Effective potential, Mori product and quantum dynamics

1998 J. Phys. A: Math. Gen. 31 L419

(http://iopscience.iop.org/0305-4470/31/22/003)

J. Phys. A: Math. Gen. **31** (1998) L419–L424. Printed in the UK PII: S0305-4470(98)93585-5

LETTER TO THE EDITOR

Effective potential, Mori product and quantum dynamics

A Cuccoli†‡, R Giachetti†§, V Tognetti†‡ and R Vaia‡‖

† Dipartimento di Fisica dell'Università di Firenze, Italy

‡ Istituto Nazionale di Fisica della Materia (INFM), Unitá di Firenze, Largo E Fermi, 2 I-50125 Firenze, Italy

§ Istituto Nazionale di Fisica Nucleare (INFN), Sezione di Firenze, Largo E Fermi, 2 I-50125 Firenze, Italy

‖ Istituto di Elettronica Quantistica del CNR Firenze, Via Panciattichi, 56/30 I-50127 Firenze, Italy

Received 22 April 1998

Abstract. We present a method that permits the calculation of the dynamical correlation functions for quantum systems. These are obtained by evaluating the generating functionals of the static moments of the relaxation functions in a self-consistent approximation that can be obtained by an appropriate extension of the effective potential theory.

The thermodynamics of quantum systems has been widely studied by the effective potential theory [1, 2]. This treatment has proved to be very accurate to determine equilibrium properties [3–5], but encounters quite a number of theoretical and practical difficulties in being applied to dynamical phenomena. An extension of the formalism uniquely based on ingenuity does not allow for a serious control of the results and slips easily into *ad hoc* or even erroneous assumptions. On the other hand it is self-evident that an adequate way for calculating quantum dynamical correlations would be highly welcome. It is our purpose to fill this gap and to provide an effective method to calculate dynamical quantities in terms of path integrals. We shall mainly be concerned with the Kubo relaxation functions, that naturally appear in the framework of Mori theory [6]. These functions are obtained by suitably defined scalar products, the Mori products

$$R_{A,B}(t) = (\hat{A}|\hat{B}(t)) = \int_0^{\beta\hbar} \mathrm{d}u \, \langle \hat{A}(0)\hat{B}(t + \mathrm{i}u)\rangle \tag{1}$$

where the observables $\hat{A}$ and $\hat{B}$ are taken such that $\langle\hat{A}\rangle = \langle\hat{B}\rangle = 0$, and braces denote the thermodynamic average. The Laplace transform of equation (1), in turn, has a continued fraction representation whose coefficients are static normalized relaxation functions, i.e. time-independent normalized Mori products of derivatives of the dynamical variables $\hat{A}(t)$ and $\hat{B}(t)$. In particular, the self-relaxation function $\Xi_0(t) = (\hat{F}_0|\hat{F}_0)^{-1}(\hat{F}_0(t)|\hat{F}_0)$ of a Hermitian operator $\hat{F}_0(t)$ can be Laplace transformed and expanded in a continued fraction, namely $\Xi_j(z) = (z + \delta_{j+1}\Xi_{j+1}(z))^{-1}$, where $\delta_{j+1} = (\hat{F}_j|\hat{F}_j)^{-1}(\hat{F}_{j+1}|\hat{F}_{j+1})$ and $\hat{F}_j$ denotes the so-called jth fluctuating force. The quantities $(\hat{F}_j|\hat{F}_j)$, can be related to a combination of the first $2(j+1)$ frequency moments i.e. the coefficients of the time-series expansion of $\Xi_0(t)$. While $(\hat{F}_j|\hat{F}_j)$ with $j \neq 0$ can be expressed in terms of static correlations, the quantity $(\hat{F}_0|\hat{F}_0)$ requires the direct evaluation of the Mori product.

0305-4470/98/220419+06$19.50

Indeed, experiments measure the spectral shape, given by the Fourier transform of the dynamic correlation function, related to $\Xi_0(z)$ by the 'detailed balance' principle:

$$\mathcal{S}(\omega) = (\hat{F}_0|\hat{F}_0)\frac{\omega}{1-\mathrm{e}^{-\beta\omega}}\frac{1}{\pi}\Re(\Xi_0(z=\mathrm{i}\omega)). \tag{2}$$

Therefore, the calculation of $\mathcal{S}(\omega)$ can be approached from the knowledge of the static quantities δ_j up to a sufficiently large number $j = J$ [7], supported by some insight into the long-time behaviour of the continued fraction termination $\Xi_J(t)$ [5, 8, 7].

