 - \ln(1 - \rho).$$

This expression will be compared with the one obtained by Kac [4] for the single phase region in the limit $\gamma \to 0$. It is not difficult to see that in this case there is no transition phase, since for any value of the fugacity, there are two equal minima, as can be seen in (24). In consequence p is a monotone non-decreasing function of the density.

We pause here to make a brief comment about the biophysical application of this lattice gas model with a pair repulsive potential. It is known that certain biopolymers in solution show a typical secondary structure, i.e. the Puling and Corey [9] α-helix. Each repeating unit (monomer) of this structure can appear charged or uncharged depending on environmental variables such as pH, ionic strength, etc. In particular, if all monomers are equal, then only the repulsive interaction (of Coulombic origin) between similarly charged monomers will appear. The incorporation of this electrostatic effect into a statistical mechanics model involves certain difficulties, i.e. the Coulombic interaction is long range in nature and is not easily taken into account in

an essentially nearest-neighbour model. However, we have been able to include this effect in a theoretical model which is based on two hypotheses.

(a) A one-dimensional α-helix representation is assumed.

(b) The repulsive interaction between similarly charged monomers are taken into account in the grand partition function through a repulsive Kac type potential.

Through hypothesis (a) we can see the above-mentioned processes, i.e. the equilibrium between charged and uncharged monomers, as a one-dimensional lattice gas.

Through hypothesis (b), we introduce a long-range interaction which is characteristic of Coulombic interaction i.e. evaluating the grand partition function in the limit $\gamma \to 0$.

The analytic solution of the above theoretical model is given by (23). Through its application we have been able to prove that, if we take into account two essential aspects of the Coulombic interaction in homobiopolymers, i.e. repulsive and long range, even omitting the real structure of the interaction potential, we can find analytical information free of fitting parameters [6].

Furthermore, we have been able to show that the study of more complex phenomena, such as the helix-coil transitions induced by pH change, can be explained if we use (23) as a statistical weight to take into account the Coulombic origin contribution to the grand partition function [7]. It is important to point out that in both cases we obtain good agreement between theoretical and experimental data.

3. Properties of the non-Hermitian kernel for γ small

If we are interested in studying the eigenvalue problem to the lowest order in γ it is known [8] that equation (3) can be reduced to the study of the following differential equation (where the prime denotes differentiation with respect to x)

$$\psi'' + (\tilde{E} - q(x))\psi = 0 \tag{25}$$

where we put

$$E^{(<)} = \exp[\gamma(\tfrac{1}{2} - \tilde{E})] \tag{26}$$

and

$$\gamma q(x) = \tfrac{1}{4}\gamma x^2 - \ln\{1 + \lambda \exp[(\hat{\nu}\gamma)^{1/2}x]\}, \tag{27}$$

If we want to go beyond the lowest order in γ, one must use the Baker-Hausdorf formula [4] or follow a perturbation technique similar to that used by Kac *et al* [3].

On the other hand, if we choose the repulsive potential ($\alpha < 0$) the non-Hermitian kernel $K^{(>)}(x, y)$ given by (5) replaces $K^{(<)}(x, y)$ in the integral equation given by (3). In this case, the problem to solve, to the lowest order in γ, is

$$-\psi'' + (q(\mathrm{i}x) - \xi)\psi = 0 \tag{28}$$

where

$$E^{(>)} = \exp[\gamma(\tfrac{1}{2} - \xi)] \tag{29}$$

and

$$\gamma q(\mathrm{i}x) = \tfrac{1}{4}\gamma x^2 - \ln\{1 + \lambda \exp[\mathrm{i}(\hat{\nu}\gamma)^{1/2}x]\}. \tag{30}$$

Equation (28) can be seen as a function $F(\psi, q(\mathrm{i}x), \xi)$ which verified

$$F(\psi, q(\mathrm{i}x), \xi) = 0 \tag{31}$$

over all the points in the imaginary axis. Then take into account that $q(ix)$ is an analytic function of x for γ small, $0<\lambda\neq 1$ and for any value of $\hat{\nu}$, even at $\hat{\nu}=0$, and if we assume that ψ is analytic, we can easily prove (using the analytic prolongation theorem) that the (31) verifies

$$F(\tilde{\psi}, q(x), \xi^*)=0 \tag{32}$$

over all the points in the real axis. Naturally, we can see equation (32) as

$$-\tilde{\psi}''+(q(x)-\xi^*)\tilde{\psi}=0 \tag{33}$$

where now

$$\gamma q(x)=\tfrac{1}{4}\gamma x^2+\ln\{1+\lambda\ \exp[(\hat{\nu}\gamma)^{1/2}x]\} \tag{34}$$

and

$$\xi^*=-\xi. \tag{35}$$

It follows that, to order γ, the maximum eigenvalue is given by

$$\ln E_0^{(>)}=q_{\min}+O(\gamma) \tag{36}$$

with

$$q_{\min}=\ln(1+\lambda\ e^{\eta})+\eta^2/4\hat{\nu}$$

with η given by (24).

Since the function $q(x)$ possesses a unique minimum, independent of the value of the $\hat{\nu}$ parameter, and take into account that (33) possesses analytic eigenstates and eigenvalues, by the analytic prolongation theorem, we can conjecture that the non-Hermitian kernel could be expanded as

$$K^{(>)}(x, y)=\sum_{i=1}^{\infty}\xi_i\psi_i(x)\psi_i(y)$$

for small but non-zero γ.

So far we have assumed γ small but we have said nothing about the validity of the analytic continuation when γ vanishes. If we compare the maximum eigenvalue obtained through the above analysis with the one obtained in the preceding section, i.e. for $\gamma\to 0$, we find a suggestive resemblance between them. However, rigorous proof that the spanning properties for the non-Hermitian kernel persist, or not, in $\gamma=0$ would represent some of the mathematical difficulties still to be overcome, and furthermore an essential link between our intuition and the facts.

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