Finding Minimum-Energy Configurations of Lennard-Jones Clusters Using an Effective Potential

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We study the multiple minima problem for Lennard-Jones clusters using an effective potential which is a function of the mean position $\bar{x}$ and fluctuation σ at finite temperature. It is shown that this method smooths the potential energy hypersurface and facilitates the search for the global minimum. The method is applied to small Lennard-Jones clusters from 2 to 19 atoms and is shown to give accurate results.

1. Introduction

In many physical and chemical problems, finding the most stable structure is reduced to finding the minima of a complex multidimensional hypersurface. The most important and tempting problem of this kind is the determination of the tertiary structure of proteins, which is assumed to correspond to the global minimum of free energy. Other problems that involve multidimensional optimization are the study of the most stable structure of Lennard-Jones clusters and finding of the ground state of spin glasses. While all these problems can in principle be stated in a very simple mathematical form, the solution is considerably complicated because of the occurrence of myriads of local minima, which renders most minimalization procedures impractical. The complexity soon reaches the stage where an exhaustive search of all minima of the hypersurface is no longer manageable. To tackle this so-called “multiple minima problem”, a number of techniques have been developed.

Simulated annealing[1] searches the potential energy hypersurface by molecular dynamics or a Monte Carlo method, starting at a high temperature, which allows the method to cross energy barriers of the order kT. The system is then gradually cooled, thereby decreasing the thermal fluctuations, until the system is finally trapped in the global minimum (or a local minimum).

Recently, a different approach to multidimensional optimization was explored. Instead of locating the global minimum on the original hypersurface, the hypersurface is smoothly deformed into a surface that has a smaller number of local minima (or, in the extreme, only one global minimum). Minimization is then carried out on this simplified surface. After location of the global minimum on the simplified surface, the position of this minimum is followed as the deformation of the hypersurface is reversed, until one reaches a minimum on the original surface. Although there is no proof or justification for the assumption that the global minimum will always map back onto the global minimum, the method is very appealing and has been known to give accurate results in a number of cases. In one approach,[2,3] the hypersurface to be minimized is deformed by diffusion: the original function is considered as an initial concentration, which then diffuses according to the diffusion equation. By this diffusion process, energy barriers are flattened, while wells in the function become more shallow. This leads to the desired simplification of the surface and allows the methodology described above to be used.

An other approach is the use of the Schrödinger equation in imaginary time,[4] where one starts with the observation that the minimum of the classical potential corresponds with a maximum of the quantummechanical probability. This key observation was first made in the use of the so-called quasi-quantal methods, described in refs 5 and 6. In ref 4, the smoothing of the surface is obtained by varying the Planck constant. For large values of $\hbar$, the system is likely to tunnel trough energy barries, resulting in a simplified effective potential. The Planck constant is then gradually reduced to zero to arrive at the minimum of the original hypersurface.

Other methods using still other deformation methods include the ant−lion strategy[7] and the potential shift method.[8]

While in all methods cited thus far, the deformation is rather artificial, a number of methods exist where the deformation of the hypersurface is guided by some physical principle. This is for instance the case for the Gaussian density annealing (GDA) method,[9] where the Bloch equation for the equilibrium density distribution is approximately solved using a Gaussian ansatz. For small values of $\beta=1/kT$ this leads to a smoothing of the surface, similar to the case of simulated annealing. The mapping back to the original surface corresponds to the cooling of the system. Moreover, the deformed hypersurface now has the interpretation of the internal energy at a certain temperature, which allows one to study the physical behavior of the system as the temperature varies.

Straub and co-workers also developed a number of simulated annealing methods based on approximate solutions of the Liouville equation[10] and the Smoluchowski equation[11] which also involve a deformed potential energy hypersurface.

Another method where the potential energy surface is deformed in a more physical way is described in refs 12 and 13. In this approach, the system is considered on a spatial scale that is determined by the physical temperature. Variations of the hypersurface which are of this scale are described by Gaussian packets, while variations on smaller scales are absorbed in such a packet. It is demanded that the expectation value of a “test function” with a certain length scale is equal when calculated with the exact distribution function p_B and with a coarse-grained distribution function $\tilde{p}_\alpha$. The first three terms in the series expansion of this condition lead to a set of equations for the parameters that determine $\tilde{p}_\alpha$. We will discuss later an interesting relationship between the method proposed in this paper and the high-temperature limit of the method presented in refs 12 and 13.

