Information-theory-based solution of the inverse problem in classical statistical mechanics

Marco D'Alessandro and Francesco Cilloco
Institute for Complex Systems, National Research Council (CNR), Via del Fosso del Cavaliere 100, 00133 Rome, Italy
(Received 16 June 2010; published 30 August 2010)

We present a procedure for the determination of the interaction potential from the knowledge of the radial pair distribution function. The method, realized inside an inverse Monte Carlo simulation scheme, is based on the application of the maximum entropy principle of information theory and the interaction potential emerges as the asymptotic expression of the transition probability. Results obtained for high density monoatomic fluids are very satisfactory and provide an accurate extraction of the potential, despite a modest computational effort.

DOI: 10.1103/PhysRevE.82.021128 PACS number(s): 05.20.−y, 89.70.Cf, 61.20.Ja

I. INTRODUCTION

This paper deals with the "inverse problem" in classical statistical mechanics. Namely, we are interested in determining the interaction potential of a system from the knowledge of its radial distribution function (RDF). A basic result due to Henderson [1] states that if a system is governed by pairwise additive interactions then two potentials which give rise to the same RDF cannot be different more than a constant term. This theorem provides a theoretical support to the formulation of the inverse problem since it demonstrates the uniqueness of its solution. However, the existence of the solution is not guaranteed and furthermore the theorem does not indicate a way to find it.

Despite this general result, the solution of the inverse problem for a classical dense fluid turns out to be a difficult task to achieve. This is due mainly to the fact that in the high density regime the RDF is hardly sensitive to the detailed shape of the interaction potential and is essentially determined by its repulsive part; so the inverse functional relationship between the RDF and the interaction potential evidences a strong dependence of the latter on the input RDF. In order to expect a reliable solution of the inverse problem not only the input RDF must be provided with high precision but also the underlying theory used to formulate the inversion procedure must be very accurate. As stated by Reatto in [2] the accuracy of a satisfactory inversion scheme has be to independent both from the shape of the interaction potential and from the density of the system under inspection. If these properties are fulfilled then the interaction potentials of different systems can be consistently compared, furthermore any dependencies of the extracted potential on the thermodynamic state can be unambiguously ascribed to the effects of many-body interactions.

A generally accepted scheme for the solution of the inverse problem which fulfills these features is still lacking and, in the last three decades, several authors have proposed different approaches. A first category comprises theoretically based attempts in which the inversion scheme is defined on the basis of an integral equation theory (HNC, MHNC, etc.) of the liquid state. These pure theoretical approaches typically rely on some approximation and, due to the intrinsic difficulties depicted above, their application provides reliable results only in a limited set of cases. A considerable improvement in the accuracy of the extracted potentials has been obtained by recurring to simulation assisted procedures. These methods attempt to determine the pair interaction starting from a guessed expression of the potential which is iteratively modified on the basis of the discrepancy between the simulated pair function and the experimental data. A first result in this direction has been proposed by Schommers in [3] and later on further improvements have been achieved by Reatto, Levesque and Weiss in [4]; in this paper, the authors applied the predictor-corrector scheme, using the MHNC equation as predictor, to the Lennard-Jones fluid and to a model potential for aluminum. The convergence of the iterative potential to the correct result was found and it was checked that the use of a less accurate predictor (for example the one proposed in [3]) for the definition of the trial potential could spoil the accuracy of the procedure. Other results belonging to this class of inversion procedures comprise the empiric potential structure refinement (EPSR) proposed by Soper [5,6] and a solution due to Lyubartsev and Laaksonen [7]. The former technique performs the refinement of a reference potential using a perturbation term given by the difference between the experimental and the simulated structure factor; the latter propose a parametric dependence of the potential on a set of parameters which are determined by solving a large system of linear equations.

A further approach to the inverse problem is provided by a family of "stochastic" inversion methods in which the solution is sought as the expected value of properly extracted random variables (inverse Monte Carlo). In this simulation scheme, given the input RDF, a dynamical evolution law is defined with the aim to build a set of configurations compatible with the experimental data. So the solution of the inverse problem is brought back to the determination of a suitable transition probability which produces a "Monte-Carlo-like" dynamic. Among the various attempts in this direction we mention the reverse Monte Carlo (RMC) technique due to McGreevy and Pusztai [8] and two "absolute minimization" methods proposed by Cilloco in [9] and later on by da Silva, Svensson, Åkesson and Jönsson in [10]. Strictly speaking these methods do not provide a solution of the inverse problem since they do not allow the direct determination of the interaction potential, however the configurations produced in the inverse Monte Carlo procedure can be used to compute quantity of physical interest. It is worth mentioning that results reported in [9] represent the first application of the maximum entropy principle, indicating a possible solution based on the measurement of the three body correlation func-

tion. A further contribution is due to a technique proposed by Almarza, Lomba, and Molina [11,12] where a direct solution of the inverse problem has been obtained by performing a continuum refinement procedure of a trial interaction potential.

The purpose of this paper is to present a technique for the solution of the inverse problem based on the maximum entropy principle (ME) [13]. ME is an effective tool for setting up the equilibrium distribution of a statistical system on the basis of partial knowledge and the corresponding estimate fulfills the remarkable property of being the "maximally noncommittal with regard to the missing information." So, our solution of the inverse problem is based on the maximization of the configurational entropy constrained by the information codified in the radial pair distribution function. The procedure is realized inside an inverse Monte Carlo scheme and the interaction potential emerges as the asymptotic expression of the transition probability.

