A NEW ALGORITHM OF SOLVING THE LADO PERTURBATION METHOD

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A new numerical procedure was proposed for solving the Lado perturbation method which speeds up the computations several times. The procedure was tested by computing the thermodynamic properties of a Lennard-Jones pair-additive fluid.

Recently, considerable advance has been reached by statistical thermodynamics in the description of structure and thermodynamic properties of simple fluids. The latest group of simple-fluid theories are the methods based on the combination of the perturbation principle with the approximations used in the solution of integral equations. To this group pertain, *e.g.*, the referenced hypernetted chain theory proposed by Lado[1], its extension and reformulation called by Smith and Henderson, the corrected integral-equation[2] and the integral-equation perturbation theory by Madden and Fitts[3]. The principle of all these theories is very similar. The Percus–Yevick approximation[4] or the hypernetted chain approximation[5] are used not for the whole computation of the system properties but only to the computation of deviations from the reference system. It can be expected these methods will yield very good results, however, they are substantially more time-consuming compared with the former perturbation theories. Such as the classical integral equations, they suffer considerably from the problems of rapid convergence of iteration procedure. Perhaps, this is just the reason why concrete results of these methods have appeared in the literature only sporadically.

The aim of this paper is to propose a numerical procedure for solution of the Lado method which would enable to speed up the computations several times. The method is applied to computations of the thermodynamic properties of a Lennard-Jones pair-additive fluid. Accuracy of the Lado method is tested by comparing with the results of parametrizations of simulated data and by testing the consistency of the thermodynamic quantities.

THEORETICAL

The fundamental principle of the Lado method is neglecting the difference of elementary diagrams of the reference and investigated systems

$$E(r) = E_0(r)\,. \tag{1}$$

Consequently it can be considered as the perturbation theory of the zeroth order in elementary diagrams and therefore as a theory in a sense of the HNC approximation. On the basis of the diagram analysis, Eq. (1) can be rearranged into the form

$$\Delta c(r) = \Delta h(r) - \ln\left[y(r)/y_0(r)\right], \tag{2}$$

where the difference of the direct correlation functions

$$\Delta c(r) = c(r) - c_0(r)\,, \tag{3}$$

the difference of the total correlation functions

$$\Delta h(r) = h(r) - h_0(r) \tag{4}$$

and the function $y(r)$ or $y_0(r)$ is defined by the relation

$$y(r) = g(r)\exp\left[\beta u(r)\right]. \tag{5}$$

Here β denotes the reduced reciprocal temperature $\beta = \varepsilon/kT$ and $u(r)$ is the pair potential. From the Ornstein–Zernike integral equation expressed in terms of the Fourier transform[6]

$$\tilde{h}(k) = \tilde{c}(k)/[1 - \varrho\tilde{c}(k)] \tag{6}$$

follows another independent relation for the difference of correlation functions:

$$\Delta\tilde{h}(k) = \chi_0^2(k)\,\Delta\tilde{c}(k)/[1 - \varrho\chi_0(k)\,\Delta\tilde{c}(k)]\,. \tag{7}$$

In preceding relations, $\sim$ denotes the Fourier transform, ϱ is the number density of the system and $\chi_0(k) = 1 + \varrho\tilde{h}(k)$ is the structural factor of the reference system. Eqs (2) and (7) form then an iteration scheme for the solution of differences of the correlation functions.

For the computation itself, Lado[1] proposes to rewrite the iteration scheme in the following way: Let us define the function

$$H(r) = \ln\left[y(r)/y_0(r)\right] = \Delta h(r) - \Delta c(r)\,. \tag{8}$$

The iteration scheme can then be rewritten as the pair of equations

$$C(r) = g_0(r)\{\exp[H(r) - \beta u_p(r)] - 1\} - H(r)\,, \tag{9}$$

$$\tilde{H}(k) = \tilde{C}(k)\{\chi_0^2(k)/[1 - \varrho\chi_0(k)\,\tilde{C}(k)] - 1\}\,, \tag{10}$$

where $u_p(r)$ is the perturbation part of the potential $u_p(r) = u(r) - u_0(r)$. Eqs (9) and (10) are equivalent to relations (2) and (7), however, they are substantially numerically more advantageous with regard to the smoothness of the function $H(r)$.

Such as in solving integral equations[7], it is necessary to use a damped iteration with a parameter $\alpha < 1$ at higher densities. If $H_n(r)$ is the n-th approximation of the solution entering Eq. (9) and $\tilde{H}'_n(k)$ the respective result of Eq. (10), we can write for the $(n + 1)$st approximation

$$H_{n+1}(r) = (1 - \alpha)\,H_n(r) + \alpha H'_n(r)\,, \tag{11}$$

where $H'_n(r)$ is a result of the back transform of $\tilde{H}'_n(k)$.