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Recently, we introduced the "effective diffused potential" (EDP)[14] as a method to approximately calculate the free energy of a system. Here also, the deformation of the hypersurface is physically motivated, instead of being just a convenient mathematical trick. The method calculates an effective potential that approximates the free energy at a certain temperature. The smoothing of the original surface is obtained by considering the system at high temperatures, where a minimum can easily be found. By subsequently lowering the temperature, the position of this minimum is followed, until one reaches the original surface. Therefore, just as in GDA[9] or in simulated annealing,[1] the parameter that controls the deformation is the physical temperature. Not only does this method fit in with the other deformation techniques, but it also allows one to approximately calculate the free energy of the system at a certain temperature. The deformed potential therefore has a clear physical interpretation. Moreover, it provides a first principle derivation of diffusion or smoothing type approach to global minimization. In this paper however, we will study the method only as a technique to isolate the global minimum on a rough and complex hypersurface. As an example, we will consider the determination of the most stable structure of clusters of Lennard-Jones atoms, which has become a standard benchmark to test the validity of a method.

In section 2, we briefly recapitulate the method to obtain the effective potential. In section 3, a simple one-dimensional example is studied to illustrate the method, and in section 4, we study clusters of Lennard-Jones atoms up to 19 atoms. The conclusions and outlook are given in section 5.

2. Effective Diffused Potential (EDP)

In this section, we outline the method to obtain the EDP. More details can be found in ref 14. Our aim is to calculate an effective potential that approximates the free energy at a certain temperature. To do this, we start from the well-known Gibbs principle,[15] which states that the free energy F for a system which is described by a potential V can be found as the solution of the following variational equation:

$$\begin{aligned} F &= \underset{\{P\}}{\mathrm{Min}}\{E(P) - kT\,S(P)\} \\ &= \underset{\{P\}}{\mathrm{Min}}\{\textstyle\int[\mathrm{d}x]\,P(x)\,V(x) + kT\int[\mathrm{d}x]\,P(x)\ln(P(x))\} \end{aligned} \quad (1)$$

This means that the free energy is given by the minimal value of the right-hand side of the above expression, where one minimizes over all normalized distribution functions $P(x)$. The function $P_{\mathrm{eq}}(x)$ that minimizes the expression is the equilibrium density distribution. The complete variational problem is of course a very impractical way of calculating the free energy. One can however restrict the minimization to a certain subspace of the space of all distribution functions, obtaining an upper bound for the free energy by minimizing in the choosen subset. A simple approximation would be to assume that the distribution is localized near a postion $\bar{x}$ and the fluctuations around this position can be described by a Gaussian with dispersion σ. This leads to the following ansatz for $P(x)$:[16]

$$P(x;\bar{x},\sigma) = \frac{1}{\sqrt{2\pi\sigma}}\exp\left(-\frac{(x-\bar{x})^2}{2\sigma}\right) \quad (2)$$

For a function of more than one coordinate, eq 2 can easily be generalized by considering a multidimensional gaussian. In this article, we will choose the N-particle distribution function as a product of one-particle Gaussian functions:

$$P(\{x\},\{\bar{x}\},\{\sigma\}) = \prod_{i=1}^{N} P(x_i;\bar{x}_i,\sigma_i) \quad (3)$$

By making the ansatz (2), the expression on the right-hand side of (1) is now reduced to a function of a finite number of variables, which allows one to find an approximation to the free energy by solving a multidimensional optimization problem. The explicit form of this (Gaussian) approximation is given by

$$F(\bar{x},\sigma,T) = \frac{1}{\sqrt{2\pi\sigma}}\int_{-\infty}^{\infty}\mathrm{d}x\,V(x)\exp\left(-\frac{(x-\bar{x})^2}{2\sigma}\right) - \frac{kT}{2}[\ln(2\pi\sigma) + 1] \quad (4)$$

Interestingly, this expression can also be found by taking the high-temperature limit of the method presented in refs 12 and 13. We note however that the equations for $\bar{x}$ and σ follow from a different physical principle. In our case, they follow straightforwardly from the Gibbs principle, while in refs 12 and 13 they express the equality of the expectation values calculated with the exact and with a coarse-grained distribution function, as discussed in the Introduction. An important difference lies in the fact that with the EDP method higher order corrections to (4) in $1/kT$ can be calculated systematically,[14] corresponding to a non-Gaussian ansatz for the distribution function.

