Dynamical calculation of the spontaneous decay constant of a cluster of identical atoms

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The dynamical method developed in a previous work [R. L. Stratonovich, Zh. Éksp. Teor. Fiz. **108**, 1326 (1995) [JETP **81**, 729 (1995)] for the purpose of calculating the average time until escape from a potential well is used to investigate the spontaneous decay of a cluster of identical atoms which attract one another. The decay constant with an arbitrary number of atoms is found for a simplified model of the interaction. The decay of a cluster of three atoms is studied in a more realistic approach for two forms of the interaction: square well and Lennard-Jones potential. © *1996 American Institute of Physics.* [S1063-7761(96)01110-9]

1. INTRODUCTION

In the present paper the dynamical method proposed in Ref. 1 for investigating escape from a potential well is elaborated for the problem of calculating the spontaneous decay constant of a cluster or a metastable molecule.

Previously, the diffusive Markov theory of the approach to a boundary was employed to solve problems associated with escape from a potential well (see, for example Refs. 2–4). However, when the number of atoms in the cluster is not too large, there are no grounds for assuming that statistically independent δ-correlated Langevin forces operate in the system, so that, strictly speaking, this theory cannot be used to investigate the spontaneous decay of such clusters and molecules. The purely dynamical method is based on the fact that the dynamical process is a fluctuational consequence of self-stochastization, i.e., dynamical chaos. If the average time until escape (decay) is much longer than the time constant for establishing a stationary or quasistationary probability distribution in phase space, then it can be assumed that for the overwhelming majority of the time the system possesses a distribution close to an equilibrium distribution in a stable system obtained from the initial distribution by a small deformation. The insertion of an additional wall at the top of the potential barrier can serve as such a deformation preventing the escape of phase points.

In Sec. 2 a simplified model of the interaction of atoms in a cluster such that the attraction between the atoms is seemingly separated from the repulsion between atoms is studied. The decay of the cluster then becomes analogous to the efflux of a gas of atoms, which repel one another, from a potential well. True, the dimensions of the well are microscopic and the velocity distribution of the atoms is not Maxwellian. In more realistic models the interatomic attraction is inseparable from the interatomic repulsion.

In the present paper we take as the equilibrium distribution in the deformed system the microcanonical distribution

$$w(q,v)=C\delta(T(v)+U(q)-E), \tag{1.1}$$

where $T(v)=T_1(p(v))$ is the kinetic energy expressed in terms of the velocity $v=\dot{q}$. It is equivalent to the distribution $w_1(q,p)=C_1\delta(H(q,p)-E)$, since the Jacobian of the transformation $p=p(v)$ is constant and can be included in the normalization constant.

A stationary distribution in the deformed system can be used to find the decay constant a of the initial system, if this constant is small. The constant a is the escape probability per unit time. In Ref. 1 the formula

$$a=\int_{\Gamma_-} w_2(x)f_\alpha(x)d\Gamma^\alpha, \tag{1.2}$$

was proposed for this constant. We shall employ this formula. Here $x=(q,p)$ or $x=(q,v)$, $f_\alpha(x)=\dot{x}_\alpha(x)$, Γ is a closed hypersurface in phase space, and Γ_- is the part of the hypersurface that corresponds to the condition of escape from a region lying inside Γ: $f_\alpha d\Gamma^\alpha>0$.

We shall employ the formula in the following variant: (1.2):

$$a=\int_{S_0} w(q,v)\,\eta(v_jn_j)v_jn_jdS_0dv, \tag{1.3}$$

where S_0 is a closed hypersurface in coordinate space, n_j is the unit outer normal vector to S_0, v_jn_j is the scalar product of multidimensional vectors, and $\eta(y)=(1+\text{sign } y)/2$. Introducing the factor $\eta(v_jn_j)$, which selects the phase points where $\Sigma_j v_jn_j>0$, is analogous to selecting the exit part Γ_- of the surface Γ in Eq. (1.2). In Eq. (1.3) $v_jn_jdS_0dv$ plays the role of $f_\alpha d\Gamma^\alpha$.

It is natural to place the hypersurface S_0, the crossing of which by an image point symbolizes the decay of a cluster, at the top of the potential barrier. This is how we proceed in the case of a square well. However, in many cases, for example, in the case of the Lennard-Jones interaction potential, the top of the barrier is at infinity. The question of where to place the boundary surface in this case is examined below in Sec. 5.

In determining the normalization constants in Eq. (1.1) and also the decay constant (1.3), it is necessary to calculate multiple integrals, whose multiplicity can be lowered to some limit. For example, in the case of a cluster consisting of three atoms there remains a triple integral that determines the normalization constant and in the case of four atoms a six-

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fold integral remains. To make it easier to calculate the integrals, in Sec. 2 a simplified model of the interaction is studied. In this model the constant a can be found for an arbitrary number N of atoms. In the limit $N\to\infty$ the result assumes a form that is well known from the diffusion theory of the approach to a boundary.

2. SPONTANEOUS DECAY CONSTANT IN THE SIMPLEST MODEL

Consider a cluster consisting of N identical atoms that is described by the Lagrangian

$$L=\frac{m_0}{2}\sum_{\alpha=1}^{N}|\dot{\mathbf{q}}_\alpha|^2-U(q), \tag{2.1}$$

where $\mathbf{q}_\alpha$ is the radius vector of the αth atom and U is the potential energy. In the case (2.1) we have the momenta $\mathbf{p}_\alpha=\partial L/\partial\dot{\mathbf{q}}_\alpha=m_0\dot{\mathbf{q}}_\alpha$ and the Hamiltonian

$$H=\frac{1}{2m_0}\sum_{\alpha=1}^{N}|\mathbf{p}_\alpha|^2+U(q).$$

In the case of pair interactions the potential energy has the form

$$U(q)=\sum_{\substack{\alpha,\beta=1\\ \alpha<\beta}}^{N}\Phi(|\mathbf{q}_\alpha-\mathbf{q}_\beta|), \tag{2.2}$$

where the sum contains $N(N-1)/2$ terms. The simplest pair interaction potential which takes account of both the attraction and repulsion between the atoms is the square well:

$$\Phi(r)=\begin{cases}\infty, & r<\sigma,\\ -\varepsilon, & \sigma<r<d,\\ 0, & r>d.\end{cases} \tag{2.3}$$

