Molecular dynamics ensemble, equation of state, and ergodicity

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The variant of the NVE ensemble known as the molecular dynamics ensemble was recently redefined by Ray and Zhang [Phys. Rev. E **59**, 4781 (1999)] to include the specification of a time invariant $\boldsymbol{G}$ (a function of phase and, explicitly, the time) in addition to the total linear momentum $\boldsymbol{M}$. We reformulate this ensemble slightly as the $NVEMR$ ensemble, in which $\boldsymbol{R}/N$ is the center-of-mass position, and consider the equation of state of the hard-sphere system in this ensemble through both the virial function and the Boltzmann entropy. We test the quasiergodic hypothesis by a comparison of old molecular dynamics and Monte Carlo results for the compressibility factor of the 12-particle, hard-disk systems. The virial approach, which had previously been found to support the hypothesis in the $NVEM$ ensemble, remains unchanged in the $NVEMR$ ensemble. The entropy S approach depends on whether $\boldsymbol{S}$ is defined through the phase integral over the energy sphere or the energy shell, the parameter θ being 0 or 1, respectively. The ergodic hypothesis is found to be supported for $\theta=0$ but not for $\theta=1$.

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Ray and Zhang [1] have noted that in an equilibrium molecular dynamics (MD) calculation for a system of N particles in a volume V with periodic boundary conditions without external forces, not only are the Hamiltonian $H(\boldsymbol{x}^N)=K(\boldsymbol{p}^N)+U(\boldsymbol{r}^N)$ and the total linear momentum $\Sigma_{i=1}^N \boldsymbol{p}_i$ invariant under the evolution in the time t of the system, but so also is the function

$$\boldsymbol{G}(\boldsymbol{x}^N(t);t)=t\sum_{i=1}^N \boldsymbol{p}_i(t)-\boldsymbol{m}\sum_{i=1}^N \boldsymbol{r}_i(t). \tag{1}$$

They therefore contend that the term ''molecular dynamics ensemble'' should refer to an NVEMG ensemble (i.e., an ensemble in which $\boldsymbol{N}$, V, the energy E, the linear momentum $\boldsymbol{M}$, and $\boldsymbol{G}$ are specified), rather than to the NVEM ensemble. [We consider here only a one-component classical system of N particles, each having mass $\boldsymbol{m}$; $\boldsymbol{r}_i$ and $\boldsymbol{p}_i$ denote the position and the momentum, respectively, of particle i. $K(\boldsymbol{p}^N)=\Sigma p_i^2/2\boldsymbol{m}$ denotes the kinetic energy and $U(\boldsymbol{r}^N)$ the potential energy; $\boldsymbol{x}^N=(\boldsymbol{r}^N,\boldsymbol{p}^N)$ denotes the phase.]

Our purpose here is, first, to state our agreement with their contention, provided that the $\boldsymbol{r}_i$ of Eq. (1) are defined as the ''infinite checkerboard'' [2,3] positions. [Otherwise, if $\boldsymbol{r}_i(t)$ were understood to be the position of particle i in the simulation cell, then it is stepwise discontinuous at the times at which the particle leaves the simulation cell through one face and reenters through the opposite face, so that $\boldsymbol{G}$ is not constant.] Furthermore, we choose to formulate the molecular dynamics ensemble somewhat differently so as to avoid the appearance of the time in the partition function.

If we are to speak of the molecular dynamics ensemble for small finite systems, we implicitly conjecture the existence of a quasiergodic theorem stating that the phase-space trajectory over a sufficiently long period of time spends equal increments of time in almost all equal elements of the phase space of the ensemble, so that the dynamical time average of any phase function should equal the corresponding ensemble average. Thus the ensemble phase space should reflect the constancy of all the time invariants of the dynamical system: the Hamiltonian through the energy parameter E, the total linear momentum $\Sigma_i \boldsymbol{p}_i$ through the momentum parameter $\boldsymbol{M}$, and the Ray-Zhang $\boldsymbol{G}$ through its initial or ensemble value (divided by $-\boldsymbol{m}$), namely the center-of-mass parameter $\boldsymbol{R}$. We write, therefore, the partition function,

$$Z_{NVEMR}=\frac{1}{C_N}\int d\boldsymbol{x}^N \boldsymbol{A}[\boldsymbol{E}-\boldsymbol{H}(\boldsymbol{x}^N)] \times\delta\left(\boldsymbol{M}-\sum_i \boldsymbol{p}_i\right)\delta\left(\boldsymbol{R}-\sum_i \boldsymbol{r}_i\right), \tag{2}$$