The contents of the paper are as follows. Section II contains a description of our method, in Sec. III we test the method in the case of a Lennard-Jones fluid and for a model of liquid aluminum. Finally in Sec. IV we discuss our results and present some final remarks.

II. THEORY

A. Statistical description of a monoatomic system

We perform a statistical analysis of a simple monoatomic system with the aim to define some quantities that will be of central interest later on in the paper. Particular emphasis will be given to the concepts of probability, likelihood, entropy, and to their mutual relationship.

Consider an homogenous and isotropic system composed of pointlike elements with average density ρ. In the following we will refer to this system as the *model*. Given an arbitrary configuration $\mathbf{x}$ of the model we can perform a local sampling of the elements pair function (PF). This means that we select a reference element and divide the space in spherical shells of width δr centered on it up to the maximum value r_M [14]; then we count the number of elements in each shell and we store these numbers in the array n_i, where $i=1,\ldots,J$.

We define a probability function $p(\mathbf{x})$ over the configuration space of the model system and collect an ensemble of s configurations extracted according to $p(\mathbf{x})$. The global sampling of the PF over the ensemble can be computed by evaluating the n_i for each configuration α and summing these local samplings shell by shell, that is

$$m_i \doteq \sum_{\alpha=1}^{s} n_i^{(\alpha)}. \tag{1}$$

Assuming that the expected PF is given by a reference function μ_i we can evaluate the probability associated to the global sampling [Eq. (1)]. Let us focus on a fixed shell k. The values of n_k obtained in two different configurations are uncorrelated and, admitting that the number of shells is large enough, the probability of finding more than one element in a single measurement can be neglected; so the shell k follows a Poisson distribution with expected value $s\mu_k$. Since there is no correlation between different shells we obtain

$$\mathcal{P}_\mu(m) = \prod_{i=1}^{J} e^{-s\mu_i} \frac{(s\mu_i)^{m_i}}{m_i!} \tag{2}$$

so the probability associated to m is given by a product of Poisson distributions. This formula describes an "open system," which can be realized as an open subset of a larger one, and elements fluctuations are possible. Conversely, if we are dealing with a closed system in which each configuration of the ensemble satisfies the further constraint,

$$\sum_{i=1}^{J} n_i = \sum_{i=1}^{J} \mu_i = N_p \tag{3}$$

the total number of elements is conserved and the probability [Eq. (2)] is reduced to a multinomial expression (see [15] and references therein):

$$\mathcal{M}_q(m) = \frac{\mathcal{P}_\mu(m)}{P(\sum_i n_i = N_p)} = N! \prod_{i=1}^{J} \frac{q_i^{m_i}}{m_i!}, \tag{4}$$

where $N \doteq sN_p$ and $q_i = \mu_i / N_p$ is the normalized reference probability distribution. Equations (2) and (4) can be interpreted as likelihood functions $\mathcal{L}(m,\mu)$ of the expected PF given the observed values m. If the number of configurations in the ensemble is very large ($s \gg 1$ which implies N, $m_i \gg 1$) we can take the logarithm of $\mathcal{L}$ and make use of the Stirling approximation up to the linear order, this gives

$$\ln \mathcal{L}_\mathcal{P}(m,\mu) \simeq -\sum_i m_i \ln \frac{m_i}{s\mu_i} + \sum_i (m_i - s\mu_i),$$

$$\ln \mathcal{L}_\mathcal{M}(m,\mu) \simeq -\sum_i m_i \ln \frac{m_i}{Nq_i}, \tag{5}$$

the two formula in Eq. (5) differ for a linear term which accounts for the fluctuations of elements.

The log-likelihood Eqs. (5) possess a nice interpretation when the number of configurations becomes infinite. Let us focus on the multinomial likelihood given by the second line of Eq. (5); in the asymptotic limit the average PF converges to the probability $p_i = m_i/N$ built over the ensemble and the likelihood can be written as

$$\lim_{s\to\infty} \frac{1}{s} \ln \mathcal{L}_\mathcal{M}(m,\mu) \simeq -N_p \sum_i p_i \ln \frac{p_i}{q_i} = -N_p D(p\,\|\,q), \tag{6}$$

we recognize that the log-likelihood is proportional to the relative entropy $D(p\|q)$ (Kullback-Leibler divergence [16]) of the ensemble distribution p with respect to the reference one. The relative entropy fulfills the properties of being positive definite and vanishing only if $p=q$. Equation (6) implies that if the global PF built over the model ensemble maximizes the likelihood with the reference function μ then, asymptotically, the distribution p minimizes the relative entropy respect to the reference probability q. We will make us of this property in the next section.

