33-765 Midterm Exam

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I hereby confirm that I have not collaborated with anybody else during completion of this exam, and I have not used external help that had been expressly excluded by the lecturer.

1. Drawing Random Numbers from any Prescribed Probability Density

Let $p(x)$ be a probability density on the real numbers, and define its *cumulative distribution function* $Q(x) := \int_{-\infty}^{x} \mathrm{d}x'\, p(x')$.

1. As a warm-up: Illustrate this definition by drawing some generic (and, pro-tip, not to singular) $p(x)$ of your choice, as well as its associated $Q(x)$ in the same diagram. Pay special attention to the values that $Q(x)$ ultimately takes.

   Note: Don't just produce the plots; explain the relation between $p(x)$ and $Q(x)$ in the context of what will matter below.

   See Figure 0.1 for the drawing. Note that $Q(x)$ must begin at $Q(-\infty) \equiv 0$ (we're assuming the distribution is defined for negative x), I drew one which was basically 0 for $x < 0$, so $Q(0) \approx 0$. Secondly, $Q(\infty) \equiv 1$ since $Q(1) \equiv \int_{-\infty}^{\infty} \mathrm{d}x'\, p(x') = 1$ by normalization. Finally, in my plot, I attempted to show a bimodal distribution. The peaks and valleys should correspond to inflection points in the CDF, and the entire CDF should be monotonically increasing.

2. Argue that if $p(x) > 0$ for all x, the equation $q = Q(x)$ can be solved for $x = Q^{-1}(q)$ (meaning $Q(x)$ is invertible).

   An function is only invertible iff it is strictly increasing or decreasing in its domain. This corresponds to its derivative being strictly positive or negative over the entire domain. The probability distribution itself is the derivative of the cumulative distribution function by definition:

   $$p(x) = \frac{\mathrm{d}Q(x)}{\mathrm{d}x}$$

   so as long as $p(x) = \frac{\mathrm{d}Q(x)}{\mathrm{d}x} > 0$ (or strictly negative), $Q(x)$ is invertible.

