Evaluating Thermodynamic Properties in LAMMPS

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date begun: March 23, 2016
date last updated: March 24, 2016

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I. Purpose of Document

The purpose of this document is to provide a practical introduction to the evaluation of thermodynamic properties in LAMMPS. The notes begin with some formal theory and conclude with practical implementation.

From an undergraduate course in thermodynamics, we have a list of thermodynamic properties of interest. Here we review them in three categories: (1) instantaneous properties immediately available in LAMMPS, (2) properties that can be reliably obtained with a little additional work, and (3) properties involving entropy.

II. Specifying the Thermodynamic State

We begin by recalling the Phase Rule that states that the number of thermodynamic degrees of freedom, *DOF*, of a system are related to the number of phases (ϕ) and the number of components, *C*.

$$DOF = C - \phi + 2 \tag{1}$$

For a single component, single phase system, $DOF = 2$, meaning that the thermodynamic state is fully specified by two variables, for example temperature, *T*, and pressure, *p*, or *T* and the number density, ρ. In fact, any two variables can be used to specify the state. For example a state could be specified by providing the enthalpy, *H*, and the ρ, but that's just not very practical. The Phase Rule is based on intensive properties, thus it does not consider the specification of N, the number of atoms or molecules, *N*, as one of the state variables. In the simulation of a single component, single phase system, we therefore specify three variables in order to fully specify the system. Below we list the four routinely accessible ensembles based on the choice of variables. In the common notation, simulation volume, *V*, an extensive variable is specified, but this does not trouble us since the number density is related to the system volume via, $\rho = N/V$.

- NVE, microcanonical ensemble
- NVT, canonical ensemble
- NpT, isobaric-isothermal ensemble
- NpH, isobaric-isenthalpic ensemble

In undergraduate thermodynamic courses, we ordinarily use the symbol, *U*, to represent the internal energy, whereas in statistical mechanics, the symbol, *E*, is used. Here, $U = E$.

In a multicomponent single-phase system, the phase rule provides that each additional species adds an additional degrees of thermodynamic freedom, $DOF = C + 1$. Typically, this means that we specify the number of each type of atom or molecule, which specifies not *C* but only *C*-1 degrees of freedom. It is easiest to see this in terms of the intensive presentation of the N of each species, namely the mole fraction (or equivalently atom fraction) of component *i*, x_i.

$$x_i \equiv \frac{N_i}{\sum_{j=1}^{C} N_j} \tag{2}$$

Since the mole fractions are constrained to sum to unity,

$$\sum_{j=1}^{C} x_j = 1 \tag{3}$$

only C-1 of the mole fractions are independent. Thus there remain two additional thermodynamic degrees of freedom, such as T and p or T and ρ.

As you increase the number of phases, the thermodynamic degrees of freedom decrease. In a single component two-phase system, $DOF = 1$. Specifying one variable, say the temperature, fully defines the thermodynamic state. In terms of vapor-liquid equilibrium, specifying the boiling temperature specifies the vapor pressure, which is the pressure at which the vapor and liquid can co-exist at that temperature.

III. Evaluating Thermodynamic Properties

III.A. Instantaneous Properties

The solution of the classical equations of motion results exclusively in a set of trajectories, which are comprised of atomic positions, **r**, and velocities, **v**, (or equivalently momenta, **p**) as a function of time, *t*. Every thermodynamic property is formulated as a function of these trajectories. Since, classical thermodynamics is a continuum theory formulated without knowledge of the atomic nature of matter, it does not provide relationships between thermodynamic quantities and atomic trajectories. For that we require statistical mechanics, sometimes called statistical thermodynamics, when limited to equilibrium systems. We make no attempt here to derive any of these relationships. We simply present some relationships and link them to variables available in LAMMPS.

- **number of particles of component i, Ni**

In the four ensembles described above, the number of particles (atoms or molecules) is held constant. Therefore, this extensive variable is always an input to the simulation. It is a constant and has no fluctuation during the course of the simulation.

- **mole or atom fraction of component *i*, x_i**

Since the number of particles is a fixed input, per equation (2), the mole fractions are also fixed inputs.

- **volume of the system, *V***

In the NVE and NVT ensembles, the volume of the simulation cell is a fixed input. It does not fluctuate with time. In the NpT and NpH ensembles, the volume fluctuates in response to the barostat.

- **temperature, *T***

The temperature is related to the kinetic energy, *KE*, via the equipartition theorem. The kinetic energy is related to the velocities via classical mechanics.

$$\frac{3}{2}NkT = KE = \frac{1}{2}\sum_{i=1}^{N}\sum_{\alpha=1}^{3} m_i v_{i,\alpha}^2 \tag{4}$$

Unlike the volume, the temperature fluctuates in all four ensembles. The NVT and NpT ensembles, in which the temperature is specified, are controlled by thermostats that do not keep the temperature exactly at the set point temperature at all times. Instead, a proper thermostat allows the temperature to fluctuate about the set point temperature in a manner that is still capable of rigorously generating trajectories that correspond to the ensemble.