It is useful to rewrite Eq. (6) in term of radial distribution functions. The model RDF $g(r_i)$ and its reference counterpart $g_0(r_i)$ are defined by normalizing the ensemble average and the expected reference function μ by the average value of particle per shell, respectively. So we have

$$g(r_i) = \lim_{s\to\infty} \frac{1}{s} \frac{m_i}{4\pi\rho r_i^2 \delta r} \quad g_0(r_i) = \frac{\mu_i}{4\pi\rho r_i^2 \delta r} \tag{7}$$

Plugging Eq. (7) in Eq. (6) and passing to the continuum limit provides an expression for the relative entropy that will be widely used in the following:

$$K_{\mathcal{M}}(g \parallel g_0) = \lim_{s\to\infty} \frac{1}{2s} \ln \mathcal{L}_{\mathcal{M}}(m,\mu) \simeq = -\frac{\rho}{2} \int d\mathbf{r} g(r) \ln \frac{g(r)}{g_0(r)}, \tag{8}$$

where the extra factor $\frac{1}{2}$ has been inserted to avoid a double counting of the number of independent distances between pairs of elements. The same analysis can be repeated starting from the first line of Eq. (5); performing the asymptotic limit and recasting the result in term of RDFs gives

$$K_{\mathcal{P}}(g \parallel g_0) = \lim_{s\to\infty} \frac{1}{2s} \ln \mathcal{L}_{\mathcal{P}}(m,\mu) \simeq -\frac{\rho}{2} \int d\mathbf{r} \left\{ g(r) \ln \frac{g(r)}{g_0(r)} - [g(r) - g_0(r)] \right\}, \tag{9}$$

which provides the relative entropy between the RDFs when elements fluctuations are taken into account.

A last comment regards the meaning of this construction when a uniform reference distribution $q_i = 1/J$ is employed. In this case Eq. (4) provides the number of occurrences of the global PF Eq. (1) up to a constant factor and the relative entropy $D(p\|q)$ reduces to the Shannon entropy [17] up to an additive constant. Expressing this condition in terms of RDFs supplies the measurement of the relative entropies [Eqs. (8) and (9)] respect to the "noninformative" reference system $g_0 \equiv 1$,

$$S_{\mathcal{M}}^{(2)} = K_{\mathcal{M}}(g \parallel 1) \quad S_{\mathcal{P}}^{(2)} = K_{\mathcal{P}}(g \parallel 1) \tag{10}$$

exploiting Eqs. (8) and (9) we recognize that the entropies [Eq. (10)] exactly reproduce the two-body contribution to the Boltzmann entropy expansion in the canonical ensemble [18] and in the grand canonical ensemble [19,20], respectively.

B. Maximum entropy solution of the inverse problem

We consider a monoatomic system whose interactions are governed by a genuine pairwise additive potential $\phi(r)$ and assume that for a given condition of temperature T and density ρ the RDF of the system $g_0(r)$ is known. We refer to this system as the *target*. The interaction potential of the system is supposed to be unknown, only the RDF is given.

We propose a solution of the inverse problem based on the maximum entropy principle [13] constrained by the information encoded in the RDF of the target system. Namely we build a probability distribution p in the model system which fulfills the properties of maximizing the Shannon entropy consistently with the condition of vanishing relative entropy with respect to $g_0(r)$,

$$K(g \parallel g_0) = 0, \tag{11}$$

where the model RDF $g(r)$ is obtained by averaging the global PF [Eq. (1)] over an ensemble of configuration extracted according to p. Formally this task is achieved by computing the maximum of the functional,

$$\mathcal{F}\{p\} = S\{p\} + \alpha K(g\{p\} \parallel g_0), \tag{12}$$

where $S\{p\}$ is the Shannon entropy,

$$S\{p\} = -\sum_n p_n \ln p_n \tag{13}$$

and α is a Lagrange multiplier. The stationary point of Eq. (12) provides the equilibrium distribution constrained by the target RDF and we will show that the knowledge of this function allows to introduce a notion of interaction potential in the model system. This quantity will be identified with the target potential thus providing a solution of the inverse problem.

1. Low density solution

In the low density limit the general strategy previously described can be easily carried out. In order to evaluate the stationary point of the functional (12), we perform an expansion of the Shannon entropy in correlation functions. Leaving aside the ideal-gas contribution which does not depend on the configurational degrees of freedom we have

$$S\{p\} = \sum_{n\geq 2} S^{(n)}. \tag{14}$$

Formula (14) provides an expansion of the excess entropy organized in powers of the density and in the low density limit the whole series is dominated by the two-body contribution $S^{(2)}$.

The solution of the inverse problem is straightforward and proceeds in two steps. First of all we maximize the two-body Shannon entropy assuming that the dynamics in the model system is governed by an (unknown) pairwise additive potential $\phi_m(r)$. For pairwise additive interactions the configurational part of the internal energy can be expressed as

$$U = \frac{\rho}{2} \int d\mathbf{r} g(r) \phi_m(r) \tag{15}$$

so the ME estimate of the two-body entropy functional subjected to the average value of the internal energy is given by the stationary configuration of the functional,

$$\mathcal{F}\{g\} = S_{\mathcal{P}}^{(2)} + \alpha \left[\frac{\rho}{2} \int d\mathbf{r} g(r) \phi_m(r) - U \right] \tag{16}$$

maximizing [Eq. (16)] and imposing the constraint [Eq. (15)] together with the thermodynamic relation $\beta = \partial S / \partial U$ provides the solution,

$$g(r) = e^{-\beta\phi_m(r)}, \tag{17}$$

which is the ME estimate of the two-body equilibrium distribution for a system with pairwise interactions [21]. We recognize the first order contribution in the cluster expansion of the RDF.