We note that the expression 4 can be written as a sum of two terms:

$$F(\bar{x},\sigma,T) = U_{\mathrm{eff}}(\bar{x},\sigma,T) - kT\,S_{\mathrm{eff}}(\bar{x},\sigma,T) \quad (5)$$

These two terms can be interpreted as an effective internal energy and an effective entropy, respectively. These are the internal energy and the entropy in our approximation.

The parameters $\bar{x}$ and σ can be found by solving the minimum equations:

$$\begin{aligned} \partial F(\bar{x},\sigma,T)/\partial\bar{x} &= 0 \\ \partial F(\bar{x},\sigma,T)/\partial\sigma &= 0 \end{aligned} \quad (6)$$

The free energy corresponds to the global minimum of these equations. Other solutions can be seen as metastable states which disappear as the temperature rises. This is similar to the method of Gaussian packet states.[12,13] The relationship and hierarchy of these states was made explicit in an interesting paper by Oresic and Shalloway.[13] In this paper, we will mainly be concerned with finding the global minimum however. The meaning of other solutions will not be discussed here.

Equation 6 leads to the following equation for σ:

$$\frac{1}{\sigma} = \frac{1}{kT}\frac{1}{\sqrt{2\pi\sigma}}\int_{-\infty}^{\infty}\mathrm{d}x\,V(x)\left[\frac{(x-\bar{x})^2}{\sigma^2} - \frac{1}{\sigma}\right]\exp\left(-\frac{(x-\bar{x})^2}{2\sigma}\right) \quad (7)$$

Upon substituting the solution $\sigma(\bar{x},T)$ of (7) into (4), one obtains a function that depends only on $\bar{x}$. We will denote this function as $V_{\mathrm{eff}}^{D}(\bar{x},T)$ and call it the effective diffused potential (EDP). The free energy of the system can now be found by minimizing this function:

$$V_{\mathrm{eff}}^{D}(\bar{x},T) = \frac{1}{\sqrt{2\pi\sigma(\bar{x},T)}}\int_{-\infty}^{\infty}\mathrm{d}x\,V(x)\exp\left(-\frac{(x-\bar{x})^2}{2\sigma(\bar{x},T)}\right) - \frac{kT}{2}[\ln(2\pi\sigma(\bar{x},T)) + 1] \quad (8)$$