where

$$\int d\boldsymbol{x}^N=\int_V d\boldsymbol{r}^N\int d\boldsymbol{p}^N, \tag{3}$$

for E positive, $M^2<2E/\boldsymbol{m}$, and $\boldsymbol{R}/N$ lying within the system volume. This contrasts with the Ray-Zhang partition function, $\Phi(E,V,N,\boldsymbol{M},\boldsymbol{G})$, which in our notation becomes the similar

$$Z'_{NVEMG}=\frac{1}{C'_N}\int d\boldsymbol{x}^N \boldsymbol{A}[E-H(\boldsymbol{x}^N)]\delta\left(\boldsymbol{M}-\sum \boldsymbol{p}_i\right) \times\delta\left(\boldsymbol{G}-t\sum \boldsymbol{p}_i+\boldsymbol{m}\sum \boldsymbol{r}_i\right). \tag{4}$$

[$\delta(\boldsymbol{x})$ is the Dirac δ function; if $\boldsymbol{x}$ is a vector, it is the product of the δ functions of its components. $\boldsymbol{A}(x)$ is the unit step function defined in Eq. (28) below. C_N and C'_N are dimensional constants that we omit in the following discussion. The appearance of the step function corresponds to our $\theta=0$ in Eq. (24) below.] But the two expressions are readily seen to be equivalent if and only if one interprets the particle positions in the rightmost factor to be the positions $\boldsymbol{r}_i(t;\boldsymbol{x}^N)$ at time t on the trajectory initiated at $\boldsymbol{x}^N$. If instead one interprets the positions to be those specified by $\boldsymbol{r}^N$, the variable of integration, and t to be an arbitrary parameter, then for fixed $\boldsymbol{M}$ and $\boldsymbol{G}$ the rightmost δ function vanishes through-

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out configuration space for those t for which $-(\boldsymbol{G}-t\boldsymbol{M})/mN$ lies outside the system volume and agrees with Eq. (2) for values of t for which $\boldsymbol{R}/N=-(\boldsymbol{G}-t\boldsymbol{M})/mN$ lies in the system volume. We believe then Eq. (2) to be preferable. We regret having previously overlooked the fact that the constancy of the total linear momentum under periodic boundary conditions implies the time invariance of $\boldsymbol{G}$.

Secondly, we wish to reconsider the relation that we previously gave [2–4] between the molecular dynamics and the NVT ensemble equations of state for hard-sphere systems when the molecular dynamics results are assumed to be related by a quasiergodic theorem to the ''molecular dynamics ensemble'' average (previously the $NVEM$, now the $NVEMR$ ensemble). In [2], and less satisfactorily in [3] [in which we started from the usual virial theorem $dpV=2(\overline{K}-\overline{W})$, and replaced $\overline{K}$ with the kinetic energy in the center-of-mass reference frame by an ad hoc argument], we derived (for a general value of $\boldsymbol{M}$) the usual ''virial'' expression

$$dp_{\mathrm{MD}}V=2(\hat{E}-\overline{W}) \tag{5}$$

for the molecular dynamics pressure p_{MD} by considering the average momentum transfer across a surface element moving with the velocity of the center of mass, $\boldsymbol{v}_0=\boldsymbol{M}/Nm$. [We also noted that ''virial equation'' is something of a misnomer for Eq. (5), and showed that a systematic consideration of the checkerboard virial function leads to a rather novel expression for the equation of state.] $\hat{E}=E-M^2/2Nm$ is the kinetic energy in the center-of-mass reference frame, and

$$\overline{W}=-\lim_{t\to\infty}\frac{1}{4t}\sum_{\gamma=1}^{c(t)}\boldsymbol{\sigma}_{ij}(\gamma)\cdot\Delta\boldsymbol{p}_{ij}(\gamma). \tag{6}$$

