Blog Entry (c) Tuesday, November 10, 2026, by James Pate Williams, Jr.

Reference: ***An Introduction to Statistical Thermodynamics*** (c) 1960 Terrell L. Hill Chapter 15 Imperfect Gases Section 15-2 and Hard sphere: virial coefficients page on SklogWiki - a wiki for statistical mechanics and thermodynamics

In this text I use Monte Carlo integration to calculate the three-dimensional hard spheres second and third virial coefficients for the Noble Gases. The integration is performed over a sphere with a radius of R meters. Monte Carlo integration can be done using multiple particles, the radius of the spherical enclosure, and the number of points to be used. I use the known analytic (theoretic) values of the two virial coefficients in evolutionary hill climbers to minimize the percentage error between my calculated and the analytic virial coefficients. In utilizing my evolutionary hill climber, the virial coefficients are sought using the radius of R. The evolutionary hill climber is elitist (meaning the maximum R can be eliminated if the child fitness is less than the selected parent fitness). The fitness function is the percentage error between the analytic and approximated virial coefficients. In my Monte Carlo code, I use the following stochastic variables based on a maximum of below R. The initialization lines of code in creating candidate solutions are:

double r = 50.0 * static_cast<double>(rand()) / RAND_MAX;

R[i] = r * 1.0e9 * a;

The random numbers generated are in the half-open interval [0.0, X).

```
double x1 = (R * rand()) / RAND_MAX;
double x2 = (R * rand()) / RAND_MAX;
double y1 = (R * rand()) / RAND_MAX;
double y2 = (X * rand()) / RAND_MAX;
double z1 = (R * rand()) / RAND_MAX;
double z2 = (R * rand()) / RAND_MAX;
double r12 = std::sqrt(
    std::pow(x1 - x2, 2.0) +
    std::pow(y1 - y2, 2.0) +
    std::pow(z1 - z2, 2.0));
```

```
Second Virial Coefficient for Noble Gases
Monte Carlo Integration is Used
Number of Points 1000000
Number of Generations 100
Population 15
Atom    B2 Analytic              B2 Approximate
Helium  4.991529959631652e-31    4.746262969973750e-31
Neon    9.193891844681553e-31    9.389661736988127e-31
Argon   5.996856363941208e-30    6.084097770330035e-30
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```
Krypton 1.141817295374476e-29   1.024347598892477e-29
Xenon   2.110667714580750e-29   2.089759387613367e-29
Radon   2.895291789548353e-29   2.199174718615131e-29
Atom    B2 % Error
Helium  4.913663578932052e+00
Neon    2.129347349455961e+00
Argon   1.454785659256500e+00
Krypton 1.028795911201130e+01
Xenon   9.906024914744022e-01
Radon   2.404307135626605e+01
Time taken 119 seconds
Third Virial Coefficient for Noble Gases
Monte Carlo Integration is Used
Number of Points 1000000
Number of Generations 100
Population 15
Atom    B3 Analytic             B3 Approximate
Helium  1.557210708618773e-61   1.559494764378819e-61
Neon    5.282977953231373e-61   4.751157230882232e-61
Argon   2.247642890608885e-59   2.000176661696957e-59
Krypton 8.148417100101773e-59   9.065567501636736e-59
Xenon   2.784323875858453e-58   2.894691493555528e-58
Radon   5.239196591641317e-58   6.326902909422479e-58
Atom    B3 % Error
Helium  1.466760886888691e-01
Neon    1.006668449229187e+01
Argon   1.101003321950710e+01
Krypton 1.125556522534306e+01
Xenon   3.963892945573590e+00
Radon   2.076093726882674e+01
Coefficient Table Fit B3/B2^2
Atom      Analytic                Approximate
Helium  6.250000000000000e-01   6.922776761995107e-01
Neon    6.250000000000000e-01   5.388892357537087e-01
Argon   6.250000000000000e-01   5.403510337179364e-01
Krypton 6.250000000000000e-01   8.639732344823379e-01
Xenon   6.250000000000001e-01   6.628415362596742e-01
Radon   6.250000000000001e-01   1.308192639953331e+00
Time taken 252 seconds

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e (process 7088) exited with code 0 (0x0).