One can show[14] that the Gaussian free energy (4) corresponds

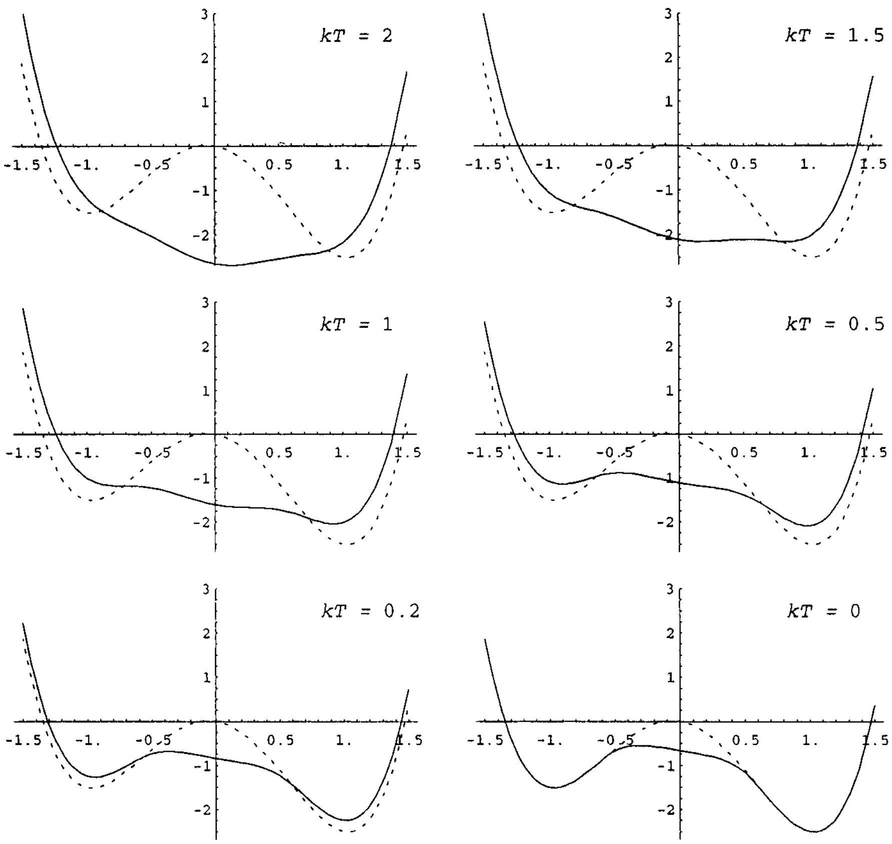

Figure 1. Effective diffused potential (solid line) compared with the potential energy (dashed line) for different values of *kT*.

to the first two terms in the high-temperature expansion of a convex effective potential $V_{\text{eff}}(\bar{x},\sigma)$ where $\bar{x}$ and σ are the mean position and the fluctuation. Higher order corrections can in principle be calculated. Furthermore, $V^D_{\text{eff}}(\bar{x},T)$ (8), obtained by minimizing (4) with respect to σ is an approximation to the exact effective potential $V_{\text{eff}}(\bar{x},T)$, which is convex in $\bar{x}$.

A closer look at the effective potential (8) reveals some simularities with the diffusion equation method (DEM) described in refs 2 and 3. In the DEM, the potential is deformed by considering the original function as an initial concentration, which is then allowed to diffuse according to the multidimensional diffusion equation in order to simplify the potential energy hypersurface. The effective potential (8) can be viewed as originating from the potential energy $V(x)$ by some sort of diffusion proces. Only in our method, the diffusion times can be different for different coordinates, which was not possible in the original DEM. Also the diffusion times are not chosen arbitrarily in order to obtain a deformation that is sufficient to easily find the global minimum, but they are determined in such a way that they correspond with a minimum of free energy. They depend not only on the temperature but also on the configuration of the system. Most importantly, the effective potential (8) that can be found using this method has a physical interpretation, which is not the case for the diffused potential in refs 2 and 3. The EDP is an approximation for the exact free energy, which separates in an energetic and an entropic contribution, as can be seen from eq 5.

3. A One-Dimensional Example

We will first study a one-dimensional example in order to illustrate the method outlined above. We consider an asymmetric double-well potential $V(x)$:

$$V(x) = 2x^4 - 4x^2 - \frac{1}{2}x \tag{9}$$

The Gaussian approximation to the free energy (4) is given by

$$F(\bar{x},\sigma,T) = -\frac{kT}{2}(\ln(2\pi\sigma) + 1) + 6\sigma^2 + \sigma(12\bar{x}^2 - 4) + V(\bar{x}) \tag{10}$$

The equation that determines σ can be solved exactly in this case and leads to the following form for $\sigma(\bar{x},T)$:

$$\sigma(\bar{x},T) = \frac{\sqrt{(12\bar{x}^2 - 4)^2 + 24kT} - (12\bar{x}^2 - 4)}{24} \tag{11}$$

Which in turn leads to the following effective potential:

$$V^D_{\text{eff}}(\bar{x},T) = -(kT/2)\ln(\sigma(\bar{x},T)) + 6\sigma(\bar{x},T)^2 + \sigma(\bar{x},T)(12\bar{x}^2 - 4) + V(\bar{x}) \tag{12}$$

In Figure 1, we have plotted this effective potential for different values of *kT*. A number of observations can be made from the form of the effective potential at different temperatures.