It can be represented as a sum of two terms $\Phi_1(r)+\Phi_2(r)$, where $\Phi_1(r)=\infty$ for $r<\sigma$, $\Phi_1(r)=0$ for $r>\sigma$, and $\Phi_2(r)=-\varepsilon\,\eta(d-r)$. The term $\Phi_1(r)$ corresponds to the repulsion between absolutely rigid spheres with diameter σ and $\Phi_2(r)$ corresponds to attraction. Now we shall greatly simplify the problem, setting

$$U=\sum_{\alpha<\beta}\Phi_1(|\mathbf{q}_\alpha-\mathbf{q}_\beta|)+\Phi_2(\max_\alpha|\mathbf{q}_\alpha|), \tag{2.4}$$

i.e., we change the mechanism of attraction. The role of the sum $\Sigma\Phi_1(|\mathbf{q}_\alpha-\mathbf{q}_\beta|)$ is to ensure dynamical chaos in the system. After dynamical chaos is ensured, it can be assumed that the constant σ is small. The microcanonical distribution (1.1) in the case of the potential (2.4) can be written as

$$w(q,v)=\begin{cases}C\delta\left(\sum_\alpha|v_\alpha|^2-2m_0^{-1}(E+\varepsilon)\right) & \text{for } q\in R'-R'',\\ 0 \text{ outside } R'-R''.\end{cases} \tag{2.5}$$

Here R' denotes the region in the $3N$-dimensional space where $|\mathbf{q}_1|<d,\ldots,|\mathbf{q}_N|<d$ and R'' denotes the part in the region R' where $|\mathbf{q}_\alpha-\mathbf{q}_\beta|<\sigma$ holds for at least one pair of indices (α,β). It is easy to see that the volume of $R_0=R'-R''$ equals

$$V_0=\int_{R'}d\mathbf{q}_1\ldots d\mathbf{q}_N\prod_{\alpha<\beta}[1+f(\mathbf{q}_\alpha-\mathbf{q}_\beta)].$$

Here we have $f(\mathbf{r})=-1$ for $r<\sigma$ and $f(\mathbf{r})=0$ for $r>\sigma$. It is convenient to write $\Sigma=V^{-N}V_0$, where $V=4\pi d^3/3$. The integral over R' can be written as

$$V^N\Sigma=\sum\prod_{j=1}^{N}\frac{1}{m_j!}(Vb_j)^{m_j}$$

(see Eq. (2.4) from Ref. 5). Here, the summation extends over all different sets of values of m_j satisfying the condition

$$\sum_j jm_j=N,$$

where b_j are the well-known cluster integrals (Eqs. (2.5) and (4.2) from Ref. 5). The normalization constant C in Eq. (2.5) is determined from the condition

$$C\int_{R_0}dq\int d\mathbf{v}\,\delta\left(v^2-2\frac{E_0}{m_0}\right)=CV_0\Omega_{3N}\int_0^\infty\delta\left(v^2-2\frac{E_0}{m_0}\right)v^{3N-1}dv=1. \tag{2.6}$$

Here, v is the magnitude of the $3N$-dimensional vector $\mathbf{v}=(\mathbf{v}_1,\ldots,\mathbf{v}_N)$ and $E_0=E+\varepsilon$. We have transformed to hyperspherical coordinates. The integration over angles has resulted in the appearance of the explicit solid angle Ω_{3N} in $3N$-dimensional space. It can be determined, e.g., by the formulas of Ref. 6 (p. 287). The integration in Eq. (2.6) is easily completed:

$$\int_0^\infty\delta\left(v^2-2\frac{E_0}{m_0}\right)v^{3N-2}\frac{dv^2}{2}=\frac{1}{2}\left(\frac{2E_0}{m_0}\right)^{(3N-2)/2}$$

Therefore

$$C=2V_0^{-1}\Omega_{3N}^{-1}(2E_0/m_0)^{-(3N-2)/2}. \tag{2.7}$$

To define the decay constant $a=1/\tau_{av}$ by the inverse average lifetime τ_{av} until the detachment of the first atom, we employ Eq. (1.4), where

$$v_jn_j=\sum_j v_jn_j=\mathbf{v}\cdot\mathbf{n}$$

is the scalar product of $3N$-dimensional vectors.

In our case we must make a stipulation with respect to the formula (1.3). The problem is that the distribution (2.5) appearing in the integrand undergoes a jump at the boundary surface S_0 on account of Eq. (2.4). For this reason, the integrand must be determined more accurately. We shall take $w(q,v)$ to be the values of this function outside the region R_0. There the potential energy equals zero. Therefore, in Eq. (1.3) we set

$$w(q,v)=C\delta\left(\sum_\alpha|\mathbf{v}_\alpha|^2-2\frac{E}{m_0}\right). \tag{2.8}$$

If, however, $w(q,v)$ is taken to be $C\delta(\Sigma_\alpha|\mathbf{v}_\alpha|^2-2E_0/m_0)$, which corresponds to the interior points of the region R_0, then $\eta(\mathbf{v}\cdot\mathbf{n})$ must be replaced by $\eta(\mathbf{v}\cdot\mathbf{n}-\sqrt{2\varepsilon/m_0})$. The last factor will select only the velocities at which an atom approaching the potential barrier is capable of overcoming the barrier. This happens when the kinetic energy $m_0(\mathbf{v}\cdot\mathbf{n})^2/2$ of its degree of freedom perpendicular to $\mathbf{n}$ is greater than ε.

In our case the surface S_0 decomposes into N sections

$$S_0=\sum_{\alpha=1}^{N} S_\alpha. \tag{2.9}$$

Here, S_α is a hypersurface, determined by the equation $|\mathbf{q}_\alpha|=d$, in $3N$-dimensional space, while the other vectors $\mathbf{q}_1,...,\mathbf{q}_{\alpha-1},\mathbf{q}_{\alpha+1},...,\mathbf{q}_N$ are less than d in magnitude. The contributions from different sections S_α are the same on account of the symmetry of the problem. Therefore we can put the expression (1.3) into the form

$$a=N\int w(q,v)\eta(\mathbf{v}_1\cdot\mathbf{l}_1)\mathbf{v}_1\mathbf{l}_1 dK_1 \times d\mathbf{q}_2...d\mathbf{q}_2...d\mathbf{q}_N d\mathbf{v}_1...d\mathbf{v}_N, \tag{2.10}$$

where we have written $\mathbf{v}_1=\mathbf{q}_1$, $\mathbf{l}_1=\mathbf{q}_1/q_1$, and K_1 is a sphere determined by the equation $|\mathbf{q}_1|=d$.

