Improved formulation of the effective-potential Monte Carlo method

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We show that the analytical result underlying the improved formulation of the effective-potential Monte Carlo method presented in a recent paper can be obtained in a simple way by resorting to the theory of Gaussian integrals.

A recent paper has been devoted to the investigation of an improved formulation of the effective-potential Monte Carlo (EPMC) method for three-dimensional crystals.[1] The main purpose of that paper was to describe an analytical and computational version of the effective-potential theory which is able to overcome some earlier formulations of it.[2–6] Remarking that the new formalism is very appealing from a computational point of view, the aim of this paper is to show that the analytical result underlying it can be obtained in a much simpler way by resorting to the theory of N-dimensional Gaussian integrals. In order to demonstrate this, we begin by recalling here the main features of the general formulation of the effective-potential theory for a three-dimensional crystal.[2–6] The method relies on a variationally approximated expression for the quantum partition function, which turns out to be written in a classical-like form through the employment of an effective potential. Therefore the method provides a tool for dealing with the quantum behavior of thermodynamic observables by means of the standard techniques of classical statistical mechanics, such as the Monte Carlo method, for example. The downside of this approach resides in the difficulties of the computational scheme for the evaluation of the effective potential. Some approximations must be introduced in order to make the calculations feasible. Within the so-called low coupling approximation (LCA),[7–9,2–6] which so far has been retained in all applications, the expression for the effective potential at a temperature $\beta=1/KT$ reads

$$V_{\rm eff}(\mathbf{x})=\widetilde{V}(\mathbf{x})-\sum_a \frac{m}{2}\alpha_a\omega_a^2+\frac{1}{\beta}\sum_a \ln\left(\frac{\sinh f_a}{f_a}\right), \quad (1)$$

where

$$\omega_a^2\delta_{ab}=\frac{1}{m}\sum_{ij} U_{ai}\frac{\partial^2\widetilde{V}}{\partial x_i\partial x_j}(\mathbf{x}_0)U_{bj}, \quad (2)$$

$$\alpha_a=\frac{\hbar}{2m\omega_a}\left(\coth f_a-\frac{1}{f_a}\right), \quad (3)$$

and $f_a=\beta\hbar\omega_a/2$. In these equations $V(\mathbf{x})$ is the interaction potential of the system evaluated at $\mathbf{x}\equiv\{x_i\}$, that is, at the instantaneous position in the N-dimensional configurational space, and $\mathbf{x}_0$ denotes the equilibrium configuration. Moreover, the subscripts a,b refer to the normal modes of the crystal obtained through the orthogonal matrix $\mathbf{U}\equiv\{U_{ai}\}$. Furthermore, the tilde appearing in Eqs. (1) and (2) denotes the broadening of the function $f(\mathbf{x})$ over the variables $\boldsymbol{\xi}\equiv\{\xi_a\}$,

$$\widetilde{f}(\mathbf{x})=\int f(\mathbf{x}+\mathbf{U}^T\boldsymbol{\xi})\prod_a\left\{\frac{d\xi_a}{[2\pi\alpha_a]^{1/2}}\exp\left(-\frac{\xi_a^2}{2\alpha_a}\right)\right\}, \quad (4)$$

due to the so-called quantum renormalization parameters α_a which are related to the pure quantum contribution to the (quadratic) fluctuation of the normal modes. In several applications the interaction potential $V(\mathbf{x})$, whose Gaussian smoothing appears in Eqs. (1) and (2), has been expanded up to finite order in the parameters α_a.[9,2–5] The formulation described in Ref. 1 explores the possibility of taking into account in the computations all terms in the Taylor expansion of $V(\mathbf{x})$. After some lengthy calculations, in which the potential is expanded and eventually resummed analytically, an expression is obtained which is very manageable for computational purposes. We describe here an alternative way which allows us to obtain the same result very simply. In this approach the potential does not need to be expanded in a Taylor series. Instead, the analytical calculation can be accomplished in a few lines by employing an identity from the theory of Gaussian integrals, namely,

$$(2\pi)^{-N/2}|\mathbf{A}|^{1/2}\int d\boldsymbol{\xi}\exp\left(-\frac{1}{2}\boldsymbol{\xi}^T\cdot\mathbf{A}\cdot\boldsymbol{\xi}+\mathbf{B}^T\cdot\boldsymbol{\xi}\right)$$
$$=\exp\left(\frac{1}{2}\mathbf{B}^T\cdot\mathbf{A}^{-1}\mathbf{B}\right). \quad (5)$$