First of all, we note that at high temperatures, only one minimum remains, which is located between the two original minima of $V(\bar{x})$. Most of the structure of the original function has been wiped out. As we lower the temperature, the structure of V slowly reappears. Two shallow wells appear, which deepen as the temperature is lowered further. If we follow the unique minimum at high temperature, we are guided into the deeper well. As the temperature goes to zero, the minimum of the effective potential goes to the global minimum of the original function. This clearly illustrates the philosophy behind hypersurface deformation as a tool to find the global minimum of a function.

A second important observation is that the effective potential $V^D_{\text{eff}}(\bar{x},T)$ does not seem to reduce to the original function $V(\bar{x})$ in the limit $kT \rightarrow 0$ for all values of $\bar{x}$. Indeed, if we consider the expression 11 when $kT \rightarrow 0$, we find

$$\sigma(\bar{x},T=0) = \frac{|(12\bar{x}^2 - 4)| - (12\bar{x}^2 - 4)}{24} \tag{13}$$

This means that the diffusion time $\sigma(\bar{x},T)$ goes to zero only when $12x^2 - 4 \geq 0$. For the function V under consideration, this means $\partial^2 V/\partial x^2 \geq 0$. The method therefore seems to discriminate between convex regions ($\partial^2 V/\partial x^2 \geq 0$) and concave regions ($\partial^2 V/\partial x^2 \leq 0$). This may seem strange at first, but it reflects an important property of the exact free energy. If one could calculate the effective potential exactly (i.e., beyond the Gaussian approximation), one would find that it is everywhere convex: $\partial^2 V^D/\partial x^2 \geq 0$ for all values of x. In the limit $kT = 0$, the exact effective potential $V_{\mathrm{eff}}(\bar{x})$ is the convex envelope of $V(x)$.[14] The fact that the diffusion time remains nonzero in concave regions results in a flattening of these regions, which can be seen as a first onset towards convexity, which would have to be exact if one could calculate V_{eff} exactly (beyond the Gaussian approximation).

This property also holds for other potentials than the one considered in this paragraph, as can be seen from the equation for σ:

$$\frac{kT}{2\sigma} = \frac{\partial}{\partial\sigma}\langle V\rangle \tag{14}$$

where $\langle V\rangle$ is the gaussian internal energy U_{eff}, given by

$$\langle V\rangle = \int \mathrm{d}x\, P(x)\, V(x) = \frac{1}{\sqrt{2\pi\sigma}}\int \mathrm{d}x\, V(x) \exp\left(-\frac{(x-\bar{x})^2}{2\sigma}\right) \tag{15}$$

Because $\langle V\rangle$ is obtained from V by diffusion, it obeys the diffusion equation, which leads to

$$\frac{\partial}{\partial\sigma}\langle V\rangle = \frac{1}{2}\frac{\partial^2\langle V\rangle}{\partial\bar{x}^2} \tag{16}$$

Combining (14) and (16), we find

$$\sigma\frac{\partial^2\langle V\rangle}{\partial\bar{x}^2} = kT \tag{17}$$

Since the right-hand side of this equation is always positive, the same must hold for the left-hand side. Since $\sigma \geq 0$, this means that $\partial^2\langle V\rangle/\partial\bar{x}^2$ must also be positive for all values of $\bar{x}$. If $\bar{x}$ lies in a region where the original function V is concave, this can be achieved only by not letting $\sigma \rightarrow 0$ as $kT \rightarrow 0$, but by keeping it fixed at a value for which $\langle V\rangle$ is convex. Therefore the effective potential does not reduce to the original potential for regions that are not convex. However, since V^D does converge to the potential V for convex regions, the method can still be used to search for minima of the original function.

We note that a similar flattening of concave regions is clearly visible in the double-well potential studied in ref 4, using the Schrödinger equation in imaginary time. There the phenomenon is explained by the fact that the equations of motion for the Gaussian wave packet tend to increase the rate at which the packet expands when it is situated in a region with negative curvature, leading to a delocalization of the wave packet in these regions.