In Eq. (2.10) it is desirable to integrate first over $\mathbf{v}_2,...,\mathbf{v}_N$. We introduce into the analysis the $3(N-1)$-component vector $\mathbf{u}=(\mathbf{v}_2,...,\mathbf{v}_N)=u\boldsymbol{\nu}$ where u is its magnitude and $\boldsymbol{\nu}=\mathbf{u}/u$ is a unit vector. Transforming to hyperspherical coordinates and integrating over the angles and u gives

$$\int \delta\left(u^2+v_1^2-\frac{2E}{m_0}\right)d\mathbf{u}=\frac{1}{2}\Omega_{3N-3}\left(\frac{2E}{m_0}-v_1^2\right)^{(3N-5)/2}\eta\left(\frac{2E}{m_0}-v_1^2\right).$$

Using this equality and also the formulas (2.7) and (2.9), we obtain from the expression (2.10)

$$a=N\frac{\Omega_{3N-3}}{\Omega_{3N}}\frac{1}{V_0}\left(\frac{m_0}{2E_0}\right)^{(3N-2)/2}\int\left(\frac{2E}{m_0}-v_1^2\right)^{(3N-5)/2}\eta\left(\frac{2E}{m_0}-v_1^2\right)\eta(\mathbf{v}_1\mathbf{l}_1)\mathbf{v}_1\mathbf{l}_1 dK_1 d\mathbf{v}_1. \tag{2.11}$$

In this integral we integrate over $\mathbf{v}_1$ first, setting $v_1^2=v_\parallel^2+|v_\perp|^2$ and $d\mathbf{v}_1=dv_\parallel d\mathbf{v}_\perp$, where $v_\parallel=\mathbf{v}_1\cdot\mathbf{l}_1$ and $\mathbf{v}_\perp$ is a two-component vector lying in a plane perpendicular to $\mathbf{l}_1$. In addition, we switch to polar coordinates:

$$\mathbf{v}_\perp=(v_\perp\cos\varphi, v_\perp\sin\varphi),\quad v_\perp>0.$$

Then

$$\int_{v_1<v_0}(v_0^2-v_\parallel^2-v_\perp^2)^\kappa\eta(v_\parallel)v_\parallel d\mathbf{v}_1 = 2\pi\int_0^{v_0}dv_\parallel v_\parallel\int_0^{\sqrt{v_0^2-v_\parallel^2}}dv_\perp v_\perp(v_0^2-v_\parallel^2-v_\perp^2)^\kappa$$

$$=\frac{\pi}{2}\frac{v_0^{2(\kappa+2)}}{(\kappa+1)(\kappa+2)},$$

where $v_0=\sqrt{2E/m_0}$ and $\kappa=(3N-5)/2$. Here the integration over $\mathbf{v}_\perp$, is performed first and then the integration over $v_\parallel$ is performed. After the integration over $\mathbf{v}_1$, the integration over the sphere K_1 is trivial. Finally, we obtain from Eq. (2.11)

$$a=\frac{2\pi}{\Sigma d}\frac{\Omega_{3N-3}}{\Omega_{3N}}\left(1-\frac{1}{N}\right)^{-1}(3N-1)^{-1}\times\sqrt{\frac{2E}{m_0}}\left(1+\frac{\varepsilon}{E}\right)^{-(3N-2)/2} \tag{2.12}$$

It is convenient to write

$$E_1=2(E+\varepsilon)/3N. \tag{2.13}$$

This is twice the kinetic energy per degree of freedom of an atom inside R_0. In the case of the canonical Gibbs distribution, kT (where k is Boltzmann's constant and T is the absolute temperature) plays the role of E_1. Substituting Eq. (2.13), we obtain from Eq. (2.12) the probability per atom of an atom escaping from a cluster:

$$\frac{a}{N}=\frac{2\pi}{\Sigma}\frac{\Omega_{3N-3}}{\Omega_{3N}}N^{-3/2}\left(1-\frac{1}{N}\right)^{-1}\times\left(3-\frac{1}{N}\right)^{-1}d^{-1}m_0^{-1/2}\left(3E_1-2\frac{\Delta U}{N}\right)^{1/2}\times\left(1-\frac{2\Delta U}{3NE_1}\right)^{(3N-2)/2} \tag{2.14}$$

($\Delta U=\varepsilon$). This is the main result of this section. Holding the quantity (2.13) fixed as N and E increase, hence we obtain in the case $\sigma\ll d/N^{1/3}$ (this condition is not necessary, but it gives a simplification) the asymptotic formula

$$\frac{a}{N}\approx(2\pi)^{-1/2}d^{-1}m_0^{-1/2}(3E_1)^{1/2}\times\exp\left(-\frac{\Delta U}{E_1}+\frac{\sigma^3}{2d^3}N^2\right). \tag{2.15}$$

Here, the asymptotic formula $\Omega_M\approx(M/\pi)^{1/2}(2\pi e/M)^{M/2}$, which is valid for $M\gg1$, and Eq. (2.17) from Ref. 5 were used. Besides $b_1=1$, the cluster integral $b_2=-2\pi\sigma^3/3$ has been used.

The exponential factor $\exp(-\Delta U/E_1)$, where $E_1=kT$, in Eq. (2.15) is also given by the diffusion theory of the approach to a boundary. However, it is difficult to determine the pre-exponential factor in the multidimensional case by means of this theory. The factor $\exp[\sigma^3N^2/(2d^3)]$ is due to the rigid repulsion of the atoms, which decreases the free space available for motion and increases the frequency of collisions with the wall of the potential well. However, it should be kept in mind that as a increases, the theory becomes inapplicable.

The variable $y=d(m_0/\Delta U)^{1/2}a/N$ as a function of $E_1/\Delta U$, as described by Eqs. (2.14) and (2.15), is plotted in Fig. 1 for different values of the number N of atoms (numbers on the curves) for the case $\sigma=0$.

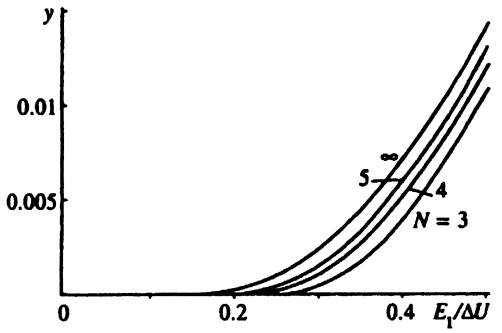

FIG. 1.

3. ELIMINATION OF THE DYNAMICAL VARIABLES OF THE CENTER OF MASS

The model examined in the preceding section is extremely simplified. We shall not use it below. First, we shall eliminate the drawback that the potential energy is not translationally invariant and we shall assume that U in Eq. (2.1) depends only on differences $\mathbf{q}_\alpha-\mathbf{q}_\beta$. Then the number of dynamical variables can be decreased by eliminating the center-of-mass variables.