Here we shall provide a functional method and an explicit formula for the *direct* evaluation of an arbitrary Mori product by an effective potential approximation, so that all the δ_j can be calculated either numerically or by suitable analytical approximations. This is particularly relevant for $(\hat{F}_0|\hat{F}_0)$, which is an external parameter of the Mori approach and could not be explicitly obtained in terms of static correlations. Moreover, our rigourous derivation of imaginary time-ordered products allows us to control the evaluation of real time correlators that can be approached by means of a 'pure quantum Gaussian' molecular dynamics, thus producing a major breakthrough in the accuracy of the computation.

We start from the generating functional in the Hamiltonian path-integral form:

$$Z[L,J] = \oint \mathcal{D}[x(u)] \int \mathcal{D}[p(u)] \exp\left[-\frac{1}{\hbar}\int_0^{\beta\hbar} \mathrm{d}u(-\mathrm{i}p(u)\dot{x}(u) + \mathcal{H}(p(u),x(u)) \right.$$
$$\left. -\hbar L(u)p(u) - \hbar J(u)x(u))\right]. \tag{3}$$

According to the effective-potential method [1, 2, 5] we consider a quadratic trial action obtained by substituting $\mathcal{H}(p(u),x(u))$ with $(1/2m)(p(u)-\eta)^2 + (m\omega^2/2)(x(u)-\xi)^2 + w$, whose parameters w, m and ω depend on the average point $(\eta,\xi) = (\beta\hbar)^{-1}(\int \mathrm{d}u\, p(u), \int \mathrm{d}u\, x(u))$ of each path. The effective Hamiltonian reads

$$\mathcal{H}_{\mathrm{eff}}(\eta,\xi) = w(\eta,\xi) + \beta^{-1}\ln(f^{-1}\sinh f) \tag{4}$$

where $f = \beta\hbar\omega/2$ rules the quantum character of the system. By defining the two-component vectors $\rho = {}^t(\eta,\xi)$ and $K(u) = {}^t(L(u),J(u))$, the approximated generating functional can be written as

$$Z_0[K] = \int \frac{\mathrm{d}\eta\,\mathrm{d}\xi}{2\pi\hbar}\mathrm{e}^{-\beta\mathcal{H}_{\mathrm{eff}}(\eta,\xi)}$$
$$\times \exp\left[\int_0^{\beta\hbar}\mathrm{d}u\,{}^t\rho K(u) + \tfrac{1}{2}\int_0^{\beta\hbar}\mathrm{d}u\int_0^{\beta\hbar}\mathrm{d}v\,{}^tK(u)\Phi(u-v)K(v)\right]. \tag{5}$$

In equation (5) we have introduced the 2×2 matrix $\Phi_{k\ell}(u-v)$ with elements $\Phi_{11}(u-v) = m^2\omega^2\Phi_{22}(u-v) = m^2\omega^2\Lambda_f(u-v)$ and $\Phi_{12}(u-v) = -\Phi_{21}(u-v) = \Gamma_f(u-v)$, where

$$\Lambda_f(u-v) = \frac{\hbar}{2m\omega\sinh f}\left[\cosh(|\omega(u-v)|-f) - \frac{\sinh f}{f}\right]$$
$$\Gamma_f(u-v) = \mathrm{i}m\frac{\partial\Lambda_f(u-v)}{\partial v} = -\frac{\mathrm{i}\hbar}{2}\frac{\sinh(|\omega(u-v)|-f)}{\sinh f}[\theta(u-v)-\theta(v-u)]. \tag{6}$$

While Λ_f is always well defined, the value of Γ_f for $u = v$ is determined only if we specify the limit $v-u\to 0^{\pm}$ that must be taken, reflecting the commutation relation of $\hat{x}$ and $\hat{p}$ at the same time. Moreover, a squared length $\alpha = \hbar/(2m\omega)(\coth f - 1/f)$ and an energy $E_\omega = m\omega^2\alpha$ are naturally defined by the parameters of the system. It is also worth observing that $\Lambda_f(0) = \Lambda_f(\beta\hbar) = \alpha$ and that $\Lambda_f(u-v)$ and $\Gamma_f(u-v)$ have a vanishing average in $[0,\beta\hbar]$.