3. What is the domain over which the function $Q^{-1}(q)$ is defined?

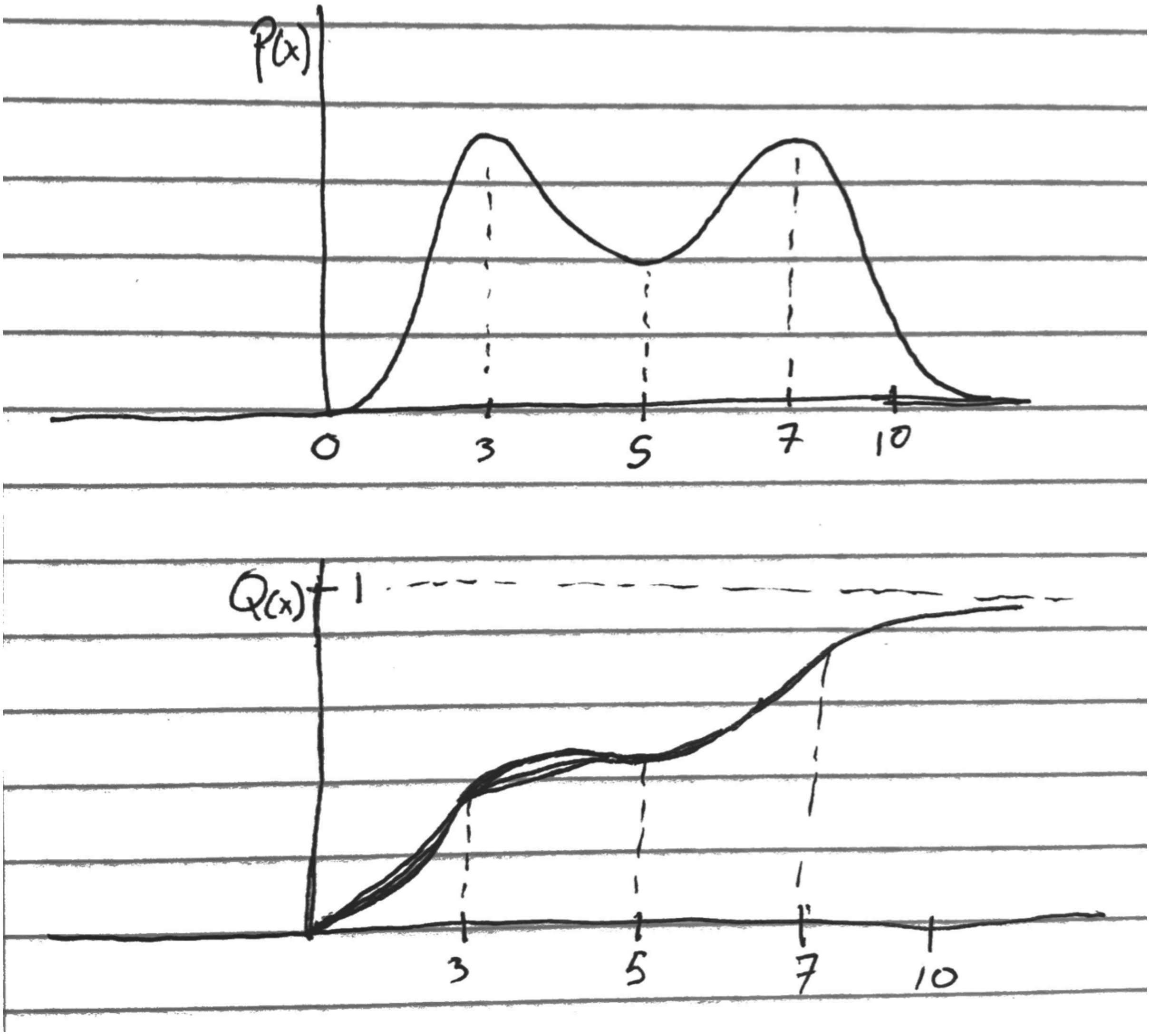

Figure 0.1: Plots of an arbitrary $p(x)$ and $Q(x)$ for Problem 1.

The CDF will increase from $Q(-\infty) \equiv 0$ to $Q(\infty) \equiv 1$ by definition, since $\int_a^a f(x)\,\mathrm{d}x \equiv 0$ and $\int_{-\infty}^{\infty} p(x)\,\mathrm{d}x \equiv 1$ if we require the probability distribution to be normalized (we do). Therefore, the domain of $Q^{-1}(q)$ is $q \in [0,1]$, since those are the maximum and minimum values obtainable from the CDF iff $p(x) > 0$.

4. Let q be a random number chosen from the interval $[0,1]$ with equal probability. Now prove the following statement, which is both interesting and practically useful: The random variable $X := Q^{-1}(q)$ has the probability density $p(x)$.

   Hint: X certainly has some probability density, let's call it $p_X(x)$. Calculate it and discover that it coincides with $p(x)$.

By transformation theory,

$$p_X(x') = \int_0^1 \mathrm{d}q\, \delta(x' - Q^{-1}(q))U(q)$$

where $U(q)$ is the uniform distribution and is equal to 1 in this domain. However, $Q^{-1}(q) \equiv x$ sampled from $p(x)$, so the δ function sets these distributions to be equal to each other.

5. As an example: If someone can give you random numbers evenly distributed on $[0, 1]$, how would you create random numbers that are distributed according to the Cauchy-Lorentz density $p_{x_0,a}(x)$ from problem 9 on homework sheet 3?

> As seen in the previous problem, we just need to feed these numbers into the inverse CDF function for the Cauchy-Lorentz distribution:
>
> $$p_{x_0,a}(x) = x_0 + a\tan\left(\pi\left(U(x) - \frac{1}{2}\right)\right)$$
>
> where $U(x)$ is, again, the uniform distribution for $x \in [0, 1]$.