We introduce new coordinates, specifically, center-of-mass and relative coordinates:

$$\mathbf{R}=\frac{1}{N}\sum_{\alpha=1}^{N}\mathbf{q}_\alpha,\quad \mathbf{r}_\sigma=\mathbf{q}_\sigma-\mathbf{q}_N,\quad \sigma=1,\ldots,N-1. \tag{3.1}$$

It is easy to invert Eq. (3.1):

$$\mathbf{q}_\sigma=\mathbf{R}+\mathbf{r}_\sigma-\frac{1}{N}\sum_{\tau=1}^{N-1}\mathbf{r}_\tau,\quad \mathbf{q}_N=\mathbf{R}-\frac{1}{N}\sum_{\tau=1}^{N-1}\mathbf{r}_\tau. \tag{3.2}$$

Substituting Eqs. (3.2) into Eq. (2.1), we obtain the Lagrangian in the new variables:

$$L=\frac{1}{2}Nm_0|\dot{\mathbf{R}}|^2+\frac{1}{2}m_0\sum_{\sigma=1}^{N-1}|\dot{\mathbf{r}}_\sigma|^2-\frac{m_0}{2N}\left|\sum_{\sigma=1}^{N-1}\dot{\mathbf{r}}_\sigma\right|^2-U. \tag{3.3}$$

The first term on the right-hand side. $Nm_0|\dot{\mathbf{R}}|^2/2$, is the kinetic energy of the center of mass of a cluster. Since the behavior of the center of mass is trivial, we shall not study its dynamical variables and we shall drop the indicated term. Then

$$L=\frac{1}{2}m_{jk}\dot{x}_j\dot{x}_k-U(x)\equiv T_2(\dot{x})-U(x), \tag{3.4}$$

where $x=(x_1,\ldots,x_n)=(\mathbf{r}_1,\ldots,\mathbf{r}_{N-1})$, i.e., we have constructed from $\mathbf{r}_1,\ldots,\mathbf{r}_{N-1}$ the vector x with $n=3(N-1)$ components. Summation over repeated indices is implied in Eq. (3.4) and below. The form of the mass matrix $\hat{M}=[m_{jl}]$ is easily seen by comparing (3.3) and (3.4):

$$\hat{M}=m_0\left(\hat{1}_n-\frac{N-1}{N}\hat{1}_3\otimes\hat{E}_{N-1}\right). \tag{3.5}$$

Here $\hat{1}_n=[\delta_{jk}]$, and

$$\hat{1}_3=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix},$$

$$\hat{1}_3\otimes\hat{E}_{N-1}=\frac{1}{N-1}\begin{pmatrix}\hat{1}_3&\hat{1}_3&\cdots&\hat{1}_3\\\hat{1}_3&\hat{1}_3&\cdots&\hat{1}_3\\\vdots&\vdots&\ddots&\vdots\\\hat{1}_3&\hat{1}_3&\cdots&\hat{1}_3\end{pmatrix}, \tag{3.6}$$

i.e., $\hat{E}_{N-1}$ is a $(N-1)\times(N-1)$ matrix, all of whose elements equal $1/(N-1)$. It is easily verified that it possesses the property

$$\hat{E}_{N-1}^2=\hat{E}_{N-1} \tag{3.7}$$

for any $N-1\geqslant 1$. Therefore, its eigenvalues all equal 0 or 1. If we write down the characteristic equation, it is easy to verify that one eigenvalue equals 1 and all others equal 0. On account of the property (3.7), any function g_0 satisfies the formula

$$g_0(a(\hat{1}_n-\hat{1}_3\otimes\hat{E}_{N-1})+b\hat{1}_3\otimes\hat{E}_{N-1})=g_0(a)(\hat{1}_n-\hat{1}_3\otimes\hat{E}_{N-1})+g_0(b)\hat{1}_3\otimes\hat{E}_{N-1}, \tag{3.8}$$

where a and b are numbers. This formula makes it possible to find $\hat{M}^{-1}$ and to switch to the momenta that are conjugate to x_j, but there is no need for us to do so, since instead of the microcanonical distribution we can study just as successfully the equivalent distribution (1.1), i.e.,

$$w(x,v)=C\delta(m_0^{-1}m_{ij}v_iv_j-2m_0^{-1}[E-U(x)]), \tag{3.9}$$

where $v_j=\dot{x}_j$. From the normalization condition for the probability density (3.9), using Eqs. (A1) and (A2) from the Appendix, we find

$$C^{-1}=\frac{1}{2}\Omega_n\left(\frac{2}{m_0}\right)^{(n-2)/2}\det{}^{-1/2}(m_0^{-1}\hat{M})\times\int_{R_0}[E-U(x)]^{(n-2)/2}\eta(E-U(x))d^nx. \tag{3.10}$$

Here the role of the factor $\eta(E-U(x))$ is to select the part of the space where $E>U(x)$, i.e., (by virtue of Eq. (3.9)) where $m_{jk}v_jv_k>0$. In Eq. (3.10) R_0 is the region of the states of the cluster.

According to Eqs. (3.6) and (3.5) and on account of what has been said above concerning the eigenvalues of the matrix $\hat{E}_{N-1}$, the matrix $\hat{M}/m_0$ possesses three eigenvalues equal to $1/N$. The remaining eigenvalues equal 1. Therefore, Eq. (3.10) assumes the form

$$C^{-1}=\frac{1}{2}\Omega_{3N-3}\left(\frac{2}{m_0}\right)^{(3N-5)/2}N^{3/2}\times\int_{R_0}[E-U(x)]^{(3N-5)/2}\eta(E-U)d^nx. \tag{3.11}$$

We now define the region R_0 of states of the cluster and the boundary S_0, the crossing of which signifies decay of the

cluster of R_0. This definition is somewhat arbitrary, because a decision must be made as to what constitutes decay of the cluster.

Let r_0 be a number. It is convenient to introduce vectors $\mathbf{q}_{\alpha\beta}=\mathbf{q}_\alpha-\mathbf{q}_\beta$ which are written as follows in the variables $\mathbf{r}_1,...,\mathbf{r}_{N-1}$: $\mathbf{q}_{\sigma\tau}=\mathbf{r}_\sigma-\mathbf{r}_\tau$ for $\sigma,\tau\leqslant N-1$ and $\mathbf{q}_{\sigma N}=\mathbf{r}_\sigma$ for $\sigma\leqslant N-1$.