If we define the two-component vectors $\hat{z} = {}^t(\hat{p}, \hat{x})$ and $y = (y_1(u), y_2(u))$, after a lengthy but straightforward calculation, the following general formula can be derived in the low-coupling approximation [5], i.e. ω independent of η and ξ:

$$\left\langle \mathcal{T}_u \left[\prod_{\nu=1}^{N} \hat{F}_\nu(\hat{z}_{i_\nu}(u_\nu)) \right] \right\rangle = \mathcal{N} \prod_{\nu=1}^{N} F_\nu \left(\frac{\delta}{\delta K_{i_\nu}} \right) Z_0[K] \Big|_{K=0}$$
$$= \mathcal{N} \int \frac{\mathrm{d}\eta\, \mathrm{d}\xi}{2\pi\hbar} \mathrm{e}^{-\beta \mathcal{H}_{\mathrm{eff}}(\eta,\xi)} \left\langle\!\!\left\langle \prod_{\nu=1}^{N} F_\nu(\rho_{i_\nu} + y_{i_\nu}(u_\nu)) \right\rangle\!\!\right\rangle. \tag{7}$$

Here, $\mathcal{N} = Z_0^{-1}[0]$ is the normalizing factor, and the double brackets denote the average over the Gaussian distribution of the variables $y_{i_\nu}(u_\nu)$, defined by the second moments

$$\langle\!\langle y_i(v) y_j(u) \rangle\!\rangle = \Phi_{ij}(u - v). \tag{8}$$

The expression (7), with the definition (8), is the key result of our paper and represents the main concern of what will follow. The discussion of these new formulae will provide a clear indication of the possibilities of their applications and will demostrate the great improvement for the actual calculation of dynamical quantities; indeed, complicated static Mori products, i.e. moments of any order, can be evaluated by this last equation. Static correlations can also be obtained performing the appropriate limit $u - v \to 0$.

In order to carry our argument on, we first look for an explicit expression for averages of two functions separately depending on momentum or displacement. A direct calculation leads from equation (7) to the following expansion:

$$\langle \mathcal{T}_2 u[\hat{A}(z_i(v))\hat{B}(z_j(u))] \rangle = \mathcal{N} \int \frac{\mathrm{d}\eta\, \mathrm{d}\xi}{2\pi\hbar} \mathrm{e}^{-\beta \mathcal{H}_{\mathrm{eff}}(\eta,\xi)} \int \frac{\mathrm{d}y\, \mathrm{d}z}{2\pi} \frac{A(y)B(z)}{[\Phi_{ii}\Phi_{jj} - \Phi_{ij}^2(u-v)]^{1/2}}$$
$$\times \exp\left\{ - \frac{\Phi_{ii}\Phi_{jj}}{2[\Phi_{ii}\Phi_{jj} - \Phi_{ij}^2(u-v)]} \right.$$
$$\left. \times \left[\frac{(y-\rho_i)^2}{\Phi_{ii}} + \frac{(z-\rho_j)^2}{\Phi_{jj}} - (y-\rho_i)\frac{\Phi_{ij}(u-v)}{\Phi_{ii}\Phi_{jj}}(z-\rho_j) \right] \right\}. \tag{9}$$

with $\Phi_{kk} \equiv \Phi_{kk}(0)$. We note that, when static quantities are approached, i.e. the two imaginary times become equal, the particular ordering of operators depending on both $\hat{p}$ and $\hat{x}$ has to be specified. Any of the two possible orders, p-left or p-right, is obtained from the equation above by simply taking the appropriate limit $v - u \to 0^{\pm}$.

The final step involved in the calculation of higher order moments is the integral expression for the average of the imaginary time-ordered product of two operators $\hat{A}$ and $\hat{B}$ at two different times u and v, both depending on momenta and displacements. Without loss of generality we can consider p-left ordered operators, so that $\hat{A} = \hat{A}_1(p(u^+))\hat{A}_2(x(u))$ and similarly for $\hat{B}$. By specializing equation (11) to this situation and with evident meaning of the notation, we obtain