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Second Virial Coefficient for Noble Gases
Monte Carlo Integration is Used
Number of Points 1000000
```

```
Number of Generations 200
Population 15
Atom    B2 Analytic              B2 Approximate
Helium  4.991529959631652e-31   4.746262969973750e-31
Neon    9.193891844681553e-31   9.170029534118779e-31
Argon   5.996856363941208e-30   6.236435043304109e-30
Krypton 1.141817295374476e-29   9.847231561108454e-30
Xenon   2.110667714580750e-29   2.073380721252408e-29
Radon   2.895291789548353e-29   2.506092616055092e-29
Atom    B2 % Error
Helium  4.913663578932052e+00
Neon    2.595452607654717e-01
Argon   3.995071164343302e+00
Krypton 1.375825536187113e+01
Xenon   1.766597038025369e+00
Radon   1.344248531005486e+01
Time taken 227 seconds
Third Virial Coefficient for Noble Gases
Monte Carlo Integration is Used
Number of Points 1000000
Number of Generations 200
Population 15
Atom    B3 Analytic              B3 Approximate
Helium  1.557210708618773e-61   1.604316208313861e-61
Neon    5.282977953231373e-61   5.148725126343071e-61
Argon   2.247642890608885e-59   2.187801927064251e-59
Krypton 8.148417100101773e-59   8.157516516598314e-59
Xenon   2.784323875858453e-58   2.797024383205959e-58
Radon   5.239196591641317e-58   5.264216394235259e-58
Atom    B3 % Error
Helium  3.024992021591651e+00
Neon    2.541233903998887e+00
Argon   2.662387508027250e+00
Krypton 1.116709709966527e-01
Xenon   4.561433193036980e-01
Radon   4.775503678151541e-01
Coefficient Table Fit B3/B2^2
Atom    Analytic                 Approximate
Helium  6.250000000000000e-01   7.121744310716679e-01
Neon    6.250000000000000e-01   6.122915106712813e-01
Argon   6.250000000000000e-01   5.625164069596026e-01
Krypton 6.250000000000000e-01   8.412588781173798e-01
Xenon   6.250000000000001e-01   6.506360763084323e-01
Radon   6.250000000000001e-01   8.381842570483780e-01
Time taken 480 seconds
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e (process 5788) exited with code 0 (0x0).
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Second Virial Coefficient for Noble Gases
Monte Carlo Integration is Used
Number of Points 1000000
Number of Generations 300
Population 15
Atom    B2 Analytic              B2 Approximate
Helium  4.991529959631652e-31   4.842899593412331e-31
Neon    9.193891844681553e-31   9.170029534118779e-31
Argon   5.996856363941208e-30   5.979188160443553e-30
Krypton 1.141817295374476e-29   1.118878767391262e-29
Xenon   2.110667714580750e-29   2.115125400775319e-29
Radon   2.895291789548353e-29   2.764459201817924e-29
Atom    B2 % Error
Helium  2.977651490051155e+00
Neon    2.595452607654717e-01
Argon   2.946244236212390e-01
Krypton 2.008949074089030e+00
Xenon   2.111979144691933e-01
Radon   4.518804916406646e+00
Time taken 330 seconds
Third Virial Coefficient for Noble Gases
Monte Carlo Integration is Used
Number of Points 1000000
Number of Generations 300
Population 15
Atom    B3 Analytic              B3 Approximate
Helium  1.557210708618773e-61   1.542371203298208e-61
Neon    5.282977953231373e-61   5.339370395451388e-61
Argon   2.247642890608885e-59   2.254435742093640e-59
Krypton 8.148417100101773e-59   8.612375200869350e-59
Xenon   2.784323875858453e-58   2.601509792945651e-58
Radon   5.239196591641317e-58   4.691844981234721e-58
Atom    B3 % Error
Helium  9.529542301778284e-01
Neon    1.067436637427609e+00
Argon   3.022211185387556e-01
Krypton 5.693843295795229e+00
Xenon   6.565833971324103e+00
Radon   1.044724321434794e+01
Coefficient Table Fit B3/B2^2
Atom    Analytic                 Approximate
Helium  6.250000000000000e-01   6.576244901936323e-01
Neon    6.250000000000000e-01   6.349632356051724e-01
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Argon    6.250000000000000e-01   6.305992067221579e-01
Krypton 6.250000000000000e-01   6.879500029091027e-01
Xenon    6.250000000000001e-01   5.815046923376688e-01
Radon    6.250000000000001e-01   6.139362606103491e-01
Time taken 690 seconds

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e (process 25368) exited with code 0 (0x0).