4. Clusters of Lennard-Jones Atoms

The study of clusters of Lennard-Jones atoms originated within the framework of nucleation theory. The most stable configurations of these clusters have since then been the subject of numerous studies. Since the number of local minima on the potential energy hypersurface grows rapidly with the number of particles in the cluster,[17] an exhaustive search is almost impossible for more than 13 particles. To study the most stable configurations, a number of growth schemes were examined to determine the most stable configuration.[19] It was found that for small numbers of particles, the most stable configurations are compact packings with a pentagonal character, rather than other common lattice structures. It is expected that for large numbers of atoms, the most stable structure will become the face-centered cubic lattice.

TABLE 1: Amplitudes and Dispersions for the Four-Gaussian Fit to the Potential (18)

	1	2	3	4
a_k	846 706.7	2 713.651	−0.715 442	−9.699 172
b_k	15.46 441	7.346 88	0.639 62	1.850 37

In this paper we want to study the most stable structures of small clusters of atoms, interacting via two-body Lennard-Jones potentials. We work with the standard form of the Lennard-Jones potential, defined as follows:

$$V_{\mathrm{LJ}}(r) = 4\left(\frac{1}{r^{12}} - \frac{1}{r^6}\right) \tag{18}$$

The complete potential funtion of the cluster is given by the sum of all possible two-body potentials:

$$V = \sum_{i>j} V_{\mathrm{LJ}}(|\vec{r}_i - \vec{r}_j|) \tag{19}$$

We make the following ansatz for the multiparticle distribution function:

$$P(\{\vec{x}\},\{\bar{\vec{x}}\},\{\sigma\}) = \prod_{i=1}^{N} \frac{1}{(2\pi\sigma_i)^{3/2}} \exp\left(-\frac{(\vec{x}_i - \bar{\vec{x}}_i)^2}{2\sigma_i}\right) \tag{20}$$

One could consider anisotropic Gaussian packets by assigning different dispersions to the x, y, and z components of the coordinates, but we will not use this possibility here.

To obtain the effective potential, we have to calculate the internal energy $\int P(x)\, V(x)$. Because the potential is divergent in the origin, the diffused potential cannot be calculated. It is however physically sensible to replace the exact potential with a form that is finite in the origin, as long as this form is a good approximation to the exact potential in the physically relevant domain. Therefore, we replace the actual two-body Lennard-Jones potential with a four-term sum of Gaussians which gives a very accurate approximation to the exact function, i.e., $V(r) \simeq \sum_{k=1}^{4} a_k \mathrm{e}^{-b_k r^2}$. The amplitudes and dispersions are taken from ref 4 and are collected in Table 1.

The internal energy is unlikely to be affected much by the regularisation when $P(x)$ is small in the "unphysical" regions (where V becomes huge). Since the atoms are well seperated, even on the smoothed surface, this condition will be fulfilled.

With the approximation $V_{\mathrm{LJ}}(r) = \sum_k a_k \mathrm{e}^{-b_k r^2}$, the internal energy is now easily calculated in closed form:

$$\int P(x)\, V(x) = \sum_{i>j}\sum_k \tilde{a}_k^{(ij)}\, \mathrm{e}^{-\tilde{b}_k^{(ij)}|\bar{\vec{r}}_i - \bar{\vec{r}}_j|^2} \tag{21}$$

with

$$\tilde{a}_k^{(ij)} = a_k/(1 + 2(\sigma_i + \sigma_j)b_k)^{3/2}$$
$$\tilde{b}_k^{(ij)} = b_k/(1 + 2(\sigma_i + \sigma_j)b_k) \qquad (22)$$

Because the clusters are not thermodynamically stable, they have to be confined to a finite volume in order to calculate the free energy, as is done in Monte Carlo simulations (see for instance ref 20). For large values of T, the entropy term drives the dispersions to infinity when no confining force is imposed. We will therefore use a confining potential in order to prevent the clusters from dissociating. This potential is a harmonic potential which biases the system toward small interatomic distances and is of the form that was also used in ref 4:

$$V_{\text{confine}} = \lambda \sum_{i>j} |\vec{r}_i - \vec{r}_j|^2 \qquad (23)$$