2. Entropy of a Discrete Gas and its Legendre Transformation

Consider a lattice with M sites, each of which can be either occupied by a particle or empty. Let's assume that exactly N sites are occupied. Don't worry about interactions—we assume they vanish. This is like an ideal gas on a lattice.

1. Calculate the total number $\Omega(N, M)$ of of ways in which N sites on this lattice can be singly occupied.

> The gas particles are not distinguishable in any way, so imagine we define an ordered set $A = \{1, 2, 3, \cdots, M\}$. The number of ways we can fill lattice sites are the number of unique subsets of A which contain N elements, since we could imagine one such configuration of particles as choosing spots in A and adding those numbers to a new set until that set had N elements. I don't idly use the word "choose" here; This is a statement of "M choose N", the definition of the binomial coefficient:
>
> $$\Omega(N, M) = \binom{M}{N} = \frac{M!}{N!(M-N)!}$$
>
> The binomial coefficient $\binom{M}{N}$ is defined as the number of ways to choose an unordered subset of N elements from a fixed set of M elements. We want this to be unordered choice because the particles are identical, and we don't want to double count all the different ways we could swap particles on the same lattice sites.

2. The total entropy is given by $S(N, M) = k_B \ln[\Omega(N, M)]$. Find an approximate expression for the entropy using the simplest version of Stirling's approximation.

> $$\begin{aligned} S(N, M) &= k_B \ln[\Omega(N, M)] \\ &= k_B \ln\left[\frac{M!}{N!(M-N)!}\right] \\ &= k_B \left[\ln M! - \ln N! - \ln(M-N)!\right] \end{aligned}$$
>
> Stirling's approximation states that, for $n >> 1$,
>
> $$\ln n! = n \ln n - n + \mathcal{O}(\ln n)$$
>
> Therefore,
>
> $$\begin{aligned} S(N, M) &\approx k_B \left[M \ln M - M - N \ln N + N - (M-N)\ln(M-N) + M - N\right] \\ &\approx k_B \left[M \ln M - N \ln N - (M-N)\ln(M-N)\right] \\ &\approx k_B \left[M \ln\left(\frac{M}{M-N}\right) - N \ln\left(\frac{N}{M-N}\right)\right] \end{aligned}$$

3. Define the fraction $N/M =: \phi \in [0,1]$ of the occupied sites and express the entropy as $S(\phi, M)$ or $\tilde{s}(\phi) = S(\phi, M)/(Mk_B)$.

$\phi \equiv \frac{N}{M} \implies N = M\phi$, so

$$\begin{aligned}
S(\phi, M) &= k_B \left[M \ln\left(\frac{M}{M - \phi M}\right) - \phi M \ln\left(\frac{\phi M}{M - \phi M}\right)\right] \\
&= k_B M \left[\ln\left(\frac{1}{1-\phi}\right) - \phi \ln\left(\frac{\phi}{1-\phi}\right)\right] \\
&= k_B M \left[-\ln(1-\phi) - \phi \ln \phi + \phi \ln(1-\phi)\right] \\
&= k_B M \left[(\phi - 1)\ln(1-\phi) - \phi \ln \phi\right]
\end{aligned}$$

or

$$\tilde{s}(\phi) = (\phi - 1)\ln(1-\phi) - \phi \ln \phi$$

4. Show that

[(i)] $S(\phi, M) = S(1-\phi, M)$ and state in words what this means.

To avoid writing k_B and M a few times, I'll show equivalently that $\tilde{s}(\phi) = \tilde{s}(1-\phi)$:

$$\begin{aligned}
\tilde{s}(1-\phi) &= ((1-\phi) - 1)\ln(1 - (1-\phi)) - (1-\phi)\ln(1-\phi) \\
&= -\phi \ln \phi + (\phi - 1)\ln(1-\phi) \\
&= \tilde{s}(\phi)
\end{aligned}$$

This is true because we could, at the beginning of the problem, have chosen $M - N$ spaces to *not* be occupied by gas particles. This would of course give the same binomial coefficient, but in terms of entropy, we could think of the vacant lattice sites in a particular microstate as being filled and vice-versa, and the entropy of the configuration shouldn't change (since we don't associate any intrinsic entropy with a gas particle existing and there are no interaction effects). ϕ is just the filling fraction for the original case and $1-\phi$ is the filling fraction if we swap the identities of vacancies and particles, which does not change the number of possible microstates of the system Ω.