- **pressure, *p***

In three-dimensions, the pressure tensor is a symmetric 3x3 tensor, with each component defined by a kinetic and potential contribution,

$$p_{\alpha\beta} = p_{KE,\alpha\beta} + p_{PE,\alpha\beta} \tag{5}$$

The kinetic contribution to the $\alpha\beta$ element of the pressure is

$$p_{KE,\alpha\beta} = \frac{1}{V}\sum_{i=1}^{N} m_i v_{i,\alpha} v_{i,\beta} \tag{6}$$

Since the velocities in different dimensions are not correlated, when $\alpha \neq \beta$, the average value of the $p_{KE,\alpha\beta}$ is zero. However, $\alpha = \beta$, we have twice the kinetic energy in that dimension.

$$p_{KE,\alpha\beta} = \frac{\delta_{\alpha\beta}}{V}\sum_{i=1}^{N} m_i v_{i,\alpha}^2 \tag{7}$$

If use the equipartition theorem relate the kinetic energy in terms of the temperature and average over all three dimensions, we have the pressure from the ideal gas law, where the potential energy is zero,

$$p = \frac{N}{V}kT = \frac{2}{3}\frac{KE}{V} = \frac{1}{3V}\sum_{i=1}^{N}\sum_{\alpha=1}^{3} m_i v_{i,\alpha}^2 \qquad \text{for ideal gas only} \tag{8}$$

Thus the potential energy contribution to the pressure can be seen as a deviation from the ideal gas.

$$p_{PE,\alpha\beta} = \frac{1}{V}\sum_{i=1}^{N} r_{i,\alpha} f_{i,\beta} \tag{9}$$

When $\alpha \neq \beta$, the average value of the $p_{PE,\alpha\beta}$ is not necessarily zero, depending on the state of stress within the system.

If the pressure tensor is not of interest, the scalar pressure reported by LAMMPS is the thermodynamic pressure,

$$p = \frac{1}{3}\sum_{\alpha=1}^{3} p_{\alpha\alpha} = \frac{1}{3V}\sum_{i=1}^{N}\sum_{\alpha=1}^{3} m_i v_{i,\alpha}^2 + \frac{1}{3V}\sum_{i=1}^{N}\sum_{\alpha=1}^{3} r_{i,\alpha} f_{i,\alpha} \tag{10}$$

Like the temperature, the pressure fluctuates in all four ensembles. The NpT and NpH ensembles, in which the pressure is specified, are controlled by barostats that do not keep the pressure exactly at the set point temperature at all times. Instead, a proper barostat allows the pressure to fluctuate about the set point pressure in a manner that is still capable of rigorously generating trajectories that correspond to the ensemble.

- **kinetic energy, *KE***

The kinetic energy is not a traditional thermodynamic variable. However, it is an important property in the atomic-level description of matter. The KE is defined by the sum of the kinetic energy of all particles in the system, as given in equation (4). In this work, the kinetic energy is defined exclusively as a function of velocities. Explicitly, the kinetic energy is not a function of particle positions.

If the system does not have net zero momentum, then there is a center of mass velocity that exists in the simulation. The kinetic energy can then be broken into two parts. Kinetic energy of the center of mass of the system and the peculiar kinetic energy, which is the sum of kinetic energy of each particle based on velocities relative to the system center of mass velocity. Importantly, when the equipartition theorem is used to calculate temperature, it relies on peculiar velocities. See the notes on thermostats to properly account for this effect.

- **potential energy, *PE***

The potential energy is not a traditional thermodynamic variable. However, it is an important property in the atomic-level description of matter. The PE is defined by the sum of all interactions between all particles in the system as given by the interaction potential. The Lennard-Jones potential, Embedded-Atom Method potential and OPLS-aa potential are all examples of interaction potentials that define the potential energy. In this work, the potential energy is defined exclusively as a function of positions. Explicitly, the potential energy is not a function of particle velocities.

- **internal energy, *U* (or total energy, *E*)**

The internal energy is the sum of the kinetic and potential energies. It is also called the total energy. Often in thermodynamics, we here of the excess internal energy, which subtracts the KE form the total energy. However, in general, the internal energy includes both contributions.

$$U = E = KE + PE \tag{11}$$

In the NVE ensemble, the internal energy should be constant, as it is a measure of the conservation of energy of the classical equations of motion. It truth it fluctuates based on the numerical approximations to the solution of these ordinary differential equations. In the other three ensembles, the internal energy fluctuates.