The second step is realized by imposing Eq. (11) which allows to evaluate the ME estimate of the interaction potential $\phi_m(r)$ constrained by the target RDF. Since the vanishing of the relative entropy implies the equality of the two RDFs we obtain

$$\beta\phi_m(r) = -\ln g_0(r), \tag{18}$$

which is the ME solution of the inverse problem at low density.

2. High density solution: A Monte Carlo approach

The correlators expansion of the excess entropy [Eq. (14)] for a high density system contains, apart from the two-body contribution, all higher order terms. Since these quantities are unknown a direct maximization procedure of the excess entropy, like the one performed in the low density limit, is unfeasible. However, if the interaction potential is pairwise additive, the RDF still codifies all the information needed to the solution of the inverse problem. This is a direct consequence of the Henderson theorem [1]: the RDF determines the interaction potential up to a constant, so its knowledge sets the whole configurational part of the phase space distribution function and all the higher order terms in the entropy expansion are theoretically determined if the two-body contribution is given. Anyhow, since the explicit computation of these terms would require the knowledge of the interaction potential, a direct maximization procedure cannot be performed and a different approach has to be adopted.

The general strategy to achieve the entropy maximization is to recur to a "Monte-Carlo-like" (MC) approach in which the configuration space of the model system is sampled along a random path. So, as in the standard Metropolis-Monte Carlo (MMC) algorithm, the dynamical evolution of the system is defined by introducing a notion of trial configurations and a transition probability between neighbor states. We shall see that the stochastic nature of the MC dynamics together with a suitable choice of the transition probability will allow to generate a path in the configuration space of the model system which maximizes the excess entropy [Eq. (13)] consistently with the relative entropy constraint [Eq. (11)].

Let us define the building blocks of this procedure. Assume that we have performed s MC iterations. For each point of the path we compute a local sampling of the PF and sum up these measurements in the global pair function (1). Then we select a reference particle and compute a local sampling of the PF $n^{(1)}$, at the same time the particle is randomly moved and the new local sampling of the PF is stored in the array $n^{(2)}$. This procedure provides two different samplings of the global PF at the level $s+1$,

$$m^{(1)} = m + n^{(1)} \quad m^{(2)} = m + n^{(2)} \tag{19}$$

the trial configuration $m^{(2)}$ is accepted with a probability

$$P_{m^{(1)}\to m^{(2)}} = \min[1, f(m^{(1)}, m^{(2)})], \tag{20}$$

where f is the transition probability which determines the stochastic evolution law. The iteration of this procedure allows to generate the whole ensemble of configurations of the model system.

Now we impose the constraint [Eq. (11)]. To achieve this task we define the transition probability by the requirement that the global PF Eq. (1) built along the path maximizes the likelihood function (5) with the reference pair function μ, defined in term of the target RDF via the relation,

$$\mu_i = 4\pi\rho r_i^2 g_0(r_i)\,\delta r \tag{21}$$

If we are able to impose this condition then Eqs. (6) guarantees that, asymptotically, the relative entropy between the model and target RDFs vanishes and the constraint [Eq. (11)] is satisfied. For this purpose we try to guess a formula for the transition probability written in term of a likelihood ratio,

$$f = e^{-\delta\lambda}, \quad \text{where} \quad \delta\lambda = \ln\frac{\mathcal{L}(m^{(1)}, \mu)}{\mathcal{L}(m^{(2)}, \mu)} \tag{22}$$

so trial samples with a likelihood higher than $m^{(1)}$ are automatically accepted, otherwise they are accepted with a probability given by f. For $s \gg 1$ we can make use of the Stirling approximation (5) for the log-likelihood terms in Eq. (22). Moreover, since the n_i are of order 1 while the m_i are of order s we can expand in power of s the logarithms appearing in Eq. (5). Performing this approximation to the first order in $1/s$ provides

$$\delta\lambda = \sum_{i=1}^{J} (n_i^{(2)} - n_i^{(1)}) \ln\frac{m_i}{s\mu_i}, \tag{23}$$

this formula can be obtained starting from both the expressions for the log-likelihood given in Eq. (5), so the transition probability [Eq. (23)] turns out to be invariant respect to the boundary condition imposed in the model system.

Equation (23) computes the difference among $n^{(1)}$ and $n^{(2)}$ weighting each shell with a term

$$e_i^{(s)} = \ln\frac{m_i}{s\mu_i} \tag{24}$$

that represents the "error" after s iterations between the reference and the measured values of the global PF. So $\delta\lambda$ realizes a feedback in the model system, since it behaves as a controller which selects the configurations in the model ensemble on the basis of the error [Eq. (24)]. This controller operates only by considering the error in actual state s and, adopting the common language of the feedback control systems [22], we will call this quantity a "proportional" controller.