[(ii)] The derivative $\frac{\partial S}{\partial \phi}$ can take any real number over the domain on which $S(\phi, M)$ is defined.

$$\begin{aligned}
\frac{\partial S}{\partial \phi} &= \frac{\partial}{\partial \phi}\left[k_B M \left[(\phi - 1)\ln(1-\phi) - \phi \ln \phi\right]\right] \\
&= k_B M \left(\left[\ln(1-\phi) - \frac{\phi - 1}{1-\phi}\right] - \left[1 + \ln \phi\right]\right) \\
&= k_B M \left(\ln(1-\phi) - \ln \phi\right)
\end{aligned}$$

$$\frac{\partial S}{\partial \phi} \to \infty \quad \text{as} \quad \phi \to 0$$

and

$$\frac{\partial S}{\partial \phi} \to -\infty \quad \text{as} \quad \phi \to 1$$

By the intermediate value theorem, $\frac{\partial S}{\partial \phi}$ must therefore take every value in $(-\infty, \infty)$ at some point for $\phi \in [0,1]$.

[(iii)] $S(\phi, M)$ is concave in ϕ. Now plot it (as a function of ϕ).

To show concavity, I will take the second derivative with respect to ϕ:

$$\begin{aligned}\frac{\partial^2 S}{\partial \phi^2} &= \frac{\partial}{\partial \phi} k_B M \left(\ln(1-\phi) - \ln \phi\right) \\ &= -k_B M \left(\frac{1}{1-\phi} + \frac{1}{\phi}\right) \\ &= \frac{k_B M}{\phi(\phi - 1)}\end{aligned}$$