Here, $\mathbf{A}$ is a positive definite square matrix of order $N\times N$ whose determinant is denoted by $|\mathbf{A}|$ and $\mathbf{B}$ is an N-dimensional vector. By Fourier transforming $f(\mathbf{x})$ in Eq. (4) and using Eq. (5) we have

$$\widetilde{f}(\mathbf{x})=\int\frac{d\mathbf{q}}{(2\pi)^N}f(\mathbf{q})\exp(\imath\mathbf{q}\cdot\mathbf{x})\int\exp(\imath\mathbf{q}\cdot\mathbf{U}^T\boldsymbol{\xi})$$
$$\times\prod_a\left\{\frac{d\xi_a}{[2\pi\alpha_a]^{1/2}}\exp\left(-\frac{\xi_a^2}{2\alpha_a}\right)\right\}$$
$$=\int\frac{d\mathbf{q}}{(2\pi)^N}f(\mathbf{q})\exp(\imath\mathbf{q}\cdot\mathbf{x})\exp\left(-\frac{1}{2}\mathbf{q}^T\cdot\mathbf{D}\cdot\mathbf{q}\right), \quad (6)$$

where $\mathbf{D}\equiv\{D_{ij}\}$ is an $N\times N$ tensor whose elements are defined by

$$D_{ij}=\sum_a U_{ia}^T\alpha_a U_{aj}. \tag{7}$$

Now, by inverse Fourier transforming $f(\mathbf{q})$ in Eq. (6) we obtain

$$\begin{aligned}\tilde{f}(\mathbf{x})&=\int d\mathbf{y}\, f(\mathbf{y})\int\frac{d\mathbf{q}}{(2\pi)^N}\exp\left(-\frac{1}{2}\mathbf{q}^T\cdot\mathbf{D}\cdot\mathbf{q}+\imath\mathbf{q}\cdot(\mathbf{x}-\mathbf{y})\right)\\&=\int d\mathbf{y}\, f(\mathbf{y})\frac{\exp\left[-\frac{1}{2}(\mathbf{y}-\mathbf{x})^T\cdot\mathbf{D}^{-1}\cdot(\mathbf{y}-\mathbf{x})\right]}{[(2\pi)^N|\mathbf{D}|]^{1/2}}\\&=\int d\mathbf{y}\, f(\mathbf{y}+\mathbf{x})\frac{\exp\left(-\frac{1}{2}\mathbf{y}^T\cdot\mathbf{D}^{-1}\cdot\mathbf{y}\right)}{[(2\pi)^N|\mathbf{D}|]^{1/2}},\end{aligned} \tag{8}$$

where the identity (5) has been used again in the integration over the variables $\mathbf{q}\equiv\{q_i\}$. It should be noted that we have not made any assumption about the particular form of the function $f(\mathbf{x})$ that is the interaction potential of the system. For a three-dimensional crystal whose potential energy consists of a pairwise central interaction, Eqs. (7) and (8) reduce, with a slightly different notation, to the results reported in Ref. 1 [Eqs. (18) and (19)], namely,

$$\tilde{f}(\mathbf{x})=\frac{1}{2}\sum_{i\neq j}\int d\mathbf{y}\, f(\mathbf{y}+\mathbf{x}_i-\mathbf{x}_j)\frac{\exp\left(-\frac{1}{2}\mathbf{y}^T\cdot\mathbf{D}_{ij}^{-1}\cdot\mathbf{y}\right)}{[(2\pi)^3|\mathbf{D}_{ij}|]^{1/2}}. \tag{9}$$

Here, the subscripts i,j label the particles of the crystal whose instantaneous positions are denoted by the three-dimensional vectors $\mathbf{x}_i\equiv\{x_{i\alpha}\}$ where $\alpha=x,y,z$ labels the Cartesian components; in addition, $\mathbf{D}_{ij}=\{D_{ij,\alpha\beta}\}$ is a 3×3 tensor defined by

$$D_{ij,\alpha\beta}=\sum_a (U_{i\alpha,a}^T-U_{j\alpha,a}^T)\alpha_a(U_{a,i\beta}-U_{a,j\beta}), \tag{10}$$

which is related to the pure quantum fluctuation of the displacement between the atoms i and j.

As described in Ref. 1, Eqs. (9) and (10) can be effectively implemented in an easy and efficient Monte Carlo algorithm. We agree that this procedure represents a meaningful step forward with respect to previous formulations whose limitation was related to the finite order expansion of the effective potential. The very simple way this formalism can be obtained through the theory of N-dimensional Gaussian integrals makes the improved formulation of the EPMC theory even more appealing for future applications.

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