The transition probability [Eq. (23)], realized as a proportional controller, suffers of a difficulty which is commonly encountered in many feedback controlled systems whenever the controller is realized only through a proportional term: the presence of an offset between the measured process variable and the target reference function. Indeed a MC simulation built with this transition probability produces a model

RDF which is a "biased" reconstruction of the target one, so the formula guessed for $\delta\lambda$ turns out to be inadeguate to enforce a complete maximization of the likelihood function $\mathcal{L}(m,\mu)$. A possible solution of this problem can be accomplished by realizing the control mechanism as a proportional-integral controller (PI) [22]. So we propose a modified expression for $\delta\lambda$ given by

$$\delta\lambda = \sum_{i=1}^{J} (n_i^{(2)} - n_i^{(1)}) u_i^{(s)} \tag{25}$$

where u_i is a function of the error [Eq. (24)] which depends on three different contributions: a proportional term that determines the reaction to the current error, an integral term which keeps into account the sum of all the former ones and a background value which allows to include *a priori* knowledge on the system. The output of the PI is given by a weighted sum of these three quantities,

$$u_i^{(s)} = k_p^{(s)} e_i^{(s)} + \sum_{\alpha=1}^{s} k_I^{(\alpha)} e_i^{(\alpha)} + u_i^{(0)}, \tag{26}$$

where k_p and k_I are the (s dependent) coefficients of the proportional and of the integral terms.

A transition probability defined in term of the PI [Eq. (26)] ensures that the model RDF converges to its reference value. Furthermore the implementation of this controller allows one to define an interaction potential in the model system. In fact, as long as the measured PF converges to its reference value, the error [Eq. (24)] goes to zero. In this limit the proportional term of [Eq. (26)] becomes negligible and the integral approaches to a constant finite value. Formally we can define the model potential as the asymptotic limit of PI controller ($\beta \equiv 1/k_B T$),

$$\beta\phi_m(r_i) = \lim_{s\to\infty} u_i^{(s)} = \sum_{\alpha=1}^{\infty} k_I^{(\alpha)} e_i^{(\alpha)} + u_i^{(0)}. \tag{27}$$

So the MC dynamics built with the PI control system behaves as a constructive tool for the computation of the model potential. During a MC simulation the model system is subjected to a transient dynamical phase in which the transition probability evolves during the path; as long as the path proceeds the PI *builds* the model potential [Eq. (27)] and the transition probability approaches to a stationary regime. Once the equilibrium has been reached the system evolves according to a stationary transition probability and behaves as a Markov chain, in which the potential is given by Eq. (27).

3. Computation of the PI coefficients

Let us come back to the issue of the correct definition of the coefficients k_p and k_I. Usually the PI parameters are tuned with the aim to ensure a fast and stable convergence of the measured process variable to its reference value. In this case we propose a criterium, for fixing these parameters, which comes again from statistical considerations. We observe that if the model system is sampled with the expected distribution [Eq. (2)], the global PF approaches to $s\mu_i$ as long as s increases. So we introduce the reduced variables x_i defined by

$$\frac{m_i}{s\mu_i} = 1 + \frac{m_i - s\mu_i}{s\mu_i} = 1 + x_i \tag{28}$$

and we expand the distribution function (2) in series around $x_i=0$. Performing this expansion together with the usual Stirling approximation provides

$$\mathcal{P}_\mu(m) \simeq \prod_{i=1}^{J} \frac{1}{\sqrt{2\pi s\mu_i}} e^{-(1/2)((m_i - s\mu_i)^2/s\mu_i)} \tag{29}$$

so for large values of s the global PF is distributed according to a product of J Gaussian distributions [23]. Since the reduced variables x_i are distributed according to a standard normal distribution, the variable defined as

$$\chi^2_{(s)} \doteq \frac{1}{J}\sum_{i=1}^{J} \frac{(m_i - s\mu_i)^2}{s\mu_i} \tag{30}$$

follows a χ-square distribution with J degrees of freedom.

So we define the PI coefficients in order to implement the condition $\chi^2=1$. Enforcing this condition in the model system guarantees that the global PF has the correct fluctuation around its average value and excludes spurious correlation among different shells. This can be done by introducing a new PI which performs a dynamic control on the coefficients k_p and k_I, so we set

$$k_p^{(s)} = c_1(\chi^2_{(s)} - 1) + c_2 \sum_{\alpha=1}^{s} (\chi^2_{(\alpha)} - 1),$$

$$k_I^{(s)} = d_1(\chi^2_{(s)} - 1) + d_2 \sum_{\alpha=1}^{s} (\chi^2_{(\alpha)} - 1), \tag{31}$$

where c_1, c_2, d_1, d_2 are the PI parameters. Further details concerning the implementation of this control mechanism will be given in Sec. III.

III. APPLICATIONS

In order to illustrate the features of the technique here proposed we have solved two systems which have been widely analyzed in the literature concerning the inversion methods [4,11]: a simple Lennard-Jones fluid and a model for liquid aluminum [24].

We briefly describe the general strategy adopted in the analysis of both systems. The target RDF has been evaluated recurring to a MMC simulation in the NVT ensemble. The configuration space of the target system is a cubic volume of linear length L with N_p pointlike particle and the periodic boundary conditions together with the minimum image convention have been adopted. The target potential $\phi(r)$ is truncated at $L/2$ and the system evolves starting from an FCC lattice; after about 5×10^2 MMC steps the energy of the system approaches to a constant value and the system evolves around equilibrium. Once at equilibrium a local sampling of the PF is performed for each configuration and the

average value of μ is built, then the target $g(r)$ is computed. Due to the minimum image convention this method provides a reliable RDF up to the edge value $r_M = L/2$. The error on the target RDF can be estimated by dividing the whole simulation in blocks and by computing the standard deviation $\delta g(r)$ between the blocks.