In the domain of ϕ, this will always be negative because $\phi - 1$ will be negative for $\phi < 1$. Therefore, the function must be concave.
See Figure 0.2 for the plot of $S(\phi, M)$. As predicted, the function is concave and symmetric about $\phi = \frac{1}{2}$, the point with maximal entropy. The entropy expectedly decreases to zero at either end, where the gas either fully occupies the lattice or there is no gas at all.

```
kB = 1;
M = 10000;
Plot[kB M ((ϕ - 1) Log[1 - ϕ] - ϕ Log[ϕ]), {ϕ, 0, 1}]
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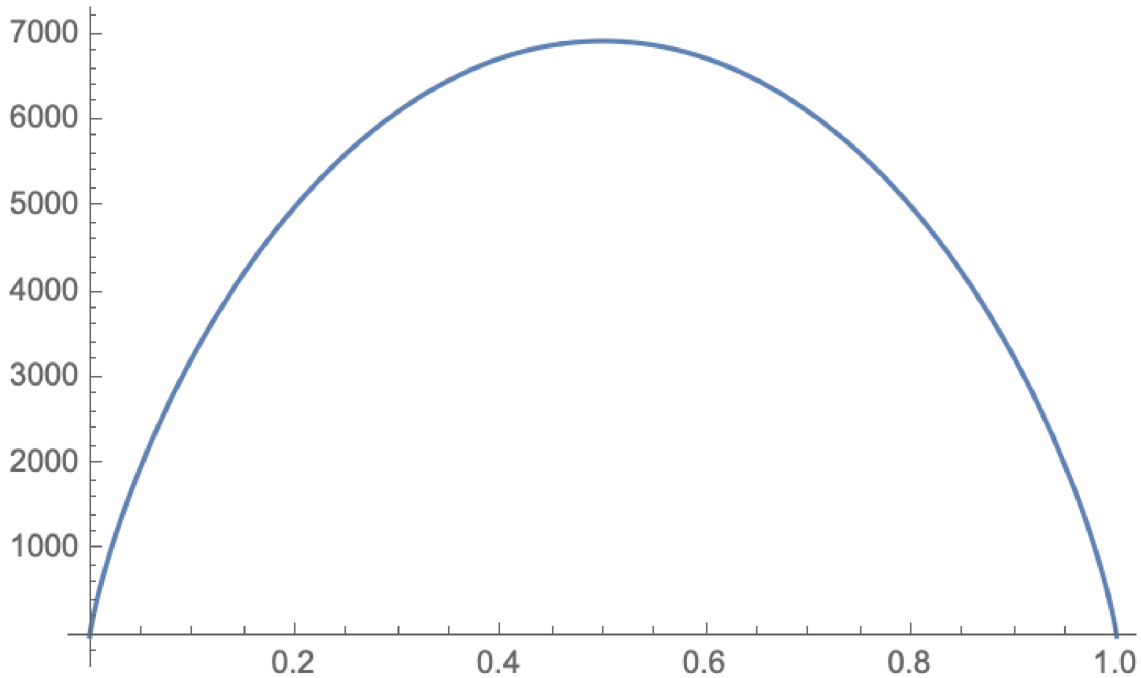

Figure 0.2: Plot for Problem 2 Part 4

5. Define $S^*(p, M)$ as the Legendre transform of $S(\phi, M)$ with respect to ϕ and calculate it. Plot it (as a function of p).

We must maximize $S(\phi, M) - \phi p$. We already know the derivative of S, so we must now solve

$$k_B M \left(\ln(1-\phi) - \ln \phi\right) - p = 0$$

in terms of ϕ:

$$\ln\left(\frac{1-\phi_0}{\phi_0}\right) = \frac{p}{k_B M}$$
$$\frac{1-\phi_0}{\phi_0} = e^{\frac{p}{k_B M}}$$
$$\implies \phi_0 = \frac{1}{1+e^{\frac{p}{k_B M}}}$$

We then insert this back into the original maximization problem:

$$\begin{aligned}
S^*(p,M) &= \max_{\phi}(S(\phi,M) - p\phi) \\
&= S(\phi_0, M) - p\phi_0 \\
&= k_B M\left((\phi_0 - 1)\ln(1-\phi_0) - \phi_0 \ln\phi_0\right) - p\phi_0 \\
&= k_B M\left(\frac{1}{1+e^{\frac{p}{k_B M}}} - 1\right)\ln\left(1 - \frac{1}{1+e^{\frac{p}{k_B M}}}\right) \\
&- \left(\frac{1}{1+e^{\frac{p}{k_B M}}}\right)\ln\left(\frac{1}{1+e^{\frac{p}{k_B M}}}\right) - \frac{p}{1+e^{\frac{p}{k_B M}}} \\
&= k_B M\left(-\frac{\ln\left(\frac{1}{e^{\frac{p}{k_B M}}+1}\right)}{e^{\frac{p}{k_B M}}+1} - \frac{e^{\frac{p}{k_B M}}}{e^{\frac{p}{k_B M}}+1}\ln\left(\frac{e^{\frac{p}{k_B M}}}{e^{\frac{p}{k_B M}}+1}\right)\right) - \frac{p}{e^{\frac{p}{k_B M}}+1} \\
&= k_B M\left(\frac{\ln\left(e^{\frac{p}{k_B M}}+1\right)}{e^{\frac{p}{k_B M}}+1} - \frac{e^{\frac{p}{k_B M}}}{e^{\frac{p}{k_B M}}+1}\left(\ln\left(e^{\frac{p}{k_B M}}\right) - \ln\left(e^{\frac{p}{k_B M}}+1\right)\right)\right) - \frac{p}{e^{\frac{p}{k_B M}}+1} \\
&= k_B M\left(\ln\left(e^{\frac{p}{k_B M}}+1\right) - \frac{e^{\frac{p}{k_B M}}}{e^{\frac{p}{k_B M}}+1}\ln\left(e^{\frac{p}{k_B M}}\right)\right) - \frac{p}{e^{\frac{p}{k_B M}}+1} \\
&= k_B M\left(\ln\left(e^{\frac{p}{k_B M}}+1\right) - \frac{e^{\frac{p}{k_B M}}}{e^{\frac{p}{k_B M}}+1}\frac{p}{k_B M}\right) - \frac{p}{e^{\frac{p}{k_B M}}+1} \\
S^*(p,M) &= k_B M \ln\left(e^{\frac{p}{k_B M}}+1\right) - p
\end{aligned}$$

See Figure 0.3 for a plot of $S^*(p,M)$ as well as the Mathematica code used to produce it. I set $k_B = 1$ since it's just an arbitrary scale factor to get units of entropy, and $M = 10000$ as an arbitrary large lattice size.

3. Generalized Harmonic/Arithmetic Mean Inequality

Consider N positive numbers x_i, associated with the weights p_i, which satisfy $0 \le p_i \le 1$ and $\sum_{i=1}^N p_i = 1$. Prove the following inequality between the generalized harmonic and the generalized arithmetic mean:

$$\left(\sum_{i=1}^N p_i \frac{1}{x_i}\right)^{-1} =: \langle\{x_i\}\rangle_{\mathrm{GH}} \le \langle\{x_i\}\rangle_{\mathrm{GA}} := \sum_{i=1}^N p_i x_i.$$

By the Cauchy-Schwartz Inequality,

$$\sum_{i=1}^N \frac{p_i}{x_i}\sum_{i=1}^N p_i x_i \ge \left(\sum_{i=1}^N \sqrt{\frac{p_i}{x_i}}\sqrt{p_i x_i}\right)^2$$