We assume that an atom is detached from a cluster when the distance of the atom from all other atoms is greater than r_0. Let the hypersurface S_0 consist of $N(N-1)$ sections:

$$S_0=\sum_{\alpha=1}^{N}\sum_{\substack{\beta=1\\ \beta\neq\alpha}}^{N} S_{\alpha\beta}.$$

On the section $S_{\alpha\beta}$ the αth atom is at the detachment limit, and the closest atom to it is the βth atom. This means that $q_{\alpha\beta}=r_0$, $q_{\alpha\gamma}>r_0$ for $\gamma\neq\beta$ and $\gamma\neq\alpha$, while the other variables $q_{\mu\nu}$, $\mu,\nu\neq\alpha$, are such that no atom has detached yet.

Since all sections $S_{\alpha\beta}$ make the same contribution to the decay constant, to obtain a the contribution from S_{1N} can be increased by a factor of $N(N-1)$:

$$a=N(N-1)\int dK_1\int_{S'_{1N}} d\mathbf{r}_2...d\mathbf{r}_{N-1}J. \tag{3.12}$$

where

$$J=\int w(x,v)\,\eta(\mathbf{v}_1\mathbf{l}_1)\mathbf{v}_1\mathbf{l}_1 d\mathbf{v}_1...d\mathbf{v}_{N-1} \tag{3.13}$$

is an integral over the velocities $\mathbf{v}_\alpha=\dot{\mathbf{r}}_\alpha$ and K_1 is the sphere $|\mathbf{r}_1|=r_0$ in three-dimensional space. In addition, $\mathbf{l}_1=\mathbf{r}_1/r_1$ is the unit outer normal vector to K_1. Equation (3.13) assumes the form

$$J=C\int g(|\mathbf{v}_1|)\,\eta(\mathbf{v}_1\mathbf{l}_1)\mathbf{v}_1\mathbf{l}_1 d\mathbf{v}_1, \tag{3.14}$$

where

$$g(|\mathbf{v}_1|)=\int \delta\left(m_0^{-1}m_{ij}v_iv_j-\frac{2}{m_0}\right.$$
$$\left.\times(E-U)\right)d\mathbf{v}_2...d\mathbf{v}_{N-1}. \tag{3.15}$$

We introduce the vector $\mathbf{u}=(\mathbf{v}_2,...,\mathbf{v}_{N-1})$ with $m=3N-6$ components. Then

$$\frac{1}{m_0}m_{ij}v_iv_j=\frac{1}{m_0}(\mathbf{v}_1^T,\mathbf{u}^T)\hat{M}\begin{pmatrix}\mathbf{v}_1\\ \mathbf{u}\end{pmatrix}$$
$$=\mathbf{v}_1^T\hat{B}\mathbf{v}_1+\mathbf{u}^T\hat{A}\mathbf{u}+2\mathbf{v}_1^T\hat{G}^T\mathbf{u},$$

and in consequence of Eqs. (3.5) and (3.6)

$$\mathbf{v}_1^T\hat{B}\mathbf{v}_1=(1-N^{-1})|\mathbf{v}_1|^2,$$

$$\hat{A}=\hat{1}_m-\frac{N-2}{N}\hat{1}_3\otimes\hat{E}_{N-2},\quad \det\hat{A}=\left(\frac{2}{N}\right)^3, \tag{3.16}$$

and $\hat{G}^T$ is simply the $3\times m$ matrix $\hat{G}^T=N^{-1}(\hat{\mathbf{1}}_3,\hat{\mathbf{1}}_3,...,\hat{\mathbf{1}}_3)$, so that

$$\mathbf{v}_1^T\hat{G}^T=(\mathbf{v}_1^T/N,\mathbf{v}_1^T/N,...,\mathbf{v}_1^T/N).$$

If we set

$$s=2m_0^{-1}(E-U)-\mathbf{v}_1^T\hat{B}\mathbf{v}_1,\quad \mathbf{b}=\hat{G}\mathbf{v}_1.$$

The integral (3.15) can be calculated using the relation (A6). According to Eqs. (3.16) and (3.8)

$$\hat{A}^{-1}=\hat{1}_m+\frac{N-2}{2}\hat{1}_3\otimes\hat{E}_{N-2}.$$

Therefore

$$\mathbf{b}^T\hat{A}^{-1}\mathbf{b}=(1-2/N)|\mathbf{v}_1|^2/2,$$

$$s+\mathbf{b}^T\hat{A}^{-1}\mathbf{b}=2m_0^{-1}(E-U)-|\mathbf{v}_1|^2/2.$$

For this reason, application of Eq. (A6) puts Eq. (3.15) into the form

$$g(|\mathbf{v}_1|)=\frac{1}{2}\Omega_{3N-6}\left(\frac{N}{2}\right)^{3/2}\left[\frac{2}{m_0}(E-U)-\frac{1}{2}v_1^2\right]^{(3N-8)/2},$$

where $v_1^2<4(E-U)/m_0$. The integration over $\mathbf{v}_1=(v_\parallel,\mathbf{v}_\perp)$ in Eq. (3.14) is performed as done in Sec. 2. The result is

$$J=4C\Omega_{3N-6}(3N-6)^{-1}(3N-4)^{-1}\left(\frac{N}{2}\right)^{3/2}\left(\frac{2}{m_0}\right)^{(3N-4)/2}$$
$$\times(E-U)^{(3N-4)/2}\eta(E-U). \tag{3.17}$$

To obtain the decay constant, it remains to substitute the expression (3.17) into Eq. (3.12).

4. CASE OF THREE ATOMS

In the case $N=3$ we have two vectors $\mathbf{r}_1$ and $\mathbf{r}_2$. Further, let $\mathbf{r}_3=\mathbf{r}_1-\mathbf{r}_2$. We denote the magnitudes of these vectors by r_1, r_2, and r_3, respectively. According to Eq. (2.2), the potential energy is $U=\Phi(r_1)+\Phi(r_2)+\Phi(r_3)$.

We now determine the region R_0 in a six-dimensional coordinate space, such that escape from this region signifies the decay of the cluster. We represent it by the sum

$$R_0=R_{123}+R_{132}+R_{213}+R_{231}+R_{312}+R_{321}. \tag{4.1}$$

Here $R_{\alpha\beta\gamma}$ is the subregion of R_0 where $r_\alpha\geqslant r_\beta\geqslant r_\Gamma$. Suppose r_0 is some number. We make $R_{\alpha\beta\gamma}$ more precise and thereby determine the region (4.1) by the inequality

$$r_\beta\leqslant r_0. \tag{4.2}$$

Therefore we assume that the cluster decays when a system consisting of two atoms and a third atom become separated by a distance r_0 or greater or all three atoms separate from one another by this distance.