In this way of solution, we reach convergence, however, the number of iterations is very high, and the consumption of computer time increases strongly with increasing density and decreasing temperature of the system. To attain substantial time-saving, we have proposed to modify the iteration scheme in the following way:

Let us assume that we know an approximate solution of Eqs (9) and (10) which is denoted by $H_1(r)$. By inserting into Eq. (9), we get the function $C_1(r)$ and from it, in terms of Eq. (10), $\tilde{H}'_1(k)$ and corresponding $H'_1(r)$. Unless $H_1(r)$ is directly the solution,

$$H_1(r) \neq H'_1(r) \tag{12}$$

holds, and the difference of these two functions is a measure of the distance $H_1(r)$ from the solution. An arbitrary successive approximation of solution $H_n(r)$ can be written as

$$H_n(r) = H_1(r) + \Delta H_n(r)\,, \tag{13}$$

where $\Delta H_n(r)$ is a comparatively small function. If we rewrite the iteration scheme in terms of deviations $\Delta H_n(r)$ we have

$$\Delta C_n(r) = g_0(r)\exp[H_1(r) - \beta u_p(r)]\{\exp[\Delta H_n(r)] - 1\} - \Delta H_n(r) \tag{14}$$

and

$$\Delta\tilde{H}'_n(k) = \Delta\tilde{C}_n(k)\,[\chi_0^2(k)/(P(k)\,P_1(k)) - 1]\,, \tag{15}$$

where

$$P_1(k) = 1 - \varrho\chi_0(k)\,\tilde{C}_1(k) \tag{16}$$

and

$$P(k) = P_1(k) - \varrho\chi_0(k)\,\Delta\tilde{C}_n(k)\,. \tag{17}$$

The differences $\Delta\tilde{C}_n(k)$ and $\Delta\tilde{H}'_n(k)$ are defined as

$$\Delta C_n(r) = C_n(r) - C_1(r) \tag{18}$$

and

$$\Delta H'_n(r) = H'_n(r) - H'_1(r)\,. \tag{19}$$

Then Eq. (*11*) turns into the equivalent relation

$$\Delta H_{n+1}(r) = (1 - \alpha)\,\Delta H_n(r) + \alpha\,\Delta H'_n(r) + \alpha[H'_1(r) - H_1(r)]\,. \tag{20}$$

Since the deviations $\Delta H(r)$ and $\Delta C(r)$ are substantially smaller functions than the original $H(r)$ and $C(r)$, it is possible, with a small accuracy loss, to use the Fourier transformation with a lower number of points for their calculations. For instance, if we extend twice the integration step, and reduce to one half the maximum distance used, the time needed for one iteration decreases approximately sixteen times. To reach reliable results, it is then suitable. after a number of these shortened iterations, to define newly the function $H_1(r)$, carry out several iteration cycles according to Eq. (*9*) and (*10*), and repeat the whole process again.

RESULTS AND DISCUSSION

The procedure proposed was checked by extensive computations for the model Lennard–Jones pontential

$$u(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]\,. \tag{21}$$

The representative results along with the details of numerical application can be found elsewhere[8]. Here we present only an illustration of speeding-up the convergence of iteration process and a brief comparison of the Lado method with smoothed simulated data on a typical liquid isochore $\varrho^* = N/V\sigma^3 = 0{\cdot}8$.

The following parameters were chosen for the computations: step in integration $\Delta r = 0{\cdot}02\sigma$ and limit integration $r_{MAX} = 6\sigma$. Here we proceeded invariably so that after 25 short iterations (*14*)–(*20*) with the parameters $r = 0{\cdot}04\sigma$ and $r_{MAX} = 3\sigma$, two long iterations (*9*)–(*11*) were always inserted. The damping factor was chosen as $\alpha = 0{\cdot}1$. To speed up the computations, $\alpha = 0{\cdot}5$ was set in each fifth iteration. With regard to the iteration character of computations, the Fourier transform was carried out by a numerical method[9] ensuring the fulfilment of condition of rever-

sibility

$$\tilde{\tilde{f}}(r) = \tilde{f}(k) = f(r) \tag{22}$$

with the inaccuracies given by finite precision of computer only. As the initial guess, the solution of exponential approximation was used which is obtained from Eqs (*9*) and (*10*) setting

$$g(r) = g_0(r)\,. \tag{23}$$

The convergences of the original and modified procedures are compared in Table I. The number of iterations is chosen always so that the time consumed by both the procedures is approximately the same. For illustration, we give also the values of the compressibility factor from virial equation

$$z = 1 - (2\pi/3)\,\varrho\beta \int_0^\infty \frac{\mathrm{d}u(r)}{\mathrm{d}r}\, g(r)\, r^3\, \mathrm{d}r\,, \tag{24}$$

the configurational energy, U, obtained from the energy equation

$$U/NkT = 2\pi\varrho\beta \int_0^\infty u(r)\, g(r)\, r^2\, \mathrm{d}r\,, \tag{25}$$

TABLE I

Convergence of the Lado method[a]