$$\langle \mathcal{T}_u[A(\hat{p}(u), \hat{x}(u))\hat{B}(\hat{p}(v), \hat{x}(v))] \rangle = \langle \mathcal{T}_u[A_1(\hat{p}(u^+))A_2(\hat{x}(u))B_1(\hat{p}(v^+))B_2(\hat{x}(v))] \rangle$$
$$= \mathcal{N} \int \frac{\mathrm{d}\eta\, \mathrm{d}\xi}{2\pi\hbar} \mathrm{e}^{-\beta \mathcal{H}_{\mathrm{eff}}(\eta,\xi)} \int \mathrm{d}^4 y\, \frac{A_1(y_1)A_2(y_2)B_1(y_3)B_2(y_4)}{(2\pi)^2 \det^{1/2}(\Psi_{ij})}$$
$$\times \exp\left[- \tfrac{1}{2} \sum_{ij} (y_i - \rho_i)\Psi_{ij}^{-1}(y_j - \rho_j) \right] \tag{10}$$

where now $\rho = {}^t(\eta, \xi, \eta, \xi)$ is a four-component vector and we have introduced the 4×4 matrix Ψ with elements $\Psi_{11} = m^2\omega^2\Psi_{22} = \Psi_{33} = m^2\omega^2\Psi_{44} = m^2\omega^2\alpha$,

$\Psi_{12} = \Psi_{21} = \Psi_{34} = \Psi_{43} = -\mathrm{i}\overline{h}/2$, $\Psi_{13} = m^2\omega^2\Psi_{24} = \Psi_{31} = m^2\omega^2\Psi_{42} = m^2\omega^2\Lambda_f(u-v)$ and $\Psi_{14} = -\Psi_{23} = -\Psi_{32} = \Psi_{41} = \Gamma_f(u-v)$.

From equation (10), when $(u-v) \to 0^+$, we find the static average,

$$\langle \hat{A}\hat{B} \rangle = \mathcal{N} \int \frac{\mathrm{d}\eta\, \mathrm{d}\xi}{2\pi\overline{h}} \langle\langle AB \rangle\rangle \mathrm{e}^{-\beta\mathcal{H}_{\mathrm{eff}}(\eta,\xi)} \tag{11}$$

indeed recovering our previous result[3, 5]†.

As far as the Mori product is concerned, the well known series expansion $(2\pi\epsilon)^{-1/2}\exp\{-x^2/(2\epsilon)\} = \sum_{n=0}^{\infty}(1/n!)(\epsilon/2)^n\delta^{(2n)}(x)$ appears to be an efficient tool to approximate the static Mori product of general operators, as well as their dynamical correlations, when the scales of the quantum fluctuations in the system, ruled by $\overline{h}$ and the natural length scale α, are small. Indeed, as the averages of $\Lambda_f(u)$ and $\Gamma_f(u)$ in $[0, \beta\overline{h}]$ vanish, we have

$$\begin{aligned}(\hat{A}(\hat{p},\hat{x})|\hat{B}(\hat{p},\hat{x})) = \mathcal{N}(\beta\overline{h}) \int \frac{\mathrm{d}\eta\, \mathrm{d}\xi}{2\pi\overline{h}} \mathrm{e}^{-\beta\mathcal{H}_{\mathrm{eff}}(\eta,\xi)} \{ &\langle\!\langle A(\eta,\xi) \rangle\!\rangle \langle\!\langle B(\eta,\xi) \rangle\!\rangle \\ &+ \tfrac{1}{2}[(m^2\omega^4 A_{pp}B_{pp} + 2m^2\omega^2 A_{px}B_{px} + A_{xx}B_{xx})\sigma_f \\ &+ (A_{pp}B_{xx} - 2A_{px}B_{px} + A_{xx}B_{pp})\mu_f] + \mathrm{o}(\alpha^2, \overline{h}^2)\}\end{aligned} \tag{12}$$

where the subscripts of A and B denote the derivatives, while σ_f and μ_f are the averages of Λ_f^2 and Γ_f^2 in $[0, \beta\overline{h}]$. Therefore, as σ_f is of order α^2 and μ_f of order $\overline{h}^2$, at the lowest order $(\hat{A}(p,x)|\hat{B}(p,x))$ reduces to the 'classical-like' average of the product of the Gaussian spreads of the two operators taken at the same order:

$$(\hat{A}(p,x)|\hat{B}(p,x)) = \mathcal{N}\beta\overline{h} \int \frac{\mathrm{d}\eta\, \mathrm{d}\xi}{2\pi\overline{h}} \langle\!\langle A(\eta,\xi) \rangle\!\rangle \langle\!\langle B(\eta,\xi) \rangle\!\rangle \mathrm{e}^{-\beta\mathcal{H}_{\mathrm{eff}}(\eta,\xi)} + \mathrm{o}(\alpha, \overline{h}). \tag{13}$$

This zeroth-order approximation was proposed in [9] with *ad hoc* assumptions and without any possible control or improvement of the accuracy.