Once the $g(r)$ has been computed the inverse procedure for the determination of the pair potential described in Sec. II can be applied. The model system is realized exactly as the target one, so the configuration spaces of the two systems are identical. The PI coefficients are dynamically defined by Eqs. (31) which ensure the correct equilibrium fluctuation of the model RDF. A direct analysis of the system response evidences that an optimal choice of the parameters appearing in Eq. (31) is given by

$$k_p^{(s)} = (\chi_{(s)}^2 - 1) + 1 \times 10^{-3} \sum_{\alpha=1}^{s} (\chi_{(\alpha)}^2 - 1),$$

$$k_I^{(s)} = 5 \times 10^{-3} k_p^{(s)}, \tag{32}$$

where the ratio between k_p and k_I has been set to a constant value. This choice guarantees a smooth convergence of the measured PF to the target reference value. It is worth noting that performing a different choice (inside a range of values which does not produce an oscillating behavior) has only the effect of changing the rate of convergence of the model system but does not affect the convergence value. Furthermore, the same set of parameters given by Eq. (32) have been used both in the analysis of the Lennard-Jones fluid and of the liquid aluminum, providing an equally good convergence independently of the details of the system.

We observe that the target RDF of both the systems under inspection exhibits a hard core structure, i.e., $g(r)=0$ for $r < r_0$. This information can be imposed in the model by introducing a hard sphere (HS) background potential, $u^{(0)}=\infty$ for $r < r_0$ and zero otherwise, which initializes the PI controller [Eq. (26)]. Due to this term any trial configuration containing particle at a distance lower than r_0 is automatically rejected. Consistently with the background potential, we choose an equilibrium HS configuration as the starting point for the MC path. Then the reverse procedure starts and the system evolves according to the transition probability [Eq. (25)]; after each iteration we compute the output of the PI [Eq. (26)] and the expression of the transition probability is updated. Since the RDF of the starting configuration is noticeably different from the reference value, the χ^2 is sensibly higher than 1 and the PI coefficients [Eq. (32)] grow very fast; this phase is characterized by a highly nonstationary dynamical evolution of the transition probability [Eq. (25)].

In order to improve the convergence of the model potential it is convenient to split the simulation into two phases. So, when the χ^2 has reached a value quite close to 1 the actual configuration and the final expression of the PI output are stored in a file and we stop the simulation. Then these quantities are used as input values for the background potential and for the initial configuration and we start the "refinement phase." Since the system is closer to equilibrium, the PI [Eq. (32)] works in a different regime with respect to the previous phase; so the system evolves smoothly to equilibrium and the transition probability approaches to its asymptotic value. This phase can be repeated many times in order to obtain a better refinement of the model potential.

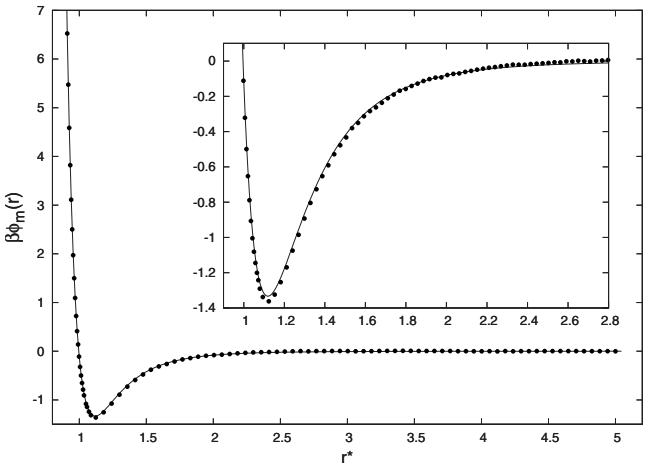

FIG. 1. Results for the Lennard-Jones system. The target potential (continuous line) and the model potential (filled circles) are plotted.

As a final check of the goodness of the results provided by this procedure we perform a standard MMC simulation using the model potential and we compare the corresponding RDF with the target one. If the difference of the two RDFs is not bigger than their intrinsical noise we conclude that the model potential [Eq. (27)] is equivalent to the target one and the reconstruction procedure stops; otherwise further refinement phases could be needed.

A. Lennard-Jones potential

The system is defined by a Lennard-Jones potential,

$$\phi_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{33}$$

with argonlike parameters $\sigma=3.405$ Å and $\epsilon/k_B T=119.76$. The MMC simulation for the determination of the target RDF is performed on a system of 864 particle at the reduced density $\rho^*=\rho\sigma^3=0.84$ and reduced temperature $T^*=k_B T/\epsilon=0.75$, near the triple point. The $g(r_i)$ has been evaluated up to $r^*=r/\sigma=5.0$ which corresponds to $L/2$; the width of the shells for the measure of the $g(r_i)$ was $\delta r=2.5\times10^{-2}$ Å and the number of measured points was 686. We performed 2×10^4 cycles after equilibration. The experimental error on the RDF was estimated by computing the standard deviation $\delta g(r_i)$ between 50 blocks of 4×10^2 cycles each. The largest value for $\delta g(r_i)$ was about 2×10^{-2} with an average value of 7×10^{-3}.