The value of λ should be sufficiently big to prevent dissociation and sufficiently small in order not to significantly disturb the minimum-energy configuration. In our calculations, we have set $\lambda = 0.01$ for all clusters, except for the smaller ones ($N \leq 7$), where λ is between 0.02 and 0.05, because these clusters seemed to require a larger value for λ in order to prevent the atoms from escaping.[21] The internal energy contribution from this confining potential is also easily calculated:

$$\lambda \sum_{i>j} |\vec{r}_i - \vec{r}_j|^2 + 3\lambda(N-1)\sum_i \sigma_i \qquad (24)$$

Using (21), (24), and (5), we find the following expression for $F(\bar{x},\sigma,T)$:

$$F(\bar{x},\sigma,T) = -\frac{kT}{2}\left[3\sum_{i=1}^{N} \ln(2\pi\sigma_i) + 3N\right] + \sum_{i>j}\sum_k \tilde{a}_k^{(ij)} e^{-\tilde{b}_k^{(ij)}|\vec{r}_i - \vec{r}_j|^2} + \lambda \sum_{i>j} |\vec{r}_i - \vec{r}_j|^2 + 3\lambda(N-1)\sum_i \sigma_i \qquad (25)$$

To find the minimum of the potential 19, the expression 25 was first minimized at high temperature (for all configurations kT was chosen equal to 3.5), starting from a random configuration in $\{\bar{x}_i\}$ and with all dispersion σ_i set equal (typically equal to 1). Minimization was carried out simultaneously in the dispersions and the coordinates, regarding the free energy (25) as a function of $4N$ parameters ($3N$ coordinates and N dispersions). After a minimum (in σ_i and $\vec{r}_i$) had been found at this temperature, the evolution of this minimum was followed as the temperature was gradually lowered according to an exponential cooling scheme $T_i = \alpha^i T_0$, with $\alpha = 0.96$. Once a minimum has been found at a certain temperature, the temperature was lowered and the found minimum configuration was used as a starting configuration for minimization at the new temperature. To find the new minimum, we used a conjugate gradient algorithm, the Fletcher−Reeves−Polak−Ribiere method.[22] After a minimum was reached for $T \simeq 0$, the confining potential was removed and the minimum configuration was further refined using the exact Lennard-Jones potential. Once a minimum has been found on the simplified surface at the highest (starting) temperature, the trajectory of this minimum is therefore fully deterministic, contrary to, for instance, simulated annealing.

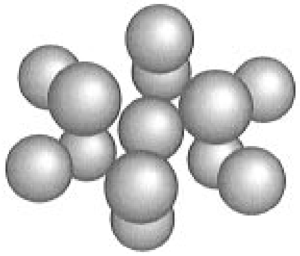

Figure 2. Minimum energy structure of the 13-atom cluster. The atoms are situated on the vertices and in the center of a Mackay icosahedron.

TABLE 2: Results from the Minimum Search of the Effective Diffused Potential, Compared with the Exact Results

no. of atoms	no. of minima	exact result	EDP	
2	1	−1.000	−1.000	+
3	1	−3.000	−3.000	+
4	1	−6.000	−6.000	+
5	2	−9.104	−9.104	+
6	2	−12.712	−12.712	+
7	4	−16.505	−16.505	+
8	8	−19.822	−19.765	−
9	18	−24.113	−23.270	−
10	57	−28.420	−28.422	+
11	145	−32.765	−32.765	+
12	366	−37.967	−37.967	+
13	988	−44.327	−44.327	+
14	∼3258	−47.845	−47.845	+
15	∼10700	−52.322	−52.322	+
19	∼2 × 10^6	−72.659	−72.659	+

To eliminate the randomness introduced by chosing a random initial configuration, the minimization was repeated from different starting positions (typically 10 for each value of N). For almost all values of N, the same minimum was recovered on every trial, indicating that the method does not significantly depend on the initial configuration. In a few cases, one of the trials would end up in a different (local) minimum. This happened very rarely (if it happened at all for a certain value of N, only one trial out of ten would “miss”) and may be due to the fact that the random configurations were chosen truely at random, without checking whether they correspond to a physically possible configuration. In ref 4 the configurations were not generated ad random but chosen by taking N atoms from an equilibrium liquid configuration of 256 atoms. The fact that our configurations were “truely” random may account for the few missed trials.