The sum is over all collisions $\gamma=1,2,\ldots,c(t)$ occurring in the time t, with $\boldsymbol{\sigma}_{ij}(\gamma)$ being the line of centers vector $\boldsymbol{r}_{ij}^*(\gamma)=\boldsymbol{r}_i(\gamma)-\boldsymbol{r}_j(\gamma)$ between the colliding particles i and j on collision γ, and with $\Delta\boldsymbol{p}_{ij}(\gamma)=\Delta\boldsymbol{p}_i(\gamma)-\Delta\boldsymbol{p}_j(\gamma)$ being the relative momentum change on that collision. Equations (5) and (6) provide the means by which the hard-sphere pressure is obtained in a typical MD calculation. (It can also be obtained from the calculated collision rate.) In reporting molecular dynamics results for a system of hard disks, Alder and Wainwright [5], Hoover and Alder [6], and we [4] chose to report the dimensionless compressibility factor

$$\frac{p_{\mathrm{MD}}V}{NkT_{\mathrm{MD}}}=\frac{dp_{\mathrm{MD}}V}{2\hat{E}}=1-\frac{\overline{W}}{\hat{E}} \tag{7}$$

taking

$$T_{\mathrm{MD}}=2\hat{E}/dNk. \tag{8}$$

(Note that any other choice for T_{MD} would give a compressibility factor that would not approach the ideal gas value as $\overline{W}\to 0$.)

To relate $(p_{\mathrm{MD}}V/NkT_{\mathrm{MD}})$ to $(p_{NVT}V/NkT)$ as estimated, e.g., by an NVT ensemble Monte Carlo (MC) calculation, we noted that the NVT ensemble compressibility factor for a general, differentiable potential energy is

$$\frac{p_{NVT}V}{NkT}=1-\frac{\langle W(\boldsymbol{r}^N)\rangle_{NVT}}{NdkT/2}, \tag{9}$$

in which

$$W(\boldsymbol{r}^N)=-\frac{1}{2}\sum_{i=1}^{N}\boldsymbol{F}_i(\boldsymbol{r}^N)\cdot\boldsymbol{r}_i \tag{10}$$

is the usual virial function, with

$$\boldsymbol{F}_i(\boldsymbol{r}^N)=-\left(\frac{\partial U(\boldsymbol{r}^N)}{\partial\boldsymbol{r}_i}\right)_{\boldsymbol{r}_j,j\neq i} \tag{11}$$

being the force exerted on particle i by the other $N-1$ particles. We postulated a quasiergodic theorem equating $\overline{W}$ with $\langle W(\boldsymbol{r}^N)\rangle_{NVEM}$, ignoring the fact that W does not appear to exist for hard spheres. We correct this by writing $\boldsymbol{F}_i$ as $d\boldsymbol{p}_i/dt$ and specializing to hard spheres and periodic boundary conditions, recognizing that the time average of W is given by $\overline{W}$ of Eq. (6). We postulate, then, a quasiergodic theorem equating $\overline{W}$ with the hard-sphere limit of $\langle W(\boldsymbol{r}^N)\rangle_{NVEM}$ for a soft interaction, say, the $q\to\infty$ of the $(\sigma/r)^q$ pair potential. We showed, for a general potential, that

$$\langle W(\boldsymbol{r}^N)\rangle_{NVT}=\frac{1}{Z_{NVT}}\int_0^\infty dE\,e^{-\beta E}\int d\boldsymbol{M}\,Z_{NVEM}\times\langle W(\boldsymbol{r}^N)\rangle_{NVEM}. \tag{12}$$

Asserting that the hard-sphere limits of the ensemble averages exist and replacing $\langle W(\boldsymbol{r}^N)\rangle_{NVEM}$ by $\overline{W}$, we obtain for hard spheres, as previously [2],

$$\frac{\langle W(\boldsymbol{r}^N)\rangle_{NVEM}}{\hat{E}}=\frac{\langle W(\boldsymbol{r}^N)\rangle_{NVT}}{(N-1)dk\,T/2}=\frac{N}{N-1}h(N/V,N), \tag{13}$$

in which

$$h(N/V,N)=-\frac{N}{V}\frac{\sigma\omega_d(\sigma)}{2d}g(\sigma,N/V,N)=-\frac{(N-1)\sigma}{2d}\langle\delta(\boldsymbol{r}_{12}-\sigma)\rangle_{NV} \tag{14}$$

is a function only of the number density N/V and N, with the dependence on the system size N expected to vanish in the thermodynamic limit. $g(\sigma,N/V,N)$ is the angle-averaged [7] pair distribution function at contact and $\omega_d(\sigma)=2\pi^{d/2}\sigma^{d-1}/\Gamma(d/2)$ is the surface area of the d-dimensional hypersphere of radius σ. Finally, we used Eqs. (7), (9), and (13) to obtain (as previously found by Hoover and Alder [6]) the relation

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$$\left(\frac{pV}{NkT}-1\right)_{\mathrm{MD}}=\frac{N}{N-1}\left(\frac{pV}{NkT}-1\right)_{NVT} \tag{15}$$

between the ''molecular dynamics equation of state'' and the *NVT* ensemble equation of state for hard spheres.