- **enthalpy, *H***

The enthalpy is defined as the sum of the internal energy and the product of pressure and volume.

$$H \equiv U + pV \tag{12}$$

All of the quantities listed in this section can evaluated at each instant in time, yielding so called instantaneous properties. Of course, what is typically important is to report the average properties. The average can be computed in a post-processing mode using the instantaneous values printed out in the LAMMPS output file. Alternatively, the averages can be computed in the LAMMPS input file using the `fix ave/time` command. See for example, the block averaging examples on the course website that compute both the average as well as the standard error using the `fix ave/time` command.

III.B. Fluctuation Properties (heat capacity, isothermal compressibility, etc.)

There are a variety of thermodynamic properties that are based on the partial derivative of property *X* with respect to property *Y*, holding property *Z* constant. Some common thermodynamic properties of this form include the constant-pressure heat capacity, C_p, the isothermal compressibility, β, and the thermal expansivity, α.

$$C_p \equiv \left(\frac{\partial H}{\partial T}\right)_{p,N} \tag{13.a}$$

$$\beta \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N} \tag{13.b}$$

$$\alpha \equiv \left(\frac{\partial V}{\partial T}\right)_{p,N} \tag{13.c}$$

The expression given above are thermodynamic definitions. Statistical mechanics provides an elegant theoretical way to evaluate these properties based on the fluctuations of properties. These fluctuations are based on the variance or covariance of the instantaneous thermodynamic properties discussed in the previous section.

For example, in the NpT ensemble, the constant pressure heat capacity is proportional to the variance of the enthalpy

$$C_p = \frac{1}{VkT^2} < {\sigma_H}^2 > \tag{14.a}$$

The isothermal compressibility is obtained through the variance of volume,

$$\beta = \frac{1}{VkT} < {\sigma_V}^2 > \tag{14.b}$$

The thermal expansion coefficient is based on the covariance of volume and enthalpy of the

$$\alpha = \frac{1}{VkT^2} < \sigma_{(V)(H)} > \tag{14.c}$$

The angled brackets indicate an ensemble average, namely an average over both all particles and time. Note that this variance is based on instantaneous values, corresponding to the square of standard deviation of the variables. Explicitly these fluctuations do not correspond to the square of the standard error generated by the block averaging procedure.

These fluctuations seem to provide an efficient method to obtain these thermodynamic properties, since we can obtain all these three properties from one single MD simulation at the desired state point. The formulae given in equation (14) are for the NpT ensemble. Other formulae exist for other ensembles.

We could also calculate C_p, β, and α using a second procedure, namely centered finite difference using average values of properties over multiple simulations. In this approach, one runs three simulations for each thermodynamic property. For example, for the heat capacity, one runs a simulation at the state point defined by (p,T), then two other simulations at $(p,T+\varepsilon)$ and $(p,T-\varepsilon)$. The choice of ε is made so that one can observe statistically valid differences in the enthalpy between the state points. Thus the heat capacity can be determined as

$$C_p = \frac{H(p,T+\varepsilon) - H(p,T-\varepsilon)}{2\varepsilon} \tag{15.a}$$

Similarly, the isothermal compressibility and thermal expansivity can be expressed as

$$\beta = -\frac{1}{V(p,T)} \frac{V(p+\varepsilon,T) - V(p-\varepsilon,T)}{2\varepsilon} \tag{15.b}$$

$$\alpha = \frac{1}{V(p,T)}\frac{V(p,T+\varepsilon)-V(p,T-\varepsilon)}{2\varepsilon} \tag{15.c}$$

A detailed comparison of these approaches is given in the following reference.

Wang, Q., Keffer, D.J., Petrovan, S., Thomas, J.B., "Molecular Dynamics Simulation of Polyethylene Terephthalate Oligomers", J. Phys. Chem. B. 114(2) 2010 pp. 786–795, doi: 10.1021/jp909762j.

Their analysis found that the finite difference approach was markedly more accurate. Any advantage thought to be gained by efficiency of obtaining the result from a single simulation was lost since, in order to get reasonable statistics from the fluctuations, one would have to run much larger systems for much longer times.

Certainly, a set of three simulations could be set up in a single LAMMPS input file to evaluate these properties via the centered-finite difference approach.

Thermodynamic relations can also be exploited to evaluate other fluctuation properties. For example, the constant volume heat capacity, C_v, is related to the above three properties via

$$C_p - C_v = VT\frac{\alpha^2}{\beta} \tag{16.a}$$

and the isentropic compressibility can be obtained from the following relation,

$$\frac{C_p}{C_v} = \frac{\beta}{\beta_s} \tag{16.b}$$

III.C. Properties including Entropy

- **entropy, S**

There are many reasons to want to know the entropy of a system. There exist some approximate ways to evaluate an entropy based on an average configuration. See for example the following two references.