The results of our method are summarized in Table 2. From Table 2 we learn that the agreement with the exactly known values is indeed very good. Only for eight- and nine-cluster atoms, the method ends up not in the global minimum but in the first excited state. In the case of an eight-atom cluster these states are very close in energy (less than 0.3%), which could explain why the method seems to miss the global minimum. We also remark that the coupling strength of the confining potential (λ) can play a role in finding the global minimum. By tuning λ to a precise value, one can sometimes make the system end up in the different minimum. We have made no attempt however to “optimize” the value of λ for each value of N.

The case of the 12-atom cluster merits special attention. Our method correctly identifies the global minimum, which is a Mackay icosahedron with one surface atom removed (see Figure 3). The DEM, on the other hand, identified a Mackay icosahedron with the central atom removed as the final structure.[3] This may be due to the fact that the DEM uses the same dispersion for all particles. This can result in a more symmetrical configuration then when particles are allowed to have different dispersions. In the case of the 12-atom cluster, the dispersion of the “central” atom is considerably smaller than that of the surface atoms, a fact that will be missed if all

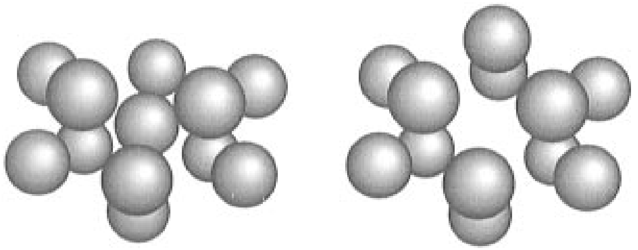

Figure 3. Minimum energy structure of the 12-atom cluster, as predicted by the effective diffused potential approach (left) and by the DEM (right). The correct structure is a Mackay icosahedron with one surface atom removed (left), while the DEM predicts a Mackay icosahedron with the central atom removed (right).

dispersion are set equal. By allowing different dispersions, our method therefore improves on a number of shortcomings of the DEM.

Finally, we note that also the minimum of the 19-atom cluster is identified correctly using our method, in contrast with the result of the DEM. Here also, there are two dispersions which are considerably smaller than the average dispersion.

5. Conclusion

We have applied the EDP method to the multiple-minima problem of Lennard-Jones clusters. It was shown how this method smooths the original surface, thereby eliminating irrelevant minima. By searching the location of the minimum at high temperature and tracking the evolution of this minimum as the temperature is lowered, we have set up a deterministic algorithm to find the global minimum on a complicated multidimensional hypersurface. The method always gives very good results, even when the global minimum is not correctly identified, as is the case for eight- and nine-atom clusters. Overall, it constitutes a considerable improvement of the diffusion equation method.[2,3]

Moreover, the method we have proposed has a physical interpretation. Since the effective potential is at every temperature an approximation of the free energy at that temperature, it can also be used to study the free energy of small clusters. This is the subject of our present research.[23] Finally, we note that the use of Smoluchowski dynamics[11] in the static limit (no time dependence) leads to equations similar to (6) and (7). We can easily combine these equations by directly minimizing in the $4N$-dimensional space of coordinates and dispersions. Also, with the method proposed in ref 11 it is not possible to approximately calculate free energies.

We also noted the relationship between our method and the high-temperature limit of the method presented in refs 12 and 13. The physical principles behind both methods are quite distinct, however, as are the computational techniques used to find the solutions. In refs 12 and 13, the equations are solved by iteration, while we perform a minimalization at each step. Also, we feel that our method offers some computational advantages. In ref 13, multidimensional integrals are evaluated using Monte Carlo integration, while in ref 12 these integrals are approximated by a factorized ansatz. This involves the tabulation of the effective two-body potential for different temperatures. While this is not problematic for Lennard-Jones clusters, it will be much harder when different types of potentials occur (e.g., Lennard-Jones potentials with coefficients dependent on the type of atom pair).

Finally, our approach follows from a simple first principle (the Gibbs principle) and allows for systematic corrections in the $1/kT$ expansion to be calculated (see ref 14).

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