The region R_0 determine above with the aid of Eqs. (4.1) and (4.2) is bounded by the five-dimensional surface

$$S_0=S_{123}+S_{132}+S_{213}+S_{231}+S_{312}+S_{321}, \tag{4.2a}$$

where $S_{\alpha\beta\gamma}$ is the section of this surface that is given by the formula

$$r_\alpha\geqslant r_\beta=r_0>r_\gamma. \tag{4.3}$$

The equation (3.11) with $N=3$ gives

$$C^{-1}=\frac{3^{3/2}}{2}\Omega_6\left(\frac{2}{m_0}\right)^2 I, \tag{4.4}$$

where I is an integral over the region R_0 and, on account of Eq. (4.1), assumes the form

$$I=\int_{R_0} f d\mathbf{r}_1 d\mathbf{r}_2 = 6I_{123} \equiv 6\int_{R_{123}} f d\mathbf{r}_1 d\mathbf{r}_2. \tag{4.5}$$

Here we used the fact that all integrals $I_{\alpha\beta\gamma}$, make the same contributions to I and

$$f=f(r_1,r_2,r_3)=[E-\Phi(r_1)-\Phi(r_2)-\Phi(r_3)]^2\eta(E - \Phi(r_1)-\Phi(r_2)-\Phi(r_3)). \tag{4.6}$$

We shall now show how the number of integrations in Eq. (4.5) can be decreased. We fix $\mathbf{r}_1$ and switch from $\mathbf{r}_2$ to spherical coordinates,

$$\mathbf{r}_2=(r_2 \sin\vartheta \sin\varphi, r_2 \sin\vartheta \cos\varphi, r_2 \cos\vartheta),$$

where ϑ is the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$ ($0\leqslant\vartheta<\pi$). Then

$$I_{123}=\int_{R_{123}} d\mathbf{r}_1 \cdot 2\pi \int dr_2 r_2^2 \int d\vartheta \sin\vartheta f \times(r_1,r_2,\sqrt{r_1^2+r_2^2-2r_1r_2\cos\vartheta}). \tag{4.7}$$

Here the integration over φ has already been performed. The condition $r_3<r_2$ can be satisfied only if

$$r_2\geqslant r_1/2 \tag{4.8}$$

(otherwise the triangle inequality is violated). Moreover, allowance must be made for the fact that $r_3>r_1-r_2$ holds for $r_1>r_2$. To replace the integration variable ϑ by r_3, we employ

$$dr_3^2=d(r_1^2+r_2^2-2r_1r_2\cos\vartheta)=2r_1r_2\sin\vartheta d\vartheta, \tag{4.9}$$

if r_1 and r_2 are fixed. Switching in the expression (4.7) from r_1 to the corresponding spherical coordinates and taking account of Eqs. (4.8), (4.9), and (4.2) and the inequality $r_3>r_1-r_2$, we obtain

$$I_{123}=8\pi^2\int_0^{r_0} dr_2 r_2 \int_{r_2}^{2r_2} dr_1 r_1 \int_{r_1-r_2}^{r_2} dr_3 r_3 f(r_1,r_2,r_3). \tag{4.10}$$

This integral can be divided into two parts: $I_{123}=I'_{123}+I''_{123}$, where

$$I'_{123}=8\pi^2\int_0^{r_0} dr_2 r_2 \int_{r_2}^{\min(r_0,2r_2)} dr_1 r_1 \int_{r_1-r_2}^{r_2} dr_3 r_3 f = 8\pi^2\int_0^{r_0} dr_1 r_1 \int_{r_1/2}^{r_1} dr_2 r_2 \int_{r_1-r_2}^{r_2} dr_3 r_3 f,$$

$$I''_{123}=8\pi^2\int_{r_0/2}^{r_0} dr_2 r_2 \int_{r_0}^{2r_2} dr_1 r_1 \int_{r_1-r_2}^{r_2} dr_3 r_3 f. \tag{4.11}$$

This partitioning is convenient in the case of the square well (2.3). For this interaction potential we must set $r_0=d$. The calculation using the formulas (4.11) for the case (2.3) with $\gamma=d/\sigma\geqslant 2$ gives

$$I'_{12}=\frac{\pi^2}{36}\sigma^6(5\gamma^6-32\gamma^3+18\gamma^2+26)(E+3\varepsilon)^2,$$

$$I''_{12}=\frac{\pi^2}{36}\sigma^6(17\gamma^6-36\gamma^2+2)(E+2\varepsilon)^2.$$

In addition, we have

$$I'_{12}=\frac{\pi^2}{6}\sigma^6(\gamma^2-1)^3(E+3\varepsilon)^2,$$

$$I''_{12}=\frac{\pi^2}{18}\sigma^6(\gamma-1)^2(8\gamma^4+16\gamma^3+33\gamma^2+34\gamma+17)(E+2\varepsilon)^2$$

for $1<\gamma\leqslant 2$. Here it is assumed that $E+3\varepsilon>0$.

We now consider the decay probability (3.12) per unit time. Since according to Eqs. (4.2a) S_0 consists of six sections, which all make the same contributions to the decay constant a, we can study the six-fold integral over the section S_{123} determined by the formula $r_2>r_1=r_0>r_3$. The relation $|\mathbf{r}_1|=r_0$ defines a sphere K_1 (in three-dimensional space). Therefore

$$a=6\int dK_1 \int_{r_2>r_0>|\mathbf{r}_1-\mathbf{r}_2|} d\mathbf{r}_2 \times \int d\mathbf{v}_1 \mathbf{v}_1\cdot\mathbf{l}_1\eta(\mathbf{v}_1\mathbf{l}_1)\int d\mathbf{v}_2 w(q,p) \tag{4.12}$$

($\mathbf{l}_1=\mathbf{r}_1/r_1$ is a unit outer normal vector to K_1). Here, the velocity integral is identical to the integral in Eq. (3.13). Therefore

$$a=6\int dK_1 \int_{r_2>r_0>r_3} d\mathbf{r}_2 J(r_2,r_3). \tag{4.13}$$

Here, allowance was made for the fact that on account of Eq. (3.17) and the relation

$$E-U|_{r_1=r_0+0}=E-\Phi(r_2)-\Phi(r_0+0)-\Phi(r_3) \tag{4.14}$$

J is a function of $r_2=|\mathbf{r}_2|$ and $r_3=|\mathbf{r}_3|$. In Eq. (4.14) we set $r_1=r_0+0$ for the case of a jump in the potential Φ at the point r_0. The potential (2.3) undergoes such a jump at $r_0=d$. It is assumed that the expression (4.14) is nonnegative, i.e., we are interested in the cases when the potential barrier has already been overcome.