Original procedure		Modified procedure				
Number of iterations	mean deviation[b]	number of iterations	mean deviation[b]	$-z$	$-F/NkT$	$-U/kT$
0	11·45	0	11·45	0·654	2·043	3·573
3	5·27	25	0·349	0·673	2·041	3·554
6	2·71	50	0·070	0·682	2·040	3·555
9	1·25	75	0·025	0·685	2·036	3·556
12	0·56	100	0·009	0·687	2·035	3·556
15	0·52	125	0·003	0·687	2·035	3·556
18	0·62	150	0·001	0·678	2·035	3·556
21	0·61	175	0·000	0·678	2·035	3·556
24	0·56	200	0·000	0·678	2·035	3·556

[a] Reduced density $N\sigma^3/V = 0{\cdot}5$, reduced temperature $\beta = 1$; [b] mean quadratic deviation of the following estimations of function $y(r)$ in per cent.

and the Helmholtz energy for which follows the relation from the Lado theory:

$$F/NkT = F_0/NkT - 2\pi\varrho \int_0^\infty \{\Delta h^2(r)/2 + \Delta h(r) -$$

$$- g(r) \ln [g(r)/g_0(r)] - g(r)\, \beta u_p(r)\}\, r^2\, dr + 1/(4\pi^2\varrho)\,.$$

$$.\int_0^\infty \{\varrho\, \Delta h(k)/\chi_0(k) - \ln [1 + \varrho\, \Delta h(k)/\chi_0(k)]\}\, k^2\, dk\,. \qquad (26)$$

The chosen density and temperature correspond to saturated liquid, where the convergence of the Lado method is especially slow. It can be seen that the procedure proposed by us converges substantially more rapidly than the original one.

To test correctness of theory, one can use a comparison with pseudoexperimental Monte Carlo data and a test of consistency of thermodynamic quantities. The values of the compressibility factor on the isochore $\varrho = 0{\cdot}8$ are compared in Table II. To obtain them, we used virial equation (*24*), equation for the Helmholtz energy (*26*) along with the relation

$$z = 1 + \varrho \left(\frac{\partial F/NkT}{\partial \varrho}\right)_\beta \qquad (27)$$

TABLE II

Values of the compressibility factor on the isochore $\varrho^* = 0{\cdot}8$

Densities	MC data z_{MC}	Lado theory z_V	z_F	z_U
0·1	3·50	3·67	3·54	—
0·2	3·70	3·95	3·78	3·78
0·3	3·67	3·91	3·74	3·78
0·4	3·54	3·78	3·55	3·64
0·5	3·33	3·49	3·26	3·40
0·6	3·03	3·20	2·93	3·11
0·7	2·64	2·88	2·54	2·75
0·8	2·19	2·36	2·12	2·36
0·9	1·71	1·95	1·73	1·94
1·0	1·24	1·52	1·24	1·48
1·1	0·74	1·00	0·72	1·01
1·2	0·22	0·56	0·21	0·52

and energy equation (25) from which the compressibility factor can be obtained by integration

$$F/NkT = F_0/NkT + \int_{\beta_0}^{\beta} \frac{U/NkT}{\beta} \, d\beta \tag{28}$$

and by following application of Eq. (27). Subscript of denotes here a reference temperature level. In this work, $\beta_0 = 0{\cdot}2$ was chosen, where the Lado method gives very good results. The table gives as well the values of the compressibility factor obtained from the parametrization of simulated data. For low temperatures, $\beta > 1$, the McDonald–Singer equation[10] and for the other temperatures, the Sýs equation[11] were used.

At high temperatures we can observe very good consistency. The values of the compressibility factor obtained by differentiating the Helmholtz energy (z_F) and those obtained in terms of the energy equation (z_U) are here nearly identical. We assume that z_F is here even more accurate than the parametrized data (z_{MC}).

On the contrary, the values of z_U and pressure equation (z_V) are in very good agreement at low temperatures. However, the mutual consistency is not a sufficient condition of correctness as it is evident on comparing with the parametrized data. The best values are namely again yielded by z_F.

REFERENCES

1. Lado F.: Phys. Rev. *A8*, 2548 (1973).
2. Smith W. R., Henderson D.: J. Chem. Phys. *69*, 319 (1978).
3. Madden W. G., Fitts D. D.: Mol. Phys. *30*, 809 (1975).
4. Percus J. K., Yevick G. L.: Phys. Rev. *110*, 1 (1958).
5. Van Leeven J. M. J., Groenveld J., De Boer J.: Physica (Utrecht) *25*, 792 (1959).
6. Watts R. O.: *A Specialist Periodical Report, Statistical Mechanics*. Billing and Sons, London 1973.
7. Broyles A. A.: J. Chem. Phys. *33*, 456 (1960).
8. Labík S., Malijevský A.: This Journal, in press.
9. Lado F.: J. Comput. Phys. *8*, 417 (1971).
10. McDonald I. R., Singer K.: Mol. Phys. *23*, 29 (1972).
11. Sýs J., Malijevský A.: This Journal *45*, 977 (1980).

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