```
kB = 1;
M = 10 000;
Plot[kB M Log[Exp[p/(kb M)] + 1] - p, {p, -100, 100 000}]
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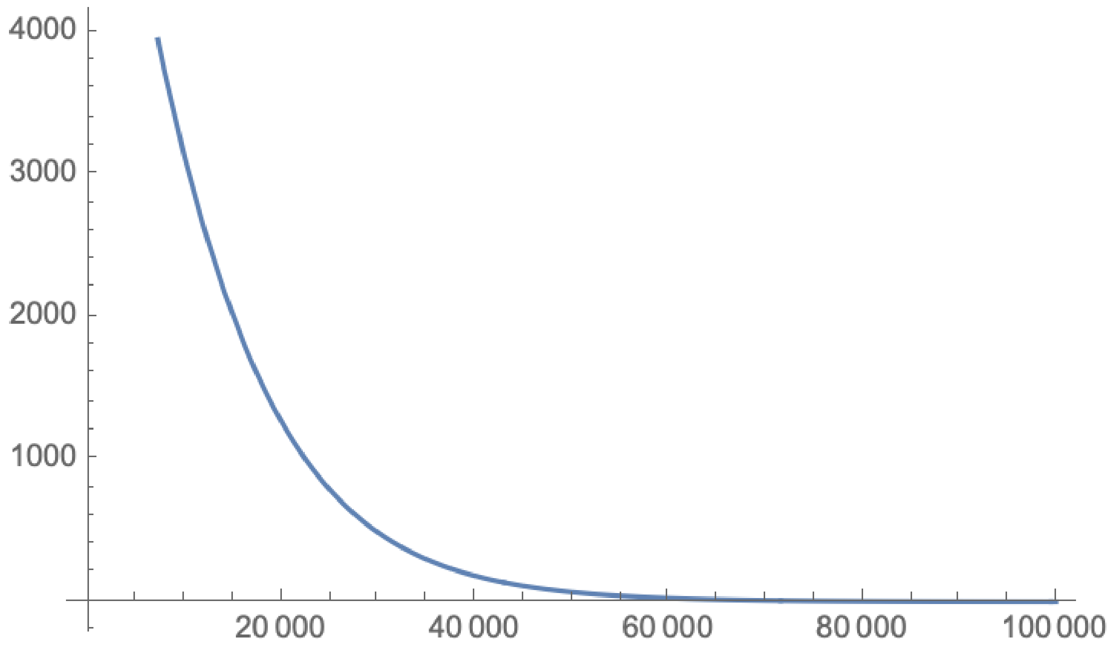