We show below for a general differentiable potential that

$$\langle W(\boldsymbol{r}^N)\rangle_{NVEMR}=\langle W(\boldsymbol{r}^N)\rangle_{NVEM}, \tag{16}$$

leading again to Eq. (15) when $\overline{W}$ is equated to $\langle W(\boldsymbol{r}^N)\rangle_{NVEMR}$ for soft spheres in the hard-sphere limit. Hoover and Alder [6] used Eq. (15) to compare the Alder and Wainwright [5] MD results with our [8] old *NVT* ensemble Monte Carlo results, both for a system of $N=12$ hard disks. It is advantageous to carry out such a comparison on as *small* a system as possible, since the ensemble differences are expected to vanish in the large system limit. The agreement was found to be reasonably good, considering the statistical errors in the two calculations, and can now be taken to support the validity of a hard-sphere, quasiergodic theorem equating the time-averaged virial to the hard-sphere limit of its *NVEMR* ensemble average.

Thirdly, we wish to mention some peculiarities associated with the various microcanonical ensembles, when the Boltzmann relation between the entropy and the partition function is used to obtain other thermodynamic functions, such as the pressure and the temperature. For a general, differentiable potential energy we have, following Pearson *et al.* [9] and omitting throughout multiplicative factors that depend only on N, m, and the dimensionality d, the partition functions

$$Z_{NVT}=Z_{NT}Q_{NVT}, \tag{17}$$

$$Z_{NT}=\int d\boldsymbol{p}^N e^{-\beta K(\boldsymbol{p}^N)}=(2m\pi kT)^{Nd/2}, \tag{18}$$

$$Q_{NVT}=\int d\boldsymbol{r}^N e^{-\beta U(\boldsymbol{r}^N)}, \tag{19}$$

$$Z_{NVE}(\theta)=\int d\boldsymbol{x}^N \Delta_\theta[E-H(\boldsymbol{x}^N)], \tag{20}$$

$$=\int d\boldsymbol{r}^N \kappa(\boldsymbol{r}^N)^{(Nd/2)-\theta}A[\kappa(\boldsymbol{r}^N)], \tag{21}$$

$$Z_{NVEM}(\theta)=\int d\boldsymbol{x}^N \Delta_\theta[E-H(\boldsymbol{x}^N)]\delta\left(\boldsymbol{M}-\sum \boldsymbol{p}_i\right), \tag{22}$$

$$=\int d\boldsymbol{r}^N \hat{\kappa}(\boldsymbol{r}^N)^{\{[(N-1)d]/2\}-\theta}A[\hat{\kappa}(\boldsymbol{r}^N)], \tag{23}$$

$$Z_{NVEMR}(\theta)=\int d\boldsymbol{x}^N \Delta_\theta[E-H(\boldsymbol{x}^N)] \times\delta\left(\boldsymbol{M}-\sum \boldsymbol{p}_i\right)\delta\left(\boldsymbol{R}-\sum \boldsymbol{r}_i\right), \tag{24}$$

$$=\frac{1}{V}Z_{NVEM}(\theta). \tag{25}$$

[To obtain Eq. (25) from Eq. (24), transform from the $\boldsymbol{r}^N=(\boldsymbol{r}_1, ..., \boldsymbol{r}_N)$ variables to new variables $\hat{\boldsymbol{r}}^N=(\hat{\boldsymbol{r}}_0,\hat{\boldsymbol{r}}_1, ..., \hat{\boldsymbol{r}}_{N-1})$ with $\hat{\boldsymbol{r}}_0=\boldsymbol{r}_0$ (the position of the center of mass) and $\hat{\boldsymbol{r}}_i=\boldsymbol{r}_i-\boldsymbol{r}_0$, $i=1,\ldots,N-1$. This being a linear transformation, the Jacobian is a constant. $U(\boldsymbol{r}^N)$ depends only on the $\hat{\boldsymbol{r}}_i$, $i=1,\ldots,N-1$. Consequently, the $\hat{\boldsymbol{r}}_0$ integration of $\delta(\boldsymbol{R}-N\boldsymbol{r}_0)$ collapses to the factor N^{-d}, which we omit. Restore the integration over $\hat{\boldsymbol{r}}_0$, and compensate by introducing a factor V^{-1}. Finally, transform back to $\boldsymbol{r}^N$, canceling the previous Jacobian, and recognize the resulting integral as Z_{NVEM}.] θ takes on only the values 0 and 1, with