For a deeper discussion of the properties of our method, we shall give explicit formulae that refer to a particle in a potential. These can be numerically computed and directly compared with the results of experiments; it is well known, for instance, that the displacement–displacement correlation function can be probed by neutron scattering. We therefore assume the Hamiltonian

$$\mathcal{H}(p,x) = p^2/2m + V(x) \qquad V(x) - V''(x_0)(x-x_0)^2/2 \equiv g v(x). \tag{14}$$

where x_0 is the absolute minimum of the potential, and the quantum coupling constant g has been defined. The effective Hamiltonian is therefore $\mathcal{H}_{\mathrm{eff}}(\eta,\xi) = \eta^2/(2m) + V_{\mathrm{eff}}(\xi)$, where m is now the particle mass, i.e. a constant, and $V_{\mathrm{eff}}(\xi) = \langle\!\langle V(\xi) \rangle\!\rangle + \beta^{-1}\ln(f^{-1}\sinh f)$.

The simplest physically relevant quantity that can be discussed is given by the imaginary time-ordered correlation of two dynamical variables $A(x)$ and $B(x)$, dependent upon the coordinates only. For standard Hamiltonians the integration over momentum can be performed and we obtain the following explicit expression for the correlation function:

$$\begin{aligned}\langle \mathcal{T}_u[A(\hat{x}(v))B(\hat{x}(u))] \rangle = \mathcal{N}\sqrt{\frac{m}{2\pi\beta\overline{h}^2}} \int \mathrm{d}\xi\, \mathrm{e}^{-\beta V_{\mathrm{eff}}(\xi)} \int \mathrm{d}y \int \mathrm{d}z\, 2A(y)B(z) \\ \times \frac{\exp\left\{-\frac{(y-z)^2}{4[\alpha-\Lambda_f(u-v)]}\right\}}{[4\pi(\alpha-\Lambda_f(u-v))]^{1/2}} \frac{\exp\left\{\frac{(y+z-2\xi)^2}{4[\alpha+\Lambda_f(u-v)]}\right\}}{[4\pi(\alpha+\Lambda_f(u-v))]^{1/2}}.\end{aligned} \tag{15}$$

† We recall that, as clearly observed in [5], the final result for the static average is independent of the particular ordering (representation) chosen for a given operator. In fact, different ordering correspond to different moments of the Gaussian spread, which lead to the same final result.

From the last equation, or by specializing equations (10) and (12), the expansion for the Mori product is finally obtained:

$$(A(\hat{x})|B(\hat{x})) = \mathcal{N}\beta\overline{h}\sqrt{\frac{m}{2\pi\beta\overline{h}^2}}\int \mathrm{d}\xi\, \mathrm{e}^{-\beta V_{\mathrm{eff}}(\xi)}\left\{A(\xi)B(\xi) + \frac{\alpha}{2}[A''(\xi)B(\xi) + A(\xi)B''(\xi)] + \frac{\alpha^2}{8}\left[A^{(iv)}(\xi)B(\xi) + A(\xi)B^{(iv)}(\xi) + \left(2 + \frac{4\sigma_f}{\alpha^2}\right)A''(\xi)B''(\xi)\right]\right\} + \mathrm{o}(\alpha^2). \tag{16}$$

Note that for the displacement–displacement correlation function only the first term in the last equation (or in equation (12)) survives and gives the total contribution to $(A(\hat{x})|B(\hat{x}))$ in the effective-potential approach. Comparing with equation (11), we have $\langle\hat{x}^2\rangle = (\beta\overline{h})^{-1}(\hat{x}|\hat{x}) + \alpha$. This shows the twofold contribution of the quantum fluctuations, i.e. the spreads of the potential and of the quantity under averaging. The Mori product takes into account the spread of the potential only. Since we can calculate the zero moment $\langle\omega\rangle^{(0)} = (\hat{x}|\hat{x})$ and since the higher moments are given by the other previous equations, the dynamic correlations $\langle\hat{x}(t)\hat{x}\rangle$ can be eventually determined by the continued fraction expansion [5–8].