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Second Virial Coefficient for Noble Gases
Monte Carlo Integration is Used
Number of Points 1000000
Number of Generations 400
Population 15
Atom     B2 Analytic              B2 Approximate
Helium   4.991529959631652e-31   4.878517321220201e-31
Neon     9.193891844681553e-31   9.113724196084460e-31
Argon    5.996856363941208e-30   5.833418147589358e-30
Krypton 1.141817295374476e-29   1.045344852864841e-29
Xenon    2.110667714580750e-29   2.079670041708083e-29
Radon    2.895291789548353e-29   3.008077012619602e-29
Atom     B2 % Error
Helium   2.264088151837731e+00
Neon     8.719664093445650e-01
Argon    2.725398215881831e+00
Krypton 8.449026205895331e+00
Xenon    1.468619274295568e+00
Radon    3.895469999893940e+00
Time taken 430 seconds
Third Virial Coefficient for Noble Gases
Monte Carlo Integration is Used
Number of Points 1000000
Number of Generations 400
Population 15
Atom     B3 Analytic              B3 Approximate
Helium   1.557210708618773e-61   1.555202054264109e-61
Neon     5.282977953231373e-61   5.173330234098379e-61
Argon    2.247642890608885e-59   2.296401325236154e-59
Krypton 8.148417100101773e-59   8.445858355613604e-59
Xenon    2.784323875858453e-58   2.706823872873888e-58
Radon    5.239196591641317e-58   5.286681014326998e-58
Atom     B3 % Error
Helium   1.289905305394091e-01
Neon     2.075490757365864e+00
Argon    2.169314121517760e+00
Krypton 3.650294920569486e+00
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Xenon   2.783440664232017e+00
Radon   9.063302331780941e-01
Coefficient Table Fit B3/B2^2
Atom    Analytic                Approximate
Helium  6.250000000000000e-01   6.534481287793473e-01
Neon    6.250000000000000e-01   6.228427862036662e-01
Argon   6.250000000000000e-01   6.748411736541898e-01
Krypton 6.250000000000000e-01   7.729023420603781e-01
Xenon   6.250000000000001e-01   6.258512538712357e-01
Radon   6.250000000000001e-01   5.842587231001383e-01
Time taken 912 seconds

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e (process 20820) exited with code 0 (0x0).