$$\Delta_0(x)=A(x), \tag{26}$$

$$\Delta_1(x)=\delta(x), \tag{27}$$

reflecting the lack of consensus (see, e.g. Pearson, *et al.* [9], and references therein; $Z_{NVE}(0)$ is their Ω, and $Z_{NVE}(1)$ is their ω) regarding the proper definition of Z_{NVE} (and, by extension, of our other microcanonical partition functions). As usual, $\beta=1/kT$, with k being the Boltzmann constant. $A(x)$ is the step function

$$A(x)=\begin{cases}0 & \text{if } x<0,\\ 1 & \text{if } x\geqslant 0.\end{cases} \tag{28}$$

In Eqs. (21) and (23),

$$\kappa(\boldsymbol{r}^N)=E-U(\boldsymbol{r}^N) \tag{29}$$

and

$$\hat{\kappa}(\boldsymbol{r}^N)=E-M^2/2mN-U(\boldsymbol{r}^N) \tag{30}$$

are the kinetic energies as functions in configuration space; their appearance as arguments in the unit step functions expresses the microcanonical constraint of fixed total energy. [In writing Eqs. (20)–(25), we have omitted for $\theta=1$ the thickness ΔE of the energy shell to which the system is supposed to be confined; it should properly be included on dimensional grounds, and we thus have ignored any dependence of it on the energy and number density of the system.]

In the *NVT* ensemble, the thermodynamic functions are obtained from the Helmholtz free energy

$$A_{NVT}=-kT\ln Z_{NVT} \tag{31}$$

through

$$dA_{NVT}=-S_{NVT}\,dT-p_{NVT}\,dV, \tag{32}$$

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giving

$$S_{NVT} = -\left(\frac{\partial A_{NVT}}{\partial T}\right)_{NV}, \tag{33}$$

$$p_{NVT} = -\left(\frac{\partial A_{NVT}}{\partial V}\right)_{NT}. \tag{34}$$

For the microcanonical ensembles, we have instead the Boltzmann relation

$$S_{NVE\ldots}(\theta) = k \ln Z_{NVE\ldots}(\theta), \tag{35}$$

and from the combined first and second law relation

$$dE = T_{NVE\ldots}(\theta) dS_{NVE\ldots}(\theta) - p_{NVE\ldots}(\theta) dV, \tag{36}$$

we have

$$T_{NVE\ldots}(\theta) = \left(\frac{\partial S_{NVE\ldots}(\theta)}{\partial E}\right)_{NV}^{-1}, \tag{37}$$

$$\frac{p_{NVE\ldots}(\theta)}{T_{NVE\ldots}(\theta)} = \left(\frac{\partial S_{NVE\ldots}(\theta)}{\partial V}\right)_{NE}. \tag{38}$$

We compute then the temperature and compressibility factor for each of the ensembles for the general differentiable potential of Eq. (11). For the canonical ensemble, the temperature is a parameter and the compressibility factor, Eq. (9), follows from Eqs. (31) and (34). For the microcanonical ensembles, we obtain temperatures given by

$$kT_{NVE}(0) = \frac{1}{Nd/2}\langle \kappa(r^N)\rangle_{NVE}, \tag{39}$$

$$kT_{NVE}(1) = \frac{1}{Nd/2-1}\left\langle \frac{1}{\kappa(r^N)}\right\rangle_{NVE}^{-1}, \tag{40}$$

$$kT_{NVEM}(0) = \frac{1}{(N-1)d/2}\langle \hat{\kappa}(r^N)\rangle_{NVEM}, \tag{41}$$

$$kT_{NVEM}(1) = \frac{1}{(N-1)d/2-1}\left\langle \frac{1}{\hat{\kappa}(r^N)}\right\rangle_{NVEM}^{-1}, \tag{42}$$

$$T_{NVEMR}(\theta) = T_{NVEM}(\theta), \tag{43}$$

in which we follow our previous procedure, as well as that of Ray and Zhang, and that of Pearson *et al.*, in defining ensemble averages independent of the value of θ used in computing the entropy, $S_{NVE\ldots}(\theta)$. In particular, the ensemble averages of a phase function $B(x^N)$ are