We wish to conclude with some remarks on another possible dynamical extension of our theory. We can assume that our system evolves with the effective Hamiltonian as found for the thermodynamic behaviour. This means that we take the commutator for its quadratic part, while we consider the Poisson brackets for the one-loop-renormalized nonlinear part. In order to do this, we have to use a representation of the operators describing the dynamical variables which permits us to unify quantum and classical dynamics, for instance, the Weyl-representation [3, 5] or the Liouvillian scheme. To better understand this point we recall in the first place that harmonic oscillators evolve by the same law in both classical and quantum dynamics; the differences between quantum and classical statistical evolution are due to the thermal occupation numbers, which are static quantities. For real systems, the quantum deviations from the harmonic behaviour are ruled by the coupling constant g, related to quantum nonlinearity. If g is vanishing, the noncommutativity of operators at different times can be neglected and equation (12) can be assumed to hold its validity at different real times, provided also that α is small enough, so that the Gaussian spreads of $\hat{A}$ and $\hat{B}$ do not overlap. At this level, the times averages of the quantities $\langle\langle\hat{A}\rangle\rangle$ and $\langle\langle\hat{B}(t)\rangle\rangle$, evolving with the effective potential $V_{\mathrm{eff}}(\xi)$ [9, 10], can provide an approximation for the time-dependent Mori product $(\hat{A}|\hat{B}(t))$. Finally its Fourier transform then gives the relaxation function $R_{A,B}(\omega)$, which is connected to the Fourier transform $C_{A,B}(\omega)$ of the dynamical correlation function $\langle\hat{A}\hat{B}(t)\rangle$ by means of the fluctuation-dissipation theorem, as in equation (2). This last operation simply restores the correct static quantum occupation numbers.

We stress that the results become exact when $g \to 0$, i.e. for quantum harmonic oscillators with a classical nonlinear interaction term. Of course, the other exact limit is the classical system. For finite values of g, the validity of this scheme also involves the amplitudes of the Gaussian fluctuations ruled by the parameter α. Therefore, there is the same behaviour found for approaching static correlators with the effective Hamiltonian [5, 11]. In that case, the lowest limit of temperature was found to be related to both parameters g and α. For the dynamic correlators, this procedure yields a good approximation for times up to the order of $\overline{h}\beta$, for which the use of the effective potential makes sense in the calculation of the static quantities at lowest order, reproducing for example a correct second moment for the displacement–displacement dynamic correlator with a well-behaved classical long-time decay.

References

[1] Giachetti R and Tognetti V 1985 *Phys. Rev. Lett.* **55** 912
Giachetti R and Tognetti V 1986 *Phys. Rev.* B **33** 7647
[2] Feynman R P and Kleinert H 1986 *Phys. Rev*. A **34** 5080
[3] Cuccoli A, Tognetti V, Verrucchi P and Vaia R 1992 *Phys. Rev.* B **46** 11 601
Cuccoli A, Tognetti V, Verrucchi P and Vaia R 1996 *Phys. Rev. Lett.* **77** 3439
[4] Cowley E R and Horton G K 1995 *Dynamic Properties of Solids* vol 7, ed G K Horton and A A Maradudin (Amsterdam: North-Holland)
[5] Cuccoli A, Giachetti R, Tognetti V, Vaia R and Verrucchi P 1995 *J. Phys.: Condens. Matter* **7** 7891
[6] Mori H 1965 *Progr. Theor. Phys.* **33** 423
Mori H 1965 *Prog. Theor. Phys.* **34** 399
[7] Cuccoli A, Maradudin A A, McGurn A R, Tognetti V and Vaia R 1992 *Phys. Rev.* B **46** 8839
Cuccoli A, Maradudin A A, McGurn A R, Tognetti V and Vaia R 1993 *Phys. Rev.* B **48** 7015
[8] Lovesey S W and Meserve R A 1972 *J. Phys. C: Solid State Phys.* **6** 79
Lee M H, Hong J and Florencio J 1987 *Phys. Scr*. T **19** 498
[9] Cao J and Voth G A 1993 *J. Chem. Phys.* **99** 10 070
Cao J and Voth G A 1994 *J. Chem. Phys.* **100** 5093
Cao J and Voth G A 1994 *J. Chem. Phys.* **100** 5106
[10] Martyna G 1996 *J. Chem. Phys.* **104** 2018
[11] Giachetti R, Tognetti V and Vaia R 1988 *Phys. Rev.* A **38** 1521