The integration in Eq. (4.13) can be represented in the form

$$a=6\cdot 8\pi^2 r_0\int_{r_0}^{2r_0} dr_2 r_2 \int_{r_2-r_0}^{r_0} dr_3 r_3 J(r_2,r_3), \tag{4.15}$$

which is reminiscent of and is derived by the same method as the expression (4.10) (if in Eq. (4.10) we drop the integration over r_2, set $r_2=r_0$, and replace the index 1 by 2). In Eq. (4.15) the integration over the sphere has already been performed. Taking account of the expression (3.17) with $N=3$, we find

$$a=48\cdot 32\frac{\sqrt{3}}{5}\pi^3 C m_0^{-5/2} L(r_0), \tag{4.16}$$

where

$$L(r_0)=r_0\int_{r_0}^{2r_0}dr_2r_2\int_{r_2-r_0}^{r_0}dr_3r_3\varphi^{5/2}(r_2,r_3)\eta(\varphi(r_2,r_3)), \tag{4.17}$$

and the function (4.14) is denoted as $\varphi(r_2,r_3)$. For the particular case of the potential (2.3), when $r_0=d=\gamma\sigma$, the last integral is

$$L(d)=(E+\varepsilon)^{5/2}d\int_d^{2d}dr_2r_2\int_{\max(\sigma,r_2-d)}dr_3r_3$$
$$=\frac{11}{24}\sigma^5\gamma(\gamma-1)\left(\gamma^3+\gamma^2+\gamma+\frac{3}{11}\right)(E+\varepsilon)^{5/2}. \tag{4.18}$$

On account of Eqs. (4.4) and (4.5) the result (4.16) assumes the form

$$a=\frac{128}{15}\frac{1}{\sqrt{m_0}}\frac{L(r_0)}{I_{123}}, \tag{4.19}$$

where I_{123} and $L(r_0)$ are defined above. We see that the decay constant increases with the amount $\Delta E=E-E_{\min}$ by which the energy E exceeds the minimum energy $E_{\min}=-\varepsilon$ required for decay. For fixed ratio $\gamma=d/\sigma$ the constant (4.19) is inversely proportional to the width of the potential well. We note that the vanishing of I_{123} as $\gamma\to1$ (when the well vanishes) not only compensates for the vanishing of the expression (4.18) but also results in an increase of a.

5. THREE ATOMS INTERACTING VIA A LENNARD-JONES POTENTIAL

In contrast to a square well, the Lennard-Jones potential

$$\Phi(r)=4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right]$$

and a number of other potentials (see Ref. 5, pp. 41–43) grow continuously for values of r larger than the value corresponding to the minimum of the potential and they approach zero asymptotically from below. The question of the choice of the limiting radius r_0 merits a special discussion. The difficulty is that the potential barrier does not possess a top where it would be natural to place the boundary surface. It will be clear below how this problem can be solved.

For the time being we limit the choice of r_0 by the condition

$$r_0\gg\sigma. \tag{5.1}$$

Moreover, we shall assume that the quantity $E_0=E+\varepsilon$ satisfies the inequality

$$E_0\ll\varepsilon, \tag{5.2}$$

as a result of which the decay constant is small. We shall show that the inequalities (5.1) and (5.2) make it possible to calculate approximately the integral (4.17) appearing in Eq. (4.16), where $\varphi=E-\Phi(r_0)-\Phi(r_2)-\Phi(r_3)$. Consider the condition $\varphi(r_2,r_3)=0$, i.e.,

$$4\left[\left(\frac{\sigma}{r_3}\right)^{12}-\left(\frac{\sigma}{r_3}\right)^{6}\right]+1=\frac{1}{\varepsilon}[E_0-\Phi(r_0)-\Phi(r_2)]\approx\frac{E_0}{\varepsilon}$$
$$+4\left(\frac{\sigma}{r_0}\right)^{6}+4\left(\frac{\sigma}{r_2}\right)^{6}, \tag{5.3}$$

where the inequalities (5.1) and $r_2>r_0$ were employed. The equation (5.3) determines the limiting points of the segment, fixed by the condition $\varphi(r_2,r_3)>0$, over which the integration over r_3 must actually be performed on account of the factor of $\eta(\varphi(r_2,r_3))$ in Eq. (4.17). But the right-hand side of Eq. (5.3) is very small on account of the inequalities (5.1), (5.2), and $r_2>r_0$. Therefore, to determine the roots of Eq. (5.3) the function on the left-hand side can be expanded in a Taylor series in powers of $r_3-\sigma_0\equiv r_3-2^{1/6}\sigma$ at the point of the minimum $r_3=\sigma_0$. It is sufficient to approximate it by the parabola

$$4\left(\frac{\sigma}{r_3}\right)^{12}-4\left(\frac{\sigma}{r_3}\right)^{6}+1\approx\frac{c_0}{\sigma^2}(r_3-\sigma_0)^2, \tag{5.4}$$

where $c_0=18\cdot2^{2/3}$. Then we find from Eq. (5.3) the integration segment

$$\sigma_0-\sigma\Delta<r_3<\sigma_0+\sigma\Delta, \tag{5.5}$$

where

$$\Delta=\frac{1}{\sqrt{c_0}}\sqrt{\frac{E_0}{\varepsilon}+4\left(\frac{\sigma}{r_0}\right)^{6}+4\left(\frac{\sigma}{r_2}\right)^{6}}.$$