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Second Virial Coefficient for Noble Gases
Monte Carlo Integration is Used
Number of Points 1000000
Number of Generations 500
Population 15
Atom    B2 Analytic             B2 Approximate
Helium  4.991529959631652e-31   4.878517321220201e-31
Neon    9.193891844681553e-31   9.246115485950217e-31
Argon   5.996856363941208e-30   5.983930411242188e-30
Krypton 1.141817295374476e-29   1.142265331662067e-29
Xenon   2.110667714580750e-29   2.116399061159089e-29
Radon   2.895291789548353e-29   2.840314873434887e-29
Atom    B2 % Error
Helium  2.264088151837731e+00
Neon    5.680254037236094e-01
Argon   2.155454777396809e-01
Krypton 3.923887730604053e-02
Xenon   2.715418698427073e-01
Radon   1.898838531989299e+00
Time taken 539 seconds
Third Virial Coefficient for Noble Gases
Monte Carlo Integration is Used
Number of Points 1000000
Number of Generations 500
Population 15
Atom    B3 Analytic             B3 Approximate
Helium  1.557210708618773e-61   1.554344458640494e-61
Neon    5.282977953231373e-61   5.274911895614227e-61
Argon   2.247642890608885e-59   2.241191084326951e-59
Krypton 8.148417100101773e-59   7.980154878456371e-59
Xenon   2.784323875858453e-58   2.759644198828087e-58
```

```
Radon   5.239196591641317e-58   5.152847423921409e-58
Atom    B3 % Error
Helium  1.840630790948647e-01
Neon    1.526801301946088e-01
Argon   2.870476581885610e-01
Krypton 2.064968196624355e+00
Xenon   8.863795352384130e-01
Radon   1.648137576239663e+00
Coefficient Table Fit B3/B2^2
Atom    Analytic                Approximate
Helium  6.250000000000000e-01   6.530877934428784e-01
Neon    6.250000000000000e-01   6.170162231957249e-01
Argon   6.250000000000000e-01   6.259012478781614e-01
Krypton 6.250000000000000e-01   6.116138737665243e-01
Xenon   6.250000000000001e-01   6.161095939978207e-01
Radon   6.250000000000001e-01   6.387255767662867e-01
Time taken 1126 seconds

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e (process 13756) exited with code 0 (0x0).
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Second Virial Coefficient for Noble Gases
Monte Carlo Integration is Used
Number of Points 1000000
Number of Generations 600
Population 15
Atom    B2 Analytic             B2 Approximate
Helium  4.991529959631652e-31   4.878517321220201e-31
Neon    9.193891844681553e-31   9.246115485950217e-31
Argon   5.996856363941208e-30   5.983930411242188e-30
Krypton 1.141817295374476e-29   1.073605514783653e-29
Xenon   2.110667714580750e-29   2.117673232745092e-29
Radon   2.895291789548353e-29   2.802215922902861e-29
Atom    B2 % Error
Helium  2.264088151837731e+00
Neon    5.680254037236094e-01
Argon   2.155454777396809e-01
Krypton 5.973966313800855e+00
Xenon   3.319100451457887e-01
Radon   3.214731827081631e+00
Time taken 670 seconds
Third Virial Coefficient for Noble Gases
Monte Carlo Integration is Used
Number of Points 1000000
Number of Generations 600
Population 15
```

```
Atom    B3 Analytic             B3 Approximate
Helium  1.557210708618773e-61   1.545501091024131e-61
Neon    5.282977953231373e-61   5.310657732611297e-61
Argon   2.247642890608885e-59   2.355437730014724e-59
Krypton 8.148417100101773e-59   8.178804388223920e-59
Xenon   2.784323875858453e-58   2.749025656503042e-58
Radon   5.239196591641317e-58   5.526429958975386e-58
Atom    B3 % Error
Helium  7.519610242744860e-01
Neon    5.239427388296015e-01
Argon   4.795905962474184e+00
Krypton 3.729225903490819e-01
Xenon   1.267748327034255e+00
Radon   5.482393384365932e+00
Coefficient Table Fit B3/B2^2
Atom    Analytic                Approximate
Helium  6.250000000000000e-01   6.493720820308622e-01
Neon    6.250000000000000e-01   6.211974800158133e-01
Argon   6.250000000000000e-01   6.578071030289931e-01
Krypton 6.250000000000000e-01   7.095783463397078e-01
Xenon   6.250000000000001e-01   6.130005987510769e-01
Radon   6.250000000000001e-01   7.037873835585562e-01
Time taken 1343 seconds

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e (process 17936) exited with code 0 (0x0).
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