The complete inverse simulation procedure took 2.4×10^4 iteration. A first phase of 6×10^3 steps was performed starting from the FCC lattice and then the refinement phase was repeated three times for 6×10^3 steps each. The result for the interaction potential is reported in Fig. 1, the maximum difference between the model potential and the Lennard-Jones reference one was less than 5×10^{-2} with an

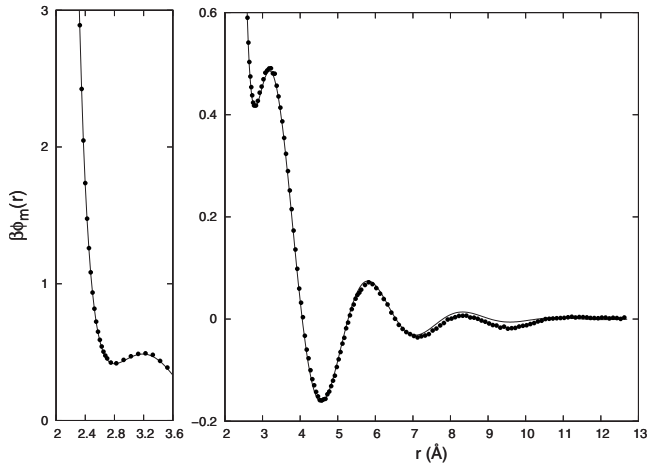

FIG. 2. Results for aluminum. The aluminum potential (continuous line) and the model potential (filled circles) are plotted.

average value of 1×10^{-2}. The average difference between the model and the target RDFs was equal to 4×10^{-3}; this value is inside the average noise of the RDF, so the model potential of Fig. 1 can be considered identical to the Lennard-Jones one.

B. Model potential of aluminum

The system is defined by a model potential for liquid aluminum [24]. The MMC simulation for the determination of the target RDF was performed on a system of 864 particle at the density $\rho=0.0527$ Å^{-3} and $T=1051$ K. The $g(r_i)$ has been evaluated up to $r=12.70$ Å which corresponds to $L/2$; the width of the shells for the measure of the $g(r_i)$ was $\delta r=2.5\times10^{-2}$ Å and the number of measured points was 508. We performed 2×10^4 cycles after equilibration. The experimental error on the RDF was estimated by computing the standard deviation $\delta g(r_i)$ between 50 blocks of 4×10^2 cycles each. The largest value for $\delta g(r_i)$ was about 2×10^{-2} with an average value of 6×10^{-3}.

The inverse simulation procedure took 2.6×10^4 iteration. A first phase of 6×10^3 steps was performed starting from the FCC lattice and then the refinement phase was repeated twice for 6×10^3 steps each and once for 8×10^3 steps. The result for the interaction potential is reported in Fig. 2, the maximum difference between the model potential and the Al model reference value was less than 2×10^{-2} with an average value of 7×10^{-3}. Even in this case the average difference between the model and the target RDFs is inside the typical noise of the RDF. Analyzing Fig. 2 we observe a difference between the target and model potential of the order of 1×10^{-2} in the range from 7 to 11 Å. This error is due to a correlated statistical fluctuation in the reconstruction procedure and can be further reduced by increasing the information content in the target RDF used as input.

IV. DISCUSSION AND CONCLUSIONS

The method presented so far supplies an accurate solution to the issue of determining the interaction potential from the radial distribution function. This technique bases its theoretical support on the maximum entropy principle of information theory which provides a general tool for the statistical inference on the basis of partial knowledge. The method is formally summarized by Eq. (12) which describes the maximization of the configurational entropy (S term) constrained by the information codified in the target system (K term). The ME solution is sought inside a Monte Carlo scheme where the maximization of configurational entropy is realized through the MC random displacements and the acceptance criterion for the trial configurations is built consistently with the physical input provided by the target RDF. The potential emerges as the asymptotic expression of the transition probability and, for pairwise potentials, it reproduces completely the interactions of the target system. This method fulfills some nice properties that, in our opinion, make it a valid tool for the extraction of potential. Actually the expression of the transition probability [Eq. (25)] is motivated only by the constraint [Eq. (11)] and does not rely on any ulterior hypothesis concerning the physical nature of the target system, so we expect that the general strategy depicted in the present paper could be of wide applicability. Nevertheless, the convergence of the model potential is ensured by a feedback control mechanism and the coefficients of [Eq. (26)] are tuned by an independent PI which operates a control on the fluctuation of the model RDF around the target reference value. This further controller avoids spurious correlations in the model RDF and guarantees that no information, besides the one codified in the target RDF, is transferred to the model during the simulation.

Results of Sec. III show that the extracted potential [Eq. (27)] accurately reproduces the original pair interaction both for the Lennard-Jones fluid and for the liquid aluminum model. A comparison between these results and the ones presented in [4,11] evidences a very satisfactory accuracy, despite a modest computational effort. This level of agreement turns out to be highly remarkable since the systems lie in the high density region of the state space where it is expected that the RDF should be quite insensitive to the details of the interaction; moreover the aluminum potential exhibits well defined oscillations even at short distances, where $\beta\phi(r)$ is still positive. As a further control we have verified that the method provides the correct results in a different region of the (ρ,T) plane; so the procedure described in Sec. III has been repeated for a Lennard-Jones fluid at $\rho^*=0.5$, $T^*=1$. As expected, the interaction potential approaches the correct result with a convergence rate even faster than in the high density case (about 1×10^4 steps were needed to obtain an accuracy comparable with the result of Fig. 1). This analysis indicates that our procedure for the solution of the inverse problem provides reliable results independently both from the density of the system and the shape of the potential under inspection, so it fulfills the requirements of a "satisfactory inversion scheme" as stated in [2].