$$\langle B(x^N)\rangle_{NVE\ldots} = \frac{\int dx^N B(x^N)\phi_{NVE\ldots}(x^N)}{\int dx^N \phi_{NVE\ldots}(x^N)}, \tag{44}$$

with (unnormalized) distribution functions

$$\phi_{NVE}(x^N) = \delta\left(E - \frac{\sum p_i^2}{2m} - U(r^N)\right), \tag{45}$$

$$\phi_{NVEM}(x^N) = \phi_{NVE}(x^N)\,\delta\left(M - \sum p_i\right), \tag{46}$$

$$\phi_{NVEMR}(x^N) = \phi_{NVEM}(x^N)\,\delta\left(R - \sum r_i\right). \tag{47}$$

For a function $B(r^N)$, such as $U(r^N)$ itself, depending only on *relative* coordinates, we have

$$\langle B(r^N)\rangle_{NVE} = \frac{\int dr^N B(r^N)\kappa(r^N)^{(Nd/2)-1} A[\kappa(r^N)]}{\int dr^N \kappa(r^N)^{(Nd/2)-1} A[\kappa(r^N)]}, \tag{48}$$

$$\langle B(r^N)\rangle_{NVEM} = \frac{\int dr^N B(r^N)\hat{\kappa}(r^N)^{\{[(N-1)d]/2\}-1} A[\hat{\kappa}(r^N)]}{\int dr^N \hat{\kappa}(r^N)^{\{[(N-1)d]/2\}-1} A[\hat{\kappa}(r^N)]}, \tag{49}$$

$$\langle B(r^N)\rangle_{NVEMR} = \langle B(r^N)\rangle_{NVEM}. \tag{50}$$

We observe from the microcanonical temperatures, Eqs. (39)–(43), that the $\theta=0$ equations express the equipartition of energy. However, for $\theta=1$ equipartition is violated, at least in the large-volume, ideal-gas limit.

The microcanonical compressibility factors follow from Eq. (38) [in the second of the equalities in Eqs. (51) and (53), we have specialized to the case of hard spheres]

$$\frac{p_{NVE}(0)V}{NkT_{NVE}(0)} = 1 - \frac{\langle W(r^N)\rangle_{NVE}}{\langle \kappa(r^N)\rangle_{NVE}} = 1 - \frac{\langle W(r^N)\rangle_{NVE}}{E}, \tag{51}$$

$$\frac{p_{NVE}(1)V}{NkT_{NVE}(1)} = 1 - \frac{N-2/d}{N}\left\langle \frac{W(r^N)}{\kappa(r^N)}\right\rangle_{NVE}, \tag{52}$$

$$\frac{p_{NVEM}(0)V}{NkT_{NVEM}(0)} = 1 - \frac{N-1}{N}\frac{\langle W(r^N)\rangle_{NVEM}}{\langle \hat{\kappa}(r^N)\rangle_{NVEM}} = 1 - \frac{N-1}{N}\frac{\langle W(r^N)\rangle_{NVEM}}{\hat{E}}, \tag{53}$$

$$\frac{p_{NVEM}(1)V}{NkT_{NVEM}(1)} = 1 - \frac{N-1-2/d}{N}\left\langle \frac{W(r^N)}{\hat{\kappa}(r^N)}\right\rangle_{NVEM}, \tag{54}$$

$$\frac{p_{NVEMR}(\theta)V}{NkT_{NVEMR}(\theta)} = \frac{p_{NVEM}(\theta)V}{NkT_{NVEM}(\theta)} - \frac{1}{N}. \tag{55}$$

We note that the *NVEMR* ensemble compressibility factor does not approach ideal-gas behavior for either value of θ.

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For hard spheres and periodic boundary conditions, the configurational integral in Eq. (19) becomes

$$Q_{NVT}=Z_{NV}=\int_{U(\boldsymbol{r}^N)=0}d\boldsymbol{r}^N=\int d\boldsymbol{r}^N\prod_{(ij)}A(r_{ij}^*-\sigma), \tag{56}$$

with Z_{NV} being independent of the temperature. The product is over the $N(N-1)/2$ distinct pairs of particle indices, and r_{ij}^* denotes the minimum image separation of the pair (ij). From Eqs. (29) and (30) we see that $\kappa(\boldsymbol{r}^N)$ and $\hat{\kappa}(\boldsymbol{r}^N)$ are positive only in the region in which $U(\boldsymbol{r}^N)$ vanishes, so Eqs. (17), (21), (23), and (25) become