D.C. Wallace, On the role of density-fluctuations in the entropy of a fluid, J. Chem. Phys. 87 (4) (1987) 2282–2284.

A. Baranyai, D.J. Evans, Direct entropy calculation from computer simulation of liquids, Phys. Rev. A 40 (7) (1989) 3817–3822

However, these efforts are fraught with sufficient difficulty and errors that they have not been accepted as a standard way to compute entropy for arbitrarily complex systems, as is the case for the instantaneous thermodynamic properties. Therefore, today, there is no easily implemented and straightforward way to calculate the entropy in a classical simulation.

- **free energies, A and G**

Since the entropy is not easily available, there is also no direct way to calculate either the Helmholtz or the Gibbs free energy from a simulation.

$$A \equiv U - TS \tag{17.a}$$

$$G \equiv H - TS = U + pV - TS \tag{17.b}$$

You should be suspicious of any article that claims to have done so.

- **chemical potential of component *i*, μ_i**

The chemical potential of component i is defined as a thermodynamic partial derivative

$$\mu_i \equiv \left(\frac{\partial G}{\partial N_i}\right)_{T,p,N_{j\neq i}} = \left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_{j\neq i}} \tag{18}$$

There are some sophisticated ways to compute the chemical potential in a simulation. We leave these techniques to a separate lecture to be presented later in the course.

- **entropy differences, ΔS**

Those of you with a fondness for thermodynamics may recall Maxwell relations. Two Maxwell relations most relevant to the calculation of entropy differences are

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial p}{\partial T}\right)_{V,N} \tag{19.a}$$

$$\left(\frac{\partial S}{\partial p}\right)_{T,N} = \left(\frac{\partial V}{\partial T}\right)_{p,N} \tag{19.b}$$

These equations can be manipulated and integrated to yield

$$\Delta S = \int_{S_1(T,V_1)}^{S_2(T,V_2)} dS = \int_{V_1}^{V_2} \left(\frac{\partial p}{\partial T}\right)_{V,N} dV \tag{20.a}$$

$$\Delta S = \int_{S_1(T,p_1)}^{S_2(T,p_2)} dS = \int_{p_1}^{p_2} \left(\frac{\partial V}{\partial T}\right)_{p,N} dp \tag{20.b}$$

In the first case, one can perform a series of simulations all at the same temperature T, in which the volume varies from V_1 to V_2. One can then compute the value of $\left(\frac{\partial p}{\partial T}\right)_{V,N}$ across this range, using for example the centered-finite difference approach described above for each simulation at (T,V_i). From this data, one can use a numerical integration scheme (such as the trapezoidal rule) to calculate an approximate value of the entropy difference. Note that this requires a series of simulations.

In the second case, one can perform a series of simulations all at the same temperature T, in which the pressure varies from p_1 to p_2. One can then compute the value of $\left(\frac{\partial V}{\partial T}\right)_{p,N} \equiv \alpha$ across this range, using for example the centered-finite difference approach described above for α at each simulation, (T,p_i). From this data, one can again use a numerical integration scheme (such as the trapezoidal rule) to calculate an approximate value of the entropy difference. Note that this requires a series of simulations.

Other thermodynamic relations can also be exploited to calculate entropy differences, such as

$$C_v = T\left(\frac{\partial S}{\partial T}\right)_{V,N} \tag{21.a}$$

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_{p,N} \tag{21.b}$$

As before, these equations can be manipulated and integrated to yield

$$\Delta S = \int_{S_1(T_1,V)}^{S_2(T_2,V)} dS = \int_{T_1}^{T_2} \frac{C_v}{T} dT \tag{22.a}$$

$$\Delta S = \int_{S_1(T_1,p)}^{S_2(T_2,p)} dS = \int_{T_1}^{T_2} \frac{C_p}{T} dT \tag{22.b}$$

Again, a series of simulations can be run, either at constant volume or constant pressure from T_1 to T_2. If the appropriate heat capacity is evaluated for each simulation, then the integral yields the change in entropy.

Once the change in entropy is known, the change in free energy can be computed directly from equation (17) since the same simulations generated values for the internal energy and enthalpy.

One (of many) examples where such an integration is done (using equation 22.a) is given in Figure 3.a. and Figure 3.b of the following reference.

McNutt, N.W., Wang, Q., Keffer, D.J., Rios, O., “Entropy-driven Structure and Dynamics in Carbon Nanocrystallites”, J. Nanoparticle Res. 16 (4) 2014 article # 2365, doi: 10.1007/s11051-014-2365-7.