10.40 Thermodynamics **Fall 2003**

Problem Set 9

#1

For 60 TIP3P (CHARMM) water molecules in a 15Å×15Å×15Å box, compute *P*, $\underline{U}$, and $\underline{C_v}$, at 300 K and at 500K, running for 1000 heat-up steps and 10,000 and 20,000 equilibrium steps. Also, compute the standard deviations of *P* and $\underline{U}$. If you split up the 20,000 step run into 4 pieces and compute the standard deviations for $\underline{C_V}$ and the averages of *P* and $\underline{U}$ of the 4 pieces, what do you get? What are the limits of these numbers as the molecular dynamics trajectory lengths get very large? Finally, what is the difference in the meaning of the standard deviations from the whole trajectory and the standard deviations of averages of pieces of the trajectory?

Solution:

The calculations were performed using the Molecular Operating Environment (MOE) program. Instructions for its use can be found in the MOE tutorial handout.

$\underline{C_V}$ is calculated using equation (10-54) in Tester & Modell.

$$\underline{C_V} = \frac{\sigma_E^2}{kT^2} \tag{1}$$

The results of the MOE calculations are shown below. The final answers for the problem are outlined in bold.

60 water molecules with the CHARMm22 potential were used in the simulation.

Table 1

Case 1: 10000 Equilibrium Steps

T (K)	300	500
<P> (kPa)	113555	192378
σ_P (kPa)	9196	13053
<U> (kcal/mol)	-8.6666	200.1928
σ_U (kcal/mol)	1.1276	1.4581
<$\underline{U}$> (kcal)	-8.6E-22	1.99E-20
σ_U (kcal)	1.12E-22	1.45E-22
$\underline{C_v}$ (kcal/K)	4.25E-23	2.56E-23
C_v (kcal/mol K)	0.426652	0.256827

Case 2: 20000 Equilibrium Steps

T (K)	300	500
<P> (kPa)	115377	192606
σ_P (kPa)	8608	11888
<U> (kcal/mol)	-6.7282	202.7188
σ_U (kcal/mol)	2.2	2.8547
<$\underline{U}$> (kcal)	-6.7E-22	2.02E-20
σ_U (kcal)	2.19E-22	2.84E-22
$\underline{C_v}$ (kcal/K)	1.62E-22	9.81E-23
C_v (kcal/mol K)	1.624086	0.984435

Table 2

Section 1: Steps 1-5000

T (K)	300	500
<P> (kPa)	112586	192888
σ_P (kPa)	10537	14480
<U> (kcal/mol)	-9.7	198.9439
σ_U (kcal/mol)	0.5031	0.8424
<$\underline{U}$> (kcal)	-9.7E-22	1.98E-20
σ_U (kcal)	5.01E-23	8.39E-23
$\underline{C}_v$ (kcal/K)	8.46E-24	8.54E-24
C_v (kcal/mol K)	0.084932	0.085724

Section 2: Steps 5001-10000

T (K)	300	500
<P> (kPa)	114524	191868
σ_P (kPa)	7509	11442
<U> (kcal/mol)	-7.6782	201.4418
σ_U (kcal/mol)	0.5783	0.6486
<$\underline{U}$> (kcal)	-7.6E-22	2.01E-20
σ_U (kcal)	5.76E-23	6.46E-23
$\underline{C}_v$ (kcal/K)	1.12E-23	5.06E-24
C_v (kcal/mol K)	0.11222	0.050818

Section 3: Steps 10001-15000

T (K)	300	500
<P> (kPa)	116514	194011
σ_P (kPa)	8334	11340
<U> (kcal/mol)	-5.6746	204.2887
σ_U (kcal/mol)	0.478	0.9538
<$\underline{U}$> (kcal)	-5.7E-22	2.04E-20
σ_U (kcal)	4.76E-23	9.5E-23
$\underline{C}_v$ (kcal/K)	7.64E-24	1.09E-23
C_v (kcal/mol K)	0.076669	0.109896

Section 4: Steps 15000-20000

T (K)	300	500
<P> (kPa)	117884	191658
σ_P (kPa)	6621	9666
<U> (kcal/mol)	-3.9049	206.2008
σ_U (kcal/mol)	0.5221	0.277
<$\underline{U}$> (kcal)	-3.9E-22	2.05E-20
σ_U (kcal)	5.2E-23	2.76E-23
$\underline{C}_v$ (kcal/K)	9.11E-24	9.23E-25
C_v (kcal/mol K)	0.091468	0.009269

The standard deviations of the values of $\underline{C}_V$ and the mean values of P and $\underline{U}$ from sections 1 through 4 of the 20,000 step run are shown below.

Table 3

Standard Deviations of the Averages

T(K)	300	500
P (kPA)	2316.255	1079.645
U (kcal/mol)	2.504309	3.186927
<$\underline{U}$> (kcal)	2.5E-22	3.18E-22
$\underline{C}_v$ (kcal/K)	1.51E-24	4.36E-24
C_v (kcal/mol K)	0.015191	0.043771

As the molecular trajectory (the length of the molecular dynamics simulation) gets very large, the value of $\underline{C}_V$ and the mean values of P, $\underline{U}$ will go to some true value for the system. The standard deviations from the whole trajectory, which are shown in table 1, are the result of inherent system fluctuations. For example, the fluctuations in the energy are related to $\underline{C}_V$ of the system. In contrast, the average values from the pieces of the trajectory, as shown in table 3, will all tend to the same value as the lengths of the pieces of the trajectory each go to infinity, so the standard deviation of the values from each of the trajectories will go to zero.