$$Z_{NVT}=(2m\pi kT)^{Nd/2}Z_{NV}, \tag{57}$$

$$Z_{NVE}(\theta)=E^{Nd/2-\theta}Z_{NV}, \tag{58}$$

$$Z_{NVEM}(\theta)=\hat{E}^{(N-1)d/2-\theta}Z_{NV}, \tag{59}$$

$$Z_{NVEMR}(\theta)=\frac{1}{V}Z_{NVEM}(\theta). \tag{60}$$

The microcanonical temperatures become

$$kT_{NVE}(\theta)=\frac{E}{Nd/2-\theta}, \tag{61}$$

$$kT_{NVEM}(\theta)=\frac{\hat{E}}{(N-1)d/2-\theta}, \tag{62}$$

$$T_{NVEMR}(\theta)=T_{NVEM}(\theta). \tag{63}$$

whether directly from Eqs. (35) and (37) or the general Eqs. (39)–(43).

For the microcanonical compressibility factors, the $\theta=1$ Eqs. (52) and (54) cannot be immediately specialized to hard spheres. Instead, we compute directly from Eqs. (31), (34), (35), (38), and (57)–(60) to obtain

$$\frac{p_{NVT}V}{NkT}=\frac{p_{NVE}(\theta)V}{NkT_{NVE}(\theta)}=\frac{p_{NVEM}(\theta)V}{NkT_{NVEM}(\theta)}=\frac{V}{N}\left(\frac{\partial\ln Z_{NV}}{\partial V}\right)_N, \tag{64}$$

$$\frac{p_{NVEMR}(\theta)V}{NkT_{NVEMR}(\theta)}=\frac{V}{N}\left(\frac{\partial\ln Z_{NV}}{\partial V}\right)_N-\frac{1}{N}, \tag{65}$$

in which the rightmost expressions are independent of θ. Indeed, it is well known (see, e.g., [3]) that

$$\frac{V}{N}\left(\frac{\partial\ln Z_{NV}}{\partial V}\right)_N=1-h(N/V,N), \tag{66}$$

with $h(N/V,N)$ given by Eq. (14). [From Eqs. (9), (53), and (64), note that we again obtain Eq. (13).]

If we hypothesize that $p_{\mathrm{MD}}=p_{NVEMR}(0)$, then from Eqs. (64) and (65) we have

$$\frac{p_{\mathrm{MD}}V}{NkT_{NVEMR}(0)}=\frac{p_{\mathrm{MD}}V}{NkT_{\mathrm{MD}}}\frac{T_{\mathrm{MD}}}{T_{NVEMR}(0)}=\frac{p_{NVT}V}{NkT}-\frac{1}{N}. \tag{67}$$

From Eqs. (8), (62), and (63) we find

$$\frac{T_{\mathrm{MD}}}{T_{NVEMR}(0)}=\frac{N-1}{N}. \tag{68}$$

Use of this in Eq. (67) gives Eq. (15), which, as already mentioned, agrees with the $N=12$ hard-disk MC and MD results. [Equivalently, we can change the definition of the MD temperature to the equipartition value $\hat{T}_{\mathrm{MD}}=T_{NVEMR}(0)=NT_{\mathrm{MD}}/(N-1)$, in which case our hypothesis takes the particularly simple form

$$\frac{p_{\mathrm{MD}}V}{Nk\hat{T}_{\mathrm{MD}}}=\frac{p_{NVEMR}(0)V}{NkT_{NVEMR}(0)}=\frac{p_{NVEMR}(1)V}{NkT_{NVEMR}(1)}.$$

This again leads to Eq. (15).]

On the other hand, if we hypothesize that $p_{\mathrm{MD}}=p_{NVEMR}(1)$, then Eqs. (64) and (65), together with Eqs. (8) and (42), lead to

$$\frac{p_{NVT}V}{NkT}=\frac{p_{\mathrm{MD}}V}{NkT_{\mathrm{MD}}}\frac{N-2}{N}+\frac{1}{N}, \tag{69}$$

which disagrees quite strongly with the MC and MD results. Thus those results tend to support the $\theta=0$ (step-function) definition of the *NVEMR* entropy and temperature. The references in Pearson *et al.* [9] contain a more thorough discussion of the arguments for and against each definition than is possible here.

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