The interpretation of the transition probability as a feedback controller represents a key point for the accomplishment of the solution discussed in the present paper. Actually, the adoption of this point of view motivates the introduction of the integral term and gives rise to the model interaction potential [Eq. (27)]. We want to point out that this is not the

only way to impose the constraint [Eq. (11)]. For example, the offset between the target reference function μ and the model global PF can be made null by using a proportional controller with an infinite value of the coefficient k_p. Pursuing this approach leads to the "pure minimization methods" [9,10] in which only trial configurations with a higher likelihood function (or with a lower χ^2 in the language of [10]) are accepted. The drawback of this approach is that, due to the lacking of the integral term, the interaction potential cannot be directly computed.

We conclude our discussion with some comments concerning the extension of this procedure to other systems than the simple monoatomic fluid analyzed in the present paper. The method is based on ME principle which holds for any system at equilibrium. For simple fluids a K term realized as the relative entropy (8,9) between the RDFs is able to constrain the whole configurational part of the probability distribution function in the model system. The information closed loop realized by the PI controller [Eq. (26)] then allows one to determine completely the interaction potential. Conversely, if we are dealing with more complex systems, that contain further degrees of freedom beside the position of the center of mass of the atoms, a ME solution is always possible, which will correspond to an effective potential. If, however, the complete target potential is sought, then it is necessary to match the relevant degrees of freedom of the systems with further involvement of information; for instance the experimental three body correlation function and the inclusion of higher order terms in the definition of K would be necessary if a three body interaction is present. As a final remark, we point out that this inversion technique has been discussed assuming that the RDF of the target system is given. However, since experimental data are expressed in term of the structure factor, a preliminary transformation to the real space RDF has to be performed in order to extract the interaction potential of a real system. This procedure may be hampered by the limited range of the structure factor or by the unsatisfactory k-resolution so, again, the use of the ME methods could reveal a useful tool to overcome those problems in optimal way.

ACKNOWLEDGMENT

The authors wish to thank Luciana Silvestri for the linguistic revision of the manuscript.

[1] R. L. Henderson, Phys. Lett. A **49**, 197 (1974).
[2] L. Reatto, Philos. Mag. A **58**, 37 (1988).
[3] W. Schommers, Phys. Rev. A **28**, 3599 (1983).
[4] L. Reatto, D. Levesque, and J. J. Weis, Phys. Rev. A **33**, 3451 (1986).
[5] A. K. Soper, J. Chem. Phys. **202**, 295 (1996).
[6] A. K. Soper, Mol. Phys. **99**, 1503 (2001).
[7] A. P. Lyubartsev and A. Laaksonen, Phys. Rev. E **52**, 3730 (1995).
[8] R. L. McGreevy and L. Pusztai, Mol. Simul. **1**, 359 (1988).
[9] F. Cilloco, J. Mol. Struct. **296**, 253 (1993).
[10] F. L. B. da Silva, B. Svensson, T. Akesson, and B. Jonsson, J. Chem. Phys. **109**, 2624 (1998).
[11] N. G. Almarza and E. Lomba, Phys. Rev. E **68**, 011202 (2003).
[12] N. G. Almarza, E. Lomba, and D. Molina, Phys. Rev. E **70**, 021203 (2004).
[13] E. T. Jaynes, Phys. Rev. **106**, 620 (1957).
[14] The configuration space of the system is assumed large enough so that for each of the sampled elements the sphere of radius r_M does not cross the boundary of the system.
[15] S. Baker and R. D. Cousins, Nucl. Instrum. Methods Phys. Res. **221**, 437 (1984).
[16] S. Kullback and R. A. Leibler, Ann. Math. Stat. **22**, 79 (1951).
[17] C. E. Shannon, Bell Syst. Tech. J. **27**, 379 (1948).
[18] H. S. Green, *The Molecular Theory of Fluids* (North-Holland, Amsterdam, 1952).
[19] R. E. Nettleton and M. S. Green, J. Chem. Phys. **29**, 1365 (1958).
[20] H. J. Raveché, J. Chem. Phys. **55**, 2242 (1971).
[21] We have used the two-body entropy expression given by Eq. (9); the same result can be obtained starting from the expression (8) but in this case a further Lagrange multiplier enforcing a normalization condition on $g(r)$ has to be introduced.
[22] A. Abramovici and J. Chapsky, *Feedback Control Systems: A Fast-Track Guide for Scientists and Engineers* (Springer, New York, 2000), p. 181.
[23] If we perform the same expansion starting from the multinomial distribution [Eq. (4)] we obtain a multivariate Gaussian distribution in which the correlations between different shells are imposed by the constraint [Eq. (3)]. However, in the asymptotic limit the off-diagonal elements of the covariance matrix become negligible and we obtain again the result (29).
[24] L. Dagens, M. Rasolt, and R. Taylor, Phys. Rev. B **11**, 2726 (1975).