Observing that the integration over r_3 cannot exceed the limits of the segment (5.5) and taking account of the integration in Eq. (4.17), we find that the integral

$$S=\int_{r_2-r_0}^{r_0}\varphi^{5/2}\eta(\varphi)r_3dr_3$$

reduces to integrating the expression $\varphi^{5/2}r_3$ from $\sigma_0-\sigma\Delta$ to $\sigma_0+\sigma\Delta$ with $0<r_2-r_0<\sigma_0-\sigma\Delta$ (first segment on the r_2 axis) and from r_2-r_0 to $\sigma_0+\sigma\Delta$ for $\sigma_0-\sigma\Delta<r_2-r_0<\sigma_0+\sigma\Delta$ (second segment). The integral $S=0$ for $r_2-r_0>\sigma_0+\sigma\Delta$ (third segment). In the subsequent integration over r_2, prescribed by Eq. (4.17), the first segment $r_0<r_2<r_0+\sigma_0-\sigma\Delta\approx r_0+\sigma_0$ makes the main contribution to L, since the length of the this segment, approximately equal to σ_0, is much greater than the length $2\sigma\Delta$ of the second segment. Therefore, the integral over the second segment can be neglected, but $\Phi(r_2)\approx\Phi(r_0)$ holds on the first segment, since on account of the inequality (5.1) the difference r_2-r_0 (which is less than $\sigma_0-\sigma\Delta\approx\sigma_0$) is much less than r_0 and therefore r_2 also. Therefore, the integration over the first segment is trivial, and from Eq. (4.17) we obtain

$$L=\frac{r_0}{2}[(r_0+\sigma_0)^2-r_0^2]\int_{\sigma_0-\sigma\Delta}^{\sigma_0+\sigma\Delta}\varphi^{5/2}(r_0,r_3)r_3dr_3. \tag{5.6}$$

We can employ the approximation (5.4) in the integrand in Eq. (5.6), after which the integral is easily calculated. This gives

$$L=\frac{5}{16}\frac{\pi\sigma\sigma_0^2}{\sqrt{c_0\varepsilon}}[E_0-2\Phi(r_0)]^3r_0^2. \tag{5.7}$$

The decrease of the factor $[E_0-2\Phi(r_0)]^3 \approx[E_0+8\varepsilon(\sigma/r_0)^6]^3$ in Eq. (5.7) with increasing r_0 is the main effect—the number of atoms which have been lost decreases as the potential barrier $2\Phi(r_0)+3\varepsilon$ increases (-3ε is the minimum value of the potential $\Phi(r_1)+\Phi(r_2)+\Phi(r_3)$). As one can see from the expression (5.7), however, there is also a secondary effect—the factor r_0^2 increases, i.e., the area of the sphere K_1 increases. It is obvious that it is pointless to increase r_0 up to values at which the secondary effect exceeds the main effect. The value of r_0 can be determined from the condition that these effects are balanced, i.e., from the condition of an extremum

$$\frac{d}{dx_0}\left[x_0\left(\frac{E_0}{8\varepsilon}+\frac{1}{x_0^3}\right)^3\right]=0$$

($x_0=r_0^2/\sigma^2$), which gives $x_0=4(\varepsilon/E_0)^{1/3}$, $r_0=2\sigma(\varepsilon/E_0)^{1/6}$. We can see that the condition (5.1) is satisfied on account of the inequality (5.2).

We shall now examine the problem of calculating the integral (4.10) in the case of the Lennard-Jones potential. It is convenient to switch in this integral to the dimensionless variables $x_1=r_1^2/\sigma^2$, $x_2=r_2^2/\sigma^2$, and $x_3=r_3^2/\sigma^2$. Then

$$I_{123}=\pi^2\varepsilon^2\sigma^6\int_0^{x_0}dx_2\int_{x_2}^{4x_2}dx_1\int_{(\sqrt{x_1}-\sqrt{x_2})^2}^{x_2}dx_3 \times\left(\frac{E}{\varepsilon}-F(x_1)-F(x_2)-F(x_3)\right)^2 \times\eta\left(\frac{E}{\varepsilon}-F(x_1)-F(x_2)-F(x_3)\right), \tag{5.8}$$

for $x_0=r_0^2/\sigma^2$ and $F(x)=4x^{-6}-4x^{-3}$. The range of integration over x_3 is limited by the condition $E/\varepsilon-F(x_1)-F(x_2)-F(x_3)>0$. The limiting points of the segment where this condition holds are easily found:

$$x_3^-=\max\left[0,\left(\frac{1}{2}-\sqrt{\frac{1}{4}+\xi}\right)^{-1/3}\right],$$

$$x_3^+=\left(\frac{1}{2}+\sqrt{\frac{1}{4}+\xi}\right)^{-1/3}.$$

Here, $\xi=[E/\varepsilon-F(x_1)-F(x_2)]/4$. Therefore, the integration over x_3 in Eq. (5.8) extends from $\max(x_3^-, x_1+x_2-2\sqrt{x_1x_2})$ to $\min(x_3^+, x_2)$. In principle, this integration can be performed analytically. The integrals over x_1 and x_2, however, can be calculated numerically on a computer.

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6. APPENDIX

Multidimensional integrals with a delta function

First, we calculate the integral

$$I_1=\int\delta(\mathbf{u}^T\hat{A}\mathbf{u}-c^2)d\mathbf{u}, \tag{A1}$$

where $\mathbf{u}$ is a m-component column vector and $\hat{A}$ is a real positive-definite $m\times m$-matrix. We switch to new integration variables $\mathbf{y}=\hat{A}^{1/2}\mathbf{u}$, where $\hat{A}^{1/2}$ is a positive-definite root of $\hat{A}$. Then Eq. (A1) assumes the form

$$I_1=\det{}^{-1/2}\hat{A}\int\delta(\mathbf{y}^T\mathbf{y}-c^2)d^my.$$

Switching to hyperspherical coordinates, we easily find that

$$I_1=\frac{1}{2}\Omega_m c^{m-2}\det{}^{-1/2}\hat{A}. \tag{A2}$$

We now consider the more complicated integral

$$I_2=\int\delta(\mathbf{u}^T\hat{A}\mathbf{u}-2\mathbf{b}^T\mathbf{u}-s)d^mu, \tag{A3}$$

where $\mathbf{b}^T$ is a m-dimensional row vector. It is easy to see that Eq. (A3) can be put into the form

$$I_2=\int\delta((\mathbf{u}^T-\mathbf{d}^T)\hat{A}(\mathbf{u}-\mathbf{d})-\mathbf{d}^T\hat{A}\mathbf{d}-s)d^mu, \tag{A4}$$

where

$$\mathbf{d}=\hat{A}^{-1}\mathbf{b}. \tag{A5}$$

Introducing the new integration variables $\tilde{\mathbf{u}}=\mathbf{u}-\mathbf{d}$ in Eq. (A4), to calculate this integral it remains only to apply Eq. (A2). This gives

$$I_2=\frac{1}{2}\Omega_m(s+\mathbf{b}^T\hat{A}^{-1}\mathbf{b})^{(m-2)/2}\det{}^{-1/2}\hat{A}, \tag{A6}$$

where Eq. (A5) was used. It is assumed that $s+\mathbf{b}^T\hat{A}^{-1}\mathbf{b}>0$, otherwise $I_2=0$.

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