Figure 0.3: Plot for Problem 2 Part 5

$$
\begin{aligned}
&= \left(\sum_{i=1}^{N} \sqrt{p_i^2} \right)^2 \\
&= \left(\sum_{i=1}^{N} p_i \right)^2 \\
&= 1^2 = 1 \implies 1 \leq \frac{\langle \{x_i\} \rangle_{\text{GA}}}{\langle \{x_i\} \rangle_{\text{GH}}} \implies \langle \{x_i\} \rangle_{\text{GH}} \leq \langle \{x_i\} \rangle_{\text{GA}}
\end{aligned}
$$

4. One of them Thermodynamic Identities. . .

Rewrite the following partial derivative in terms of the usual response functions (meaning: thermal expansion coefficient, either one of the compressibilities, either one of the specific heats), and of course any of the other functions of state, such as T, S, P, V, . . . , and possibly innocent numbers:

$$
\left. \frac{\partial U}{\partial P} \right|_{G,N} = ?
$$

Hints:

(1) The thermodynamic potential $G(T, P, N)$ is the Gibbs free energy.

(2) The answer will not look particularly pretty. Don't worry about this—it's not your fault. Instead, take pride in your thermodynamic superpowers that enable you to derive results like this.

(3) The standard Jacobi expansion is a good way to start, even if one of the new Jacobians cannot be reverse-Jacobified; Handle that obdurate one by dealing with it as an actual determinant. From then on, you can go on auto-pilot.

$$
\begin{aligned}
\left.\frac{\partial U}{\partial P}\right|_{G,N} &= \frac{\partial(U,G)}{\partial(P,G)} \\
&= \frac{\partial(U,G)}{\partial(P,T)} \underbrace{\frac{\partial(P,T)}{\partial(P,G)}}_{-\frac{1}{S}} \\
&= -\frac{1}{S}\left[\overbrace{\left.\frac{\partial U}{\partial P}\right|_T}^{*} \underbrace{\left.\frac{\partial G}{\partial T}\right|_P}_{-S} - \underbrace{\left.\frac{\partial G}{\partial P}\right|_T}_{V} \overbrace{\left.\frac{\partial U}{\partial T}\right|_P}^{\dagger} \right]
\end{aligned}
$$

$$
\begin{aligned}
* &= \left.\frac{\partial U}{\partial P}\right|_T \\
&= T \left.\frac{\partial S}{\partial P}\right|_T - P \underbrace{\left.\frac{\partial V}{\partial P}\right|_T}_{-\kappa_T V} \\
&= -T \underbrace{\left.\frac{\partial V}{\partial T}\right|_P}_{\alpha V} + P\kappa_T V \\
&= PV\kappa_T - \alpha T V
\end{aligned}
$$

$$
\begin{aligned}
\dagger &= \left.\frac{\partial U}{\partial T}\right|_P \\
&= T \underbrace{\left.\frac{\partial S}{\partial T}\right|_P}_{\frac{C_P N}{T}} - P \underbrace{\left.\frac{\partial V}{\partial T}\right|_P}_{\alpha V} \\
&= C_P N - PV\alpha
\end{aligned}
$$

Therefore

$$
\begin{aligned}
\left.\frac{\partial U}{\partial P}\right|_{G,N} &= -\frac{1}{S}\left(-S(PV\kappa_T - \alpha T V) - V(C_P N - PV\alpha)\right) \\
&= PV\kappa_T - TV\alpha + \frac{VC_P N}{S} - \frac{PV^2\alpha}{S}
\